

A Novel Reactivity Mode for Metal-Activated Dialkylcyanamide Species: Addition of *N,N'*-Diphenylguanidine to a *cis*-(R₂NCN)₂Pt^{II} Center Giving an Eight-Membered Chelated Platinoguanidine

Pavel V. Gushchin,[†] Maxim L. Kuznetsov,[‡] Matti Haukka,[§] Meng-Jiy Wang,^{||} Aleksander V. Gribanov,[⊥] and Vadim Yu. Kukushkin^{*,†,⊥}

Department of Chemistry, St. Petersburg State University, 198504 Stary Petergof, Russian Federation, Department of Chemistry, Moscow Pedagogical State University, 119021 Moscow, Russian Federation, Department of Chemistry, University of Joensuu, P.O. Box 111, FI-80101 Joensuu, Finland, Department of Chemical Engineering, National Taiwan University of Science and Technology, 43 Keelung Road, Section 4, Taipei 106, Taiwan, and Institute of Macromolecular Compounds, Russian Academy of Sciences, V. O. Bolshoi Pr. 31, 199004 St. Petersburg, Russian Federation

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The nucleophilic addition of *N,N'*-diphenylguanidine, HN=C(NHPh)₂ (DPG), to two adjacent dialkylcyanamide ligands in *cis*-[PtCl₂(NCNR₂)₂] (R = Me; R₂ = C₅H₁₀, C₄H₈O) gives unusual eight-membered chelates [PtCl₂{NH=C-(NR₂)N(Ph)C(=NH)N(Ph)C(NR₂)=NH}] (**1–3**) with trisguanidine as the cyclic ligand, in which the central guanidine =NH group remains uncoordinated. Treatment of *trans*-[PtCl₂(NCNR₂)₂] (R = R = Me; R₂ = C₅H₁₀, C₄H₈O) with 1 equiv of HN=C(NHPh)₂ in a solution (R = R = Me; R₂ = C₅H₁₀) or in a suspension (R₂ = C₄H₈O) of CHCl₃ or MeNO₂ at 20–25 °C for 20 h results in the generation of the 1,3,5-triazapentadiene monochelates [PtCl{NH=C(NR₂)N(Ph)C(NH₂)=NPh}{NCNR₂}(Cl)] (**4–6**). When any of *trans*-[PtCl₂(NCNR₂)₂] reacts with 2 equiv of DPG at 20–25 °C for 1–2 days or **4–6** are treated with 1 equiv more of HN=C(NHPh)₂ at the same temperature, the complexes bearing two chelate rings [Pt{NH=C(NR₂)N(Ph)C(NH₂)=NPh}₂](Cl)₂ (**7–9**) are formed. The formulation of the obtained complexes was supported by satisfactory C, H, and N elemental analyses, agreeable ESI⁺-MS, IR and ¹H and ¹³C{¹H} NMR spectroscopies; the structures of **1** and **2** were determined by the single-crystal X-ray diffraction. Theoretical studies (at the B3LYP level of theory) revealed that the alkyl nitrile eight-membered product is significantly less stable than the corresponding cyanamide species **1–3**, and this fact, at least partially, explains why the former was not detected in the reaction between *cis*-dinitrileplatinum(II) complexes and DPG.

Introduction

Reactions of metal-activated RC≡N species are one of the frontier areas of current research on ligand reactivity and also organic synthesis involving metal complexes. This topic has been the subject of comprehensive reviews¹ including surveys by one of us.^{2,3} In general, interest in the conversions of nitriles at metal centers stems from the possibility (i) of using RCN species as versatile synthons for the preparation

of new compounds, often unreachable in metal-free organic synthesis, via C–O, C–N, C–C, C–P, and C–S bond making, (ii) of providing an environmentally friendly metal-catalyzed hydrolytic transformation of RCN species to amides, e.g., those of industrial and pharmacological significance,³ and (iii) of synthesizing, via nucleophilic addition, diverse imino complexes.⁴

* To whom correspondence should be addressed. E-mail: kukushkin@vk2100.spb.edu.

[†] St. Petersburg State University.

[‡] Moscow Pedagogical State University.

[§] University of Joensuu.

^{||} National Taiwan University of Science and Technology.

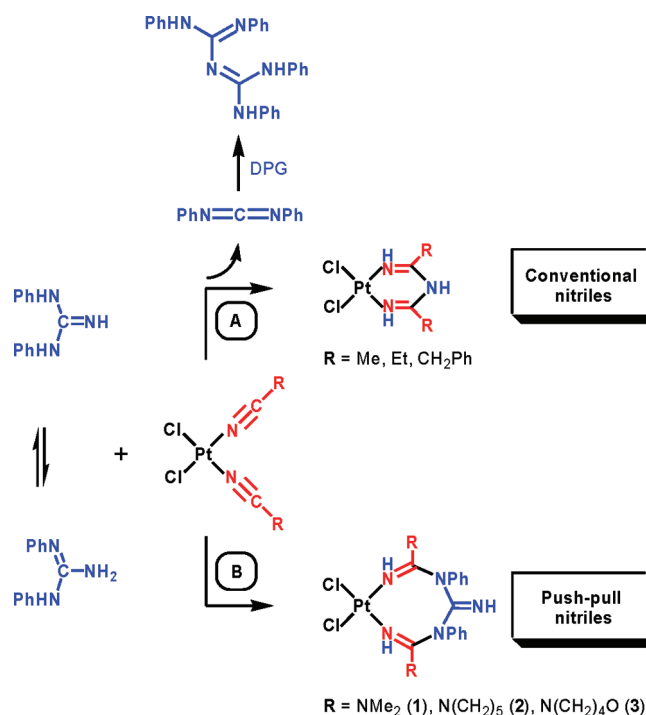
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Despite the wealth of chemistry associated with metal-bound *conventional* nitriles RCN (R = alkyl, aryl), the coordination chemistry of the so-called *push–pull* nitriles⁵ (a push–pull system is highly polarized, and it is characterized by an electron-withdrawing substituent or an electro-negative atom on one side of the multiple bond and an electron-donating substituent on the other side), such as, e.g., dialkylcyanamides R₂NCN, has so far been little explored, although data gradually accumulated in the literature indicate that the R₂NCN ligands might exhibit some exciting reactivity modes unknown for alkyl- or aryl nitrile ligands.^{6–8} This dissimilarity, in view of our general interest in the reactions of nitrile ligands,^{2,3,9–11} prompted us to distinguish reactivity differences between the push–pull and conventional nitrile species ligated to a Pt^{II} center.

We have recently reported¹¹ on the coupling between *N,N'*-diphenylguanidine, HN=C(NHPh)₂ (DPG), and coordinated

Scheme 1



nitriles in the Pt^{II} complexes *cis*- and *trans*-[PtCl₂(RCN)₂] (R = Me, Et, CH₂Ph, Ph), which proceeded rapidly under mild conditions and afforded the 1,3,5-triazapentadiene compounds. As a continuation of the project focused on the study of reactivity differences between push–pull and conventional nitrile species ligated to a Pt^{II} center, we attempted the reaction between the dialkylcyanamideplatinum(II) precursors [PtCl₂(NCNR₂)₂] and DPG and found that the process involving the dialkylcyanamide complexes proceeds in another direction than that which occurred with the structurally similar (RCN)₂Pt^{II} species. Herein we report on the study of the reaction between the Pt^{II} complexes [PtCl₂(NCNR₂)₂] and DPG, where we verified significant reactivity differences between the push–pull and conventional nitrile ligands.

Results and Discussion

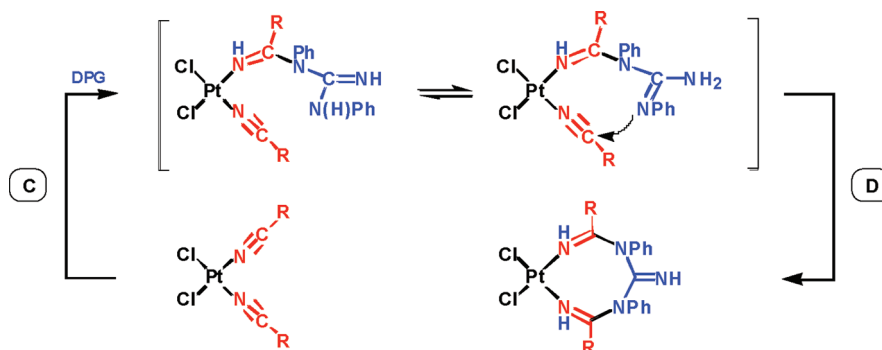
We choose as starting materials for this study the dialkylcyanamide compounds [PtCl₂(NCNR₂)₂] (R = Me; R₂ = C₅H₁₀, C₄H₈O).⁶ The route of the reaction between these species and DPG strongly depends on *cis* or *trans* configuration of the starting metal complex. Accordingly, in the sections that follow, we consider interplay between DPG and *cis*-(R₂NCN)₂Pt^{II} and then with *trans*-(R₂NCN)₂Pt^{II} centers.

Dialkylcyanamide–Guanidine Coupling at *cis*-(R₂NCN)₂-Pt^{II} Centers. We have recently reported¹¹ on the reaction of two adjacent nitrile ligands in *cis*-[PtCl₂(RCN)₂] (R = Me, Et, CH₂Ph, Ph) upon their interaction with HN=C(NHPh)₂, which afforded the 1,3,5-triazapentadiene compounds [PtCl₂{NH=C(R)NHC(R)NH}] and biguanidine (Scheme 1, route A).

In contrast to the reaction of DPG with the conventional nitrile complexes (route A), its reaction with two adjacent

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Scheme 2



dialkylcyanamide ligands in *cis*-[PtCl₂(NCNR₂)₂] (R = Me; R₂ = C₅H₁₀, C₄H₈O) in a molar ratio of 1:1 proceeds in MeNO₂ or CHCl₃ at 20–25 °C for ca. 1 day and gives unusual eight-membered chelated complexes **1–3** with trisguanidine (IUPAC name¹² for the trisguanidine ligand: *N*-[(dimethylamino)(imino)methyl]-*N'*,*N'*-dimethyl-*N,N*-diphenylimidodicarbonimidic diamide]) as the cyclic ligand, in which the central guanidine =NH group remains uncoordinated (Scheme 1, route B). If the syntheses were carried out in MeNO₂, pure complexes **1–3** were isolated in good yields (ca. 75%), while in CHCl₃, the reaction is less selective and the yields after column chromatography (or after crystallization and purification under a layer of EtOH) are 50–60%.

Thus, the novel reaction for platinum-activated dialkylcyanamide species, i.e., nucleophilic addition of DPG to two dialkylcyanamide ligands of the *cis*-(R₂NCN)₂Pt^{II} center, gives the previously unreported eight-membered chelated platinaguanidines. Chelates **1–3** exhibit surprising stability, and no transformation was observed upon keeping these complexes at 25 °C for at least 2 years. Moreover, they decompose to yield a broad spectrum of yet unidentified species upon heating in the solid phase at elevated temperatures (>160 °C; see the Experimental Section) or upon prolonged reflux in dichloroethane (ca. 83 °C; >15 h).

It is worth mentioning that five- and six-membered metal chelate rings are the most conventional ring systems in coordination chemistry insofar as they exhibit exceptional stability^{13,14} (for general consideration of the chelate effect, see refs^{15–17}). However, seven-,^{18–22} eight- (in particular, having N[⊖]N,^{19,20,23–25} P[⊖]P,^{21,26–28} S[⊖]S,^{29,30} Se[⊖]Se,³⁰ O[⊖]O,^{30–32} P[⊖]O,³³ and C[⊖]O³⁴ donor centers),^{19–35} nine-,^{20,24,27} ten-, eleven-, and twelve-membered and also complexes with trans-spanned ligands³⁶ and large metal-lamacrocycles^{22,25–35,37} are also known, albeit they are still unusual rather than common.

A plausible mechanism for the formation of eight-membered chelates (Scheme 2) apparently involves (i) an intermolecular nucleophilic attack of the Pt^{II}-activated dialkylcyanamide by the NPh center (route C) of the asymmetric³⁸ tautomer and (ii) tautomerization of the newly formed ligand followed by ring closure via intramolecular nucleophilic addition by the NPh center (route D).

One of the main reasons for the different chemical behavior of dialkylcyanamide and alkylnitrile complexes may be higher thermodynamic stability of complexes **1–3** in comparison with similar eight-membered rings derived from alkylnitrile species. Indeed, quantum-chemical calculations indicate that the Δ*G*_s value of the formation of **1** from *cis*-[PtCl₂(NCNMe₂)₂] and DPG is 10.67 kcal/mol lower than Δ*G*_s of the formation of the corresponding acetonitrile derivative *cis*-[PtCl₂{NH=C(Me)N(Ph)C(=NH)N(Ph)C(Me)=NH}] (**1'**) formed from *cis*-[PtCl₂(NCMe₂)₂] and DPG. The higher relative stability of **1–3** compared to that of the alkylnitrile derivatives is accounted for by additional resonance stabilization in the former species including cyanamide amino groups. The higher degree of bond delocalization in **1** than in **1'** is indicated by distributions of the bond orders (Wiberg bond indices; see Scheme S2 in the Supporting Information). Involvement of the NMe₂ groups of **1** in conjugation (see Scheme S3 in the Supporting Information) is confirmed by sp² orbital hybridization of the nitrogen seen from the natural bond order analysis (Table S5 in the Supporting Information) and also by X-ray data. A more detailed description of the theoretical results is given in the Supporting Information.

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Characterization of 1–3. The formulation of complexes 1–3 was supported by satisfactory C, H, and N elemental analyses and agreeable positive electrospray ionization mass spectrometry (ESI⁺-MS) data, where peaks of the molecular ion [M]⁺ and the dimer [2M]⁺ were detected. The IR spectroscopic data confirmed the hypothesis of the DPG addition to both adjacent R₂NCN ligands and rule out the possibility of the addition of DPG to only one complexed push–pull nitrile. Thus, in the IR spectra of 1–3, the strong $\nu(\text{C}=\text{N})$ bands (ca. 1620 cm^{−1}) and N–H stretching vibra-

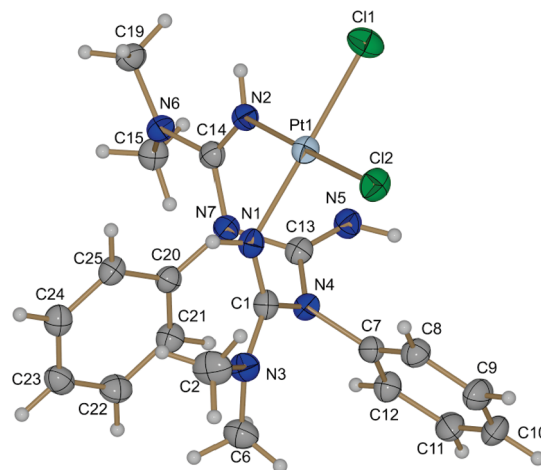


Figure 1. Thermal ellipsoid view of **1** with an atomic numbering scheme. Thermal ellipsoids are drawn with 50% probability. Selected bond lengths (Å) and angles (deg): N1–C1 1.293(4), N2–C14 1.295(4), N5–C13 1.256(4), N4–C1 1.395(4), N7–C14 1.392(4), N4–C13 1.418(4), N7–C13 1.417(4); N2–Pt1–N1 93.93(10).

tions (medium-to-strong bands at 3477–3244 cm^{−1}) are displayed and no $\nu(\text{C}\equiv\text{N})$ stretches of the dialkylcyanamide ligands were observed.

In the ¹H NMR spectra, complexes 1–3 reveal two singlets of the NH protons at ca. 7.00 and 6.00 ppm in a ratio 1:1, two doublets and three triplets in the region 7.61–7.21 ppm, corresponding to the Ph protons. Data on variable-temperature ¹H NMR indicating some dynamic processes for 1–3 are given in the Supporting Information.

Both compounds 1·CHCl₃ and 2·CHCl₃ were characterized by X-ray diffraction (Figures 1 and 2). They have a square-planar geometry, and two cis positions are occupied with eight-membered bidentate ligands, while the other two are occupied with chlorides. In the chelate rings, the CN bonds have a low degree of delocalization (Table 1) and the

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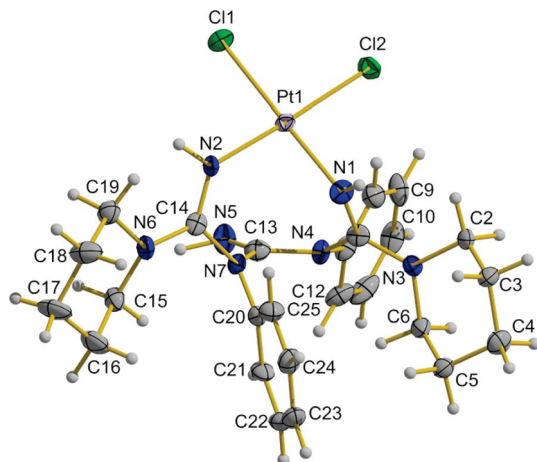


Figure 2. Thermal ellipsoid view of **2** with an atomic numbering scheme. Thermal ellipsoids are drawn with 50% probability. Selected bond lengths (Å) and angles (deg): N1–C1 1.300(10), N2–C14 1.318(10), N5–C13 1.249(11), N4–C1 1.383(10), N7–C14 1.378(10), N4–C13 1.395(11), N7–C13 1.403(11); N2–Pt1–N1 94.4(3).

Table 1. Selected Bond Lengths (Å) and Angles (deg) for **1** and **2**

	1	2
Pt1–N1	2.027(2)	2.004(7)
Pt1–N2	2.027(2)	1.970(7)
Pt1–Cl1	2.2962(8)	2.304(2)
Pt1–Cl2	2.3018(8)	2.302(2)
N1–C1	1.293(4)	1.300(10)
N2–C14	1.295(4)	1.318(10)
N4–C1	1.395(4)	1.383(10)
N4–C13	1.418(4)	1.395(11)
N5–C13	1.256(4)	1.249(11)
N7–C14	1.392(4)	1.378(10)
N1–Pt1–N2	93.93(10)	94.4(3)
Cl1–Pt1–Cl2	91.48(3)	92.32(8)

central guanidine group is not coordinated. Both **1** and **2** crystallize as a racemate, which consists of the two optical isomers (Δ - and Λ -twist-boat; Figure S1 in the Supporting Information), probably due to the conformational flexibility of the eight-membered cycles. For a detailed description of the X-ray structural data and also for the packing diagrams of the chloroform solvates (Figures S2–S6 and Table S1 in the Supporting Information).

Dialkylcyanamide–Guanidine Coupling at $trans$ -(R_2 -NCN) $_2$ Pt^{II} Centers. Earlier we reported¹¹ on the reaction between the Pt^{II}-bound conventional nitriles in the complexes $trans$ -[PtCl₂(RCN)₂] (R = Et, CH₂Ph, Ph) and DPG. When this interplay proceeds in a molar ratio of 1:2, it furnishes the monochelates [PtCl{NH=C(R)NC(NHPh)=NPh}(RCN)] (Scheme 3, route E) but with 4 equiv of DPG (Scheme 3, route G) [or the reaction of [PtCl{NH=C(R)NC(NHPh)=NPh}(RCN)] with 2 equiv of DPG (Scheme 3, route F)], and the complexes containing two bidentate 1,3,5-triazapentadiene ligands, i.e., [Pt{NH=C(R)NC(NHPh)=NPh}₂], are formed.

We now extended the coupling between DPG and the conventional nitriles at Pt^{II} centers to Pt^{II} complexes bearing the push–pull nitriles. Thus, the treatment of $trans$ -[PtCl₂(NCNR₂)₂] (R = Me; R₂ = C₅H₁₀, C₄H₈O) with 1 equiv of DPG (Scheme 3, route H) in a solution (R = R = Me; R₂ = C₅H₁₀) or in a suspension (R₂ = C₄H₈O) of CHCl₃ (or MeNO₂) at 20–25 °C for 20 h results in the generation of

the 1,3,5-triazapentadiene monochelates [PtCl{NH=C(NR₂)-N(Ph)C(NH₂)=NPh}(NCNR₂)](Cl) (**4–6**). When any of $trans$ -[PtCl₂(NCNR₂)₂] reacts with 2 equiv of DPG at 20–25 °C for 1–2 days (Scheme 3, route J) or **4–6** are treated with 1 equiv more of DPG at the same temperature, the complexes bearing two chelate rings [Pt{NH=C(NR₂)-N(Ph)C(NH₂)=NPh}₂](Cl)₂ (**7–9**) are formed. Further increasing the quantity of DPG up to a molar ratio of the reactants of 1:4 does not affect the reaction and also yields of **7–9** (Scheme 3, route I). It is worth mentioning that the coupling conditions giving the bischelates for the push–pull nitrile $trans$ -(R₂NCN)₂Pt species (Scheme 3, route J) are much milder (20–25 °C) than those for conventional nitrile $trans$ -(RCN)₂Pt complexes (75 °C) (Scheme 3, route G).

Inspecting the structures of 1,3,5-triazapentadiene species derived, on the one hand, from the conventional organonitrileplatinum(II) complexes $trans$ -[PtCl₂(RCN)₂] (R = Et, CH₂Ph, Ph),¹¹ and, on the other hand, the dialkylcyanamide-platinum(II) complexes $trans$ -[PtCl₂(NCNR₂)₂], we assumed that the conventional complexed organonitriles react with the symmetric tautomer of DPG (Scheme 3, routes E–G), while the push–pull nitrile ligands preferably react with the asymmetric tautomer of DPG (Scheme 3, routes H–J). Presumably, compounds **4–9** are generated via the previously unreported nucleophilic attack of the asymmetric tautomer³⁸ to the push–pull nitrile at the Pt^{II} center.

Characterization of the (1,3,5-Triazapentadiene)platinum(II) Complexes. The C, H, and N elemental analysis data for **4–9** favor the presence of one (**4–6**) or two (**7–9**) Cl[−] counterions, and their availability was also confirmed by the reaction with Ag⁺ that give the solid AgCl. In ESI⁺-MS, both the observed fragmentation and the isotopic pattern of the complexes correspond to those expected for **4**⁺–**6**⁺ and **7**²⁺–**9**²⁺. Comparison of the IR spectra of **4–9** with those of the starting dialkylcyanamide complexes indicates the presence of the C≡N stretching vibrations (at ca. 2290 cm^{−1}) but with a significant lesser intensity for **4–6** and the absence of ν (C≡N) bands for **7–9**. The IR spectra of **4–9** exhibit, in contrast to the starting materials $trans$ -[PtCl₂(NCNR₂)₂], strong ν (C=N) vibrations in the range of 1650–1629 cm^{−1} and N–H stretching vibrations, which emerge between 3375 and 3150 cm^{−1}.

In the ¹H NMR spectra recorded at ambient temperature, a noticeable broadening and/or some sets of signals of alkyl protons of the NR₂ amide groups of **4–9** has been observed. Thus, ¹H NMR data of **4–9** give collateral evidence favoring inversion at the N atom of NR₂ groups and/or a restricted rotation of the amide groups NR₂ (located close to the Ph rings) around the C–NR₂ bond, suggesting a significant contribution of the form with C=NR₂ double-bond character. The relevant formamidinium ions, [H(R¹)NCH=NR²(R³)]⁺,⁴²

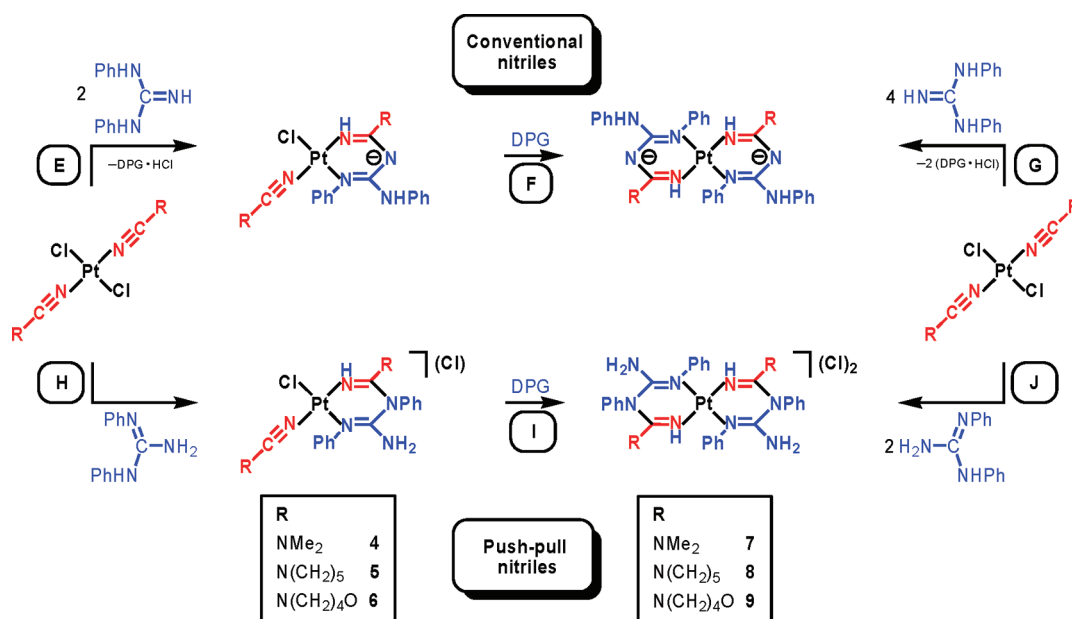
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Scheme 3



a derivative of the five-membered S_3N_2 ring (C_6H_{11})₂NC(Cl)- $NS_3N_2^+Cl^-$,⁴³ amidoozavinylidene (or amidomethyleneamide) species $Mo=N=CH(NR_2)^7$ and compound $Mo_2-(OCH_2CMe_3)_6(\mu-\eta^1, \eta^2-NCNMe_2)^{44}$ also exhibit an encumbered rotation around the C=N bond.

In the 1H NMR spectra, **4–6** exhibit two signals of the NH protons, i.e., the broad signal at ca. 10.28 ppm and the singlet in the range 5.67–5.84 ppm. The ^{13}C NMR spectra of **4–9** display resonances from two different carbons (ca. 158 and 155 ppm) of two different C=N bonds. The proposed structures of **7** and **8** were also confirmed by X-ray diffraction. However, these data will be reported separately.⁴⁵

Final Remarks. The results from this work can be summarized into three perspectives. First, the reaction between two cis-ligated R_2NCN species and DPG represents a novel reactivity mode, which has never been reported for any nitrile at any metal center. Second, the formation of eight-membered rings described in this Article appears to be specific for the push-pull nitriles R_2NCN , and this reaction was not observed for the conventional alkyl- and aryl nitriles $R'CN$. The performed quantum-chemical calculations allowed the interpretation of the different behaviors of the conventional nitrile and dialkylcyanamide complexes in their reactions with DPG, indicating that the eight-membered product is significantly less stable in the case of the alkyl nitrile derivatives $cis-(RCN)_2Pt^{II}$ in comparison with the cyanamide species $cis-(R_2NCN)_2Pt^{II}$. Third, the obtained eight-membered chelates represent a novel type of guanidines, which comprise one integrated system with the metal center. These platinaguanidines bear the free =NH moiety that can serve as a nucleophilic center in the metal-mediated

nitrile-imine (guanidine) coupling,⁴⁵ leading to multimetallic systems derived from the ligand reactions. Work focusing on the latter topic is underway in our group.

Experimental Section

Materials and Instrumentation. The guanidine $HN=C(NHPh)_2$ (Aldrich) and solvents were obtained from commercial sources and used as received. The complex $cis-[PtCl_2(NCNC_4H_8O)_2]$ was synthesized upon heating of the clathrate $Pt_6Cl_{12} \cdot 0.1C_2H_5Cl \cdot 5.7H_2O$ ⁴⁶ with $NCNC_4H_8O$ (Aldrich) (see the Experimental Section), and the obtained compound contains an admixture of the trans isomer (an isomeric cis:trans ratio obtained by 1H NMR integration is ca. 2.7:1.0). The complexes $trans-[PtCl_2(NCNR_2)_2]$ ($R = Me$; $R_2 = C_5H_{10}$, C_4H_8O) and $cis-[PtCl_2(NCNR_2)_2]$ ($R = Me$; $R_2 = C_5H_{10}$) were prepared in accordance with the published methods.⁶

Elemental analyses were obtained on a 185B Carbon Hydrogen Nitrogen Analyzer Hewlett-Packard instrument. Differential thermal analysis/thermogravimetry (DTA/TG) measurements were performed using a Perkin-Elmer (Diamond TG/DTA) derivatograph in air at a heating rate of 10 °C/min (carrier gas: air, 200 mL/min). Time-of-flight (TOF)-ESI-MS spectra were obtained on a MX-5310 mass spectrometer. IR spectra (4000–400 cm^{-1}) were recorded on a Shimadzu FTIR 8400S instrument in KBr pellets. 1H and $^{13}C\{^1H\}$ NMR spectra were measured on a Bruker-DPX 300 spectrometer at ambient temperature.

Computational Details. The full geometry optimization of all structures has been carried out in Cartesian coordinates with the help of the *Gaussian-98*⁴⁷ program package at the density functional theory level. The calculations have been performed using Becke's three-parameter hybrid exchange functional⁴⁸ in combination with the gradient-corrected correlation functional of Lee, Yang, and Parr⁴⁹ (B3LYP). A quasi-relativistic Stuttgart pseudopotential described 60 core electrons, and the appropriate contracted basis set (8s7p6d)/[6s5p3d]⁵⁰ for the Pt atom and the 6-31G* basis set for other atoms were used. The combination of the B3LYP functional and the basis set mentioned was found as a quite reasonable approximation for the investigation of properties of transition-metal complexes,^{51–53} including nitrile complexes of

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platinum,⁵¹ taking into account the low computational cost of this method and the fact that the results obtained at B3LYP agree well with those calculated at the higher correlated methods.

The Hessian matrix was calculated analytically for all optimized structures in order to prove the location of correct minima (no “imaginary” frequencies) and to estimate the zero-point-energy (ZPE) correction and thermodynamic parameters, the latter of which were calculated at 25 °C. Solvent effects were taken into account at the single-point calculations based on the gas-phase equilibrium geometries by using the polarizable continuum model (PCM)⁵⁴ in the CPCM version⁵⁵ with CHCl₃ as a solvent. For **T2a**, the dispersion–repulsion term could not be calculated with CPCM and other PCM-based models. Hence, the nonelectrostatic component for this structure was estimated as $\Delta G_{\text{non-EL}}(\text{T2a}) = \Delta G_{\text{non-EL}}(\text{T2b}) + \Delta G_{\text{non-EL}}(\text{T3a}) - \Delta G_{\text{non-EL}}(\text{T3b})$, where $\Delta G_{\text{non-EL}}$ are nonelectrostatic contributions in the solvent effects for **T2a**, **T2b**, **T3a**, and **T3b** species. The enthalpies and Gibbs free energies in solution (H_s and G_s) were estimated by the addition of the ZPE, thermal (δH_g), and also entropic (δG_g) contributions taken from the gas-phase calculations to the single-point CPCM–self-consistent-field (SCF) energy (E_s).

The starting geometries of eight- and six-membered reaction products were based on the experimental X-ray structures of **1** and **2** (this work) and [PtCl₄{NH=C(NH₂)NHC(NMe₂)=NH}].³⁹ For DPG, the most stable tautomeric form in the *E,Z* conformation, i.e., PhN=C(NH₂)N(H)Ph,⁴⁰ was considered. The equilibrium geometries and the main calculated bond lengths are in reasonable agreement with the X-ray data obtained for *trans*-[PtCl₂(NCNMe₂)₂],⁶ *cis*-[PtCl₂(NCMe)₂],⁴¹ **1**, and **2** (this work) and [PtCl₄{NH=C(NH₂)NHC(NMe₂)=NH}].³⁹ (Table S2 and Figure S7 in the Supporting Information). The maximum deviations of the theoretical and experimental parameters are 0.07 and 0.05 Å for the Pt–N and Pt–Cl bonds, respectively, whereas the difference for the other bonds does not exceed 0.037 Å, often falling within the 3σ interval of the X-ray data.

X-ray Structure Determinations. The crystals of **1** and **2** were immersed in cryo-oil, mounted in a Nylon loop, and measured at

Table 2. Crystal Data

	1	2
empirical formula	C ₂₀ H ₂₆ Cl ₅ N ₇ Pt	C ₂₆ H ₃₄ Cl ₅ N ₇ Pt
fw	722.81	816.94
temp (K)	120(2)	120(2)
λ (Å)	0.710 73	0.710 73
cryst syst	triclinic	orthorhombic
space group	<i>P</i> $\bar{1}$	<i>Pbca</i>
<i>a</i> (Å)	8.7607(2)	9.8934(7)
<i>b</i> (Å)	11.4006(3)	24.2416(13)
<i>c</i> (Å)	13.6067(3)	24.9307(18)
α (deg)	109.475(1)	90
β (deg)	93.761(1)	90
γ (deg)	104.921(1)	90
<i>V</i> (Å ³)	1220.82(5)	5979.2(7)
<i>Z</i>	2	8
ρ _{calc} (Mg/m ³)	1.966	1.815
μ (Mo Kα) (mm ^{−1})	6.316	5.171
no. of reflns	5616	36566
no. of unique reflns	5616	6000
<i>R</i> _{int}	0.0750	0.1120
<i>R</i> ^a (<i>I</i> ≥ 2σ)	0.0245	0.0467
w <i>R</i> ^b (<i>I</i> ≥ 2σ)	0.0577	0.0887

^a *R*1 = $\sum ||F_o| - |F_c|| / \sum |F_o|$. ^b w*R*2 = $[\sum (w(F_o^2 - F_c^2))^2 / \sum (w(F_o^2)^2)]^{1/2}$.

a temperature of 120 K. The X-ray diffraction data were collected by means of a Nonius Kappa CCD diffractometer using Mo Kα radiation (λ = 0.710 73 Å). The *Denzo-Scalepack*⁵⁶ or *EvalCCD*⁵⁷ program packages were used for cell refinements and data reductions. The structures were solved by direct methods using *SIR2004*⁵⁸ or *SHELXS-97*⁵⁹ with the *WinGX*⁶⁰ graphical user interface. A semiempirical absorption correction (*SORTAV*⁶¹ or *SADABS*⁶²) was applied to all data. Structural refinements were carried out using *SHELXL-97*.⁶³ In **1**, the CHCl₃ solvent molecule was severely disordered and therefore the final structural model was refined without it. The contribution of the disordered solvent to the calculated structure factors was taken into account by using the *SQUEEZE* routine of the *PLATON*⁶⁴ program. In **1**, the NH hydrogen atom H5 was located from the difference Fourier map but constrained to ride on its parent atom. In **2**, all NH hydrogen atoms were also located from the difference Fourier map and constrained on their parent atom, with *U*_{iso} = 1.5*U*_{eq} (parent atom). Other hydrogen atoms were positioned geometrically and were constrained to ride on their parent atoms, with N–H = 0.88 Å, C–H = 0.95–0.99 Å, and *U*_{iso} = 1.2–1.5*U*_{eq} (parent atom). The crystallographic details are summarized in Table 2 and selected bond lengths and angles in Table 1.

Synthetic Work. Reaction of *cis*-[PtCl₂(NCNR₂)₂] and 1 equiv of DPG in MeNO₂. *cis*-[PtCl₂(NCNR₂)₂] (R = Me; R₂ = C₅H₁₀, C₄H₈O) (0.12 mmol) and HN=C(NHPh)₂ (25.8 mg, 0.12

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mmol) were dissolved in MeNO₂ (1.0 mL), whereupon a yellow precipitate immediately began to release. The suspension formed was left to stand at 20–25 °C for 24 h without stirring, the precipitate was filtered off, washed with one 0.5-mL portion of MeNO₂ and one 1.0-mL portion of Et₂O, and dried in air at 20–25 °C. Yields were as follows: 56 mg, 75% (**1**); 59 mg, 70% (**2**); 59 mg, 70% (**3**).

Reaction of *cis*-[PtCl₂(NCNR₂)₂] and 1 equiv of DPG in CHCl₃. *cis*-[PtCl₂(NCNR₂)₂] (R = Me; R₂ = C₅H₁₀, C₄H₈O) (0.10 mmol) and HN=C(NHPh)₂ (21.3 mg, 0.10 mmol) were dissolved in CHCl₃ (1.0 mL) and left to stand at 20–25 °C for 21 h. The reaction mixture was evaporated to dryness at 20–25 °C (R = Me; R₂ = C₅H₁₀, C₄H₈O), and the greenish-beige solid residue formed was recrystallized under a layer of one 1.5-mL portion of EtOH (R₂ = C₅H₁₀, C₄H₈O), followed by centrifugation and decantation of the solution. After that, the formed pale-yellow powder (R₂ = C₅H₁₀, C₄H₈O) was washed with one 1.5-mL portion (R₂ = C₅H₁₀) or two 1.5-mL portions (R₂ = C₄H₈O) of EtOH and one 1.5-mL portion of Et₂O (R₂ = C₅H₁₀, C₄H₈O), followed by centrifugation and decantation of washing waters, and then dried in air at 20–25 °C. In the case of R = Me, the major product was isolated in analytically pure form from the reaction mixture by column chromatography on SiO₂ (silica gel 60 F₂₅₄, 0.063–0.200 mm, Merck; eluent Me₂CO:CHCl₃ = 1:1, R_f = 0.31, second fraction). Yields were as follows: 31 mg, 53% after column chromatography (R = Me, **1**); 42 mg, 61% (R₂ = C₅H₁₀, **2**); 45 mg, 67% (R₂ = C₄H₈O, **3**).

1·½CHCl₃. Anal. Calcd for C₁₉H₂₅N₇Cl₂Pt·½CHCl₃: C, 34.59; H, 3.80; N, 14.48. Found: C, 34.62; H, 4.37; N, 13.91. ESI⁺-MS: *m/z* 1235 [2M]⁺, 1198 [2M – HCl]⁺, 635 [M + H₂O]⁺, 618 [M + H]⁺. TLC: R_f = 0.31 (eluent Me₂CO:CHCl₃ = 1:1). DTA/TG: 214 °C (gradual decomposition). IR (KBr, selected bands, cm^{−1}): 3364 (m), 3277 (m, br), ν(N–H); 3043 (m-w), ν(C–H from Ar); 2936 (m-w), 2880 (m-w), 2814 (w), ν(C–H from NMe₂); 1622 (vs), ν(C=N and C=C from Ar); 746 (m-s), 711 (m-s), 690 (m), δ(C–H from Ar). ¹H NMR (CDCl₃, δ): 7.55 (d, 2H), 7.47 (t, 4H), 7.41 (d, 2H), 7.33 (t, 1H), 7.21 (t, 1H) (Ph's), 6.97 (s, 1H), 5.96 (s, 1H) (NH), 3.11 (br), 2.76 (br), 2.69 (br), 1.74 (br, 12H) (NMe₂). ¹³C{¹H} NMR (CDCl₃, δ): 159.96, 157.84, 155.44 (C=N), 139.42, 138.89 (C_{ipso}), 130.86, 129.03, 127.85, 126.65, 125.96, 124.32 (carbons in Ph), 39.38–38.21 (group of overlapping signals) (carbons in NMe₂). Crystals of **1**·CHCl₃ suitable for an X-ray diffraction study were obtained by slow evaporation of a chlorobenzene/chloroform (1:8, v/v) solution at 20–25 °C.

2. Anal. Calcd for C₂₅H₃₃N₇Cl₂Pt: C, 43.05; H, 4.77; N, 14.06. Found: C, 43.57; H, 5.11; N, 13.87. ESI⁺-MS: *m/z* 738 [M + K + 2H]⁺, 720 [M + Na]⁺, 661.5 [M – Cl]⁺. FAB⁺-MS: *m/z* 1395 [2M + H]⁺, 1359 [2M – HCl]⁺, 1286 [2M – Cl – 2HCl]⁺, 1249 [2M + H – 4HCl]⁺, 697 [M]⁺, 662 [M – Cl]⁺, 624 [M – 2HCl]⁺. TLC: R_f = 0.52 (eluent MeOH:CHCl₃ = 1:20). DTA/TG: 175 °C (gradual decomposition). IR (KBr, selected bands, cm^{−1}): 3477 (m, br), 3360 (m-s), 3254 (m-s, br), ν(N–H); 3056 (m), ν(C–H from Ar); 2938 (m-s), 2855 (m-s), ν(C–H from NC₅H₁₀); 1619 (s, br), ν(C=N and C=C from Ar); 751 (m-s), 701 (m-s), δ(C–H from Ar). ¹H NMR (CDCl₃, δ): 7.61 (d, 1H), 7.48 (t, 4H), 7.41 (d, 3H), 7.34 (t, 1H), 7.24 (t, 1H) (Ph's), 6.98 (s, 1H), 6.00 (s, 1H) (NH), 3.80 (br), 3.40 (br), 3.16 (br), 3.04 (br), 2.39 (br), 1.58 (br), 1.49 (br), 1.36 (br), 1.20 (br), 1.08 (br), 0.53 (br), 0.43 (br), 0.10 (br, 20H) (NC₅H₁₀). ¹³C{¹H} NMR (CDCl₃, δ): 160.43, 158.25, 155.83 (C=N), 140.14, 139.75 (C_{ipso}), 130.80, 129.15, 128.21, 127.70, 126.94, 124.50 (carbons in Ph), 48.75 (br), 47.98 (br) (α-CH₂), 24.86 (br) (β-CH₂), 24.18, 23.68 (γ-CH₂) (carbons in NC₅H₁₀).

Crystals of **2**·CHCl₃ suitable for an X-ray diffraction study were obtained by slow evaporation of a benzene:chloroform (1:8, v/v) solution at 20–25 °C.

3·½CHCl₃. Anal. Calcd for C₂₃H₂₉N₇Cl₂PtO₂·½CHCl₃: C, 33.42; H, 3.49; N, 11.13. Found: C, 33.61; H, 4.01; N, 11.70. ESI⁺-MS: *m/z* 1403 [2M]⁺, 702 [M]⁺. TLC: R_f = 0.62 (eluent Me₂CO:CHCl₃ = 2:1). DTA/TG: 204 °C (gradual decomposition). IR (KBr, selected bands, cm^{−1}): 3356 (m), 3269 (m), 3244 (m), ν(N–H); 3050 (w), ν(C–H from Ar); 2969 (m-w), 2913 (m-w), 2856 (m-w), ν(C–H from NC₄H₈O); 1619 (s), ν(C=N and C=C from Ar); 750 (m), 700 (m), δ(C–H from Ar). ¹H NMR (CDCl₃, δ): 7.76 (d, br, 1H), 7.55 (t, 4H), 7.43 (t, 3H), 7.32 (t, 2H) (Ph's), 7.15 (br, 1H), 6.16 (s, 1H) (NH), 3.95 (br, 1H), 3.70 (br, 1H), 3.35 (br, 9H), 3.01 (br, 1H), 2.63 (br), 2.48 (br), 2.40 (br), 2.31 (br, 4H) (16H, NC₄H₈O). Poor solubility of this compound in all common deuterated solvents and rapid solvolysis in DMSO-*d*₆, where the complex is soluble, precluded ¹³C{¹H} NMR measurements.

Reaction of *trans*-[PtCl₂(NCNR₂)₂] and 1 equiv of DPG. *trans*-[PtCl₂(NCNR₂)₂] (R = Me; R₂ = C₅H₁₀, C₄H₈O) (0.07 mmol) and HN=C(NHPh)₂ (16 mg, 0.08 mmol) were dissolved (R = Me; R₂ = C₅H₁₀) or suspended (R₂ = C₄H₈O) in CHCl₃ (1.0 mL) to give a bright-yellow solution or a suspension and left to stand at 20–25 °C for 20 h without stirring (R = Me; R₂ = C₅H₁₀) or with stirring (R₂ = C₄H₈O), respectively, to form in each case a pale-yellow solution, which was evaporated until dryness, and the yellow solid residue formed was washed with one 4.5-mL portion of a Me₂CO:Et₂O = 1:2 mixture (R = Me) or one 1.0-mL portion of Me₂CO (R₂ = C₅H₁₀), followed by centrifugation and decantation of washing waters. After that, the formed pale-yellow (R = Me) or colorless powder (R₂ = C₅H₁₀) was washed with one 2.0-mL portion of a Me₂CO:Et₂O = 1:1 mixture (R = Me) or one 1.0-mL portion of Me₂CO (R₂ = C₅H₁₀) and one 1.5-mL portion of Et₂O (R = Me), followed by centrifugation and decantation of washing waters, and dried in air at 20–25 °C (R = Me; R₂ = C₅H₁₀). In the case of R₂ = NC₄H₈O, the colorless precipitate was centrifuged, washed with one 0.5-mL portion of Me₂CO and one 0.5-mL portion of Et₂O, followed by centrifugation and decantation of washing waters, and dried in air at 20–25 °C. The yield was 5 mg (bis-chelate **9**). Then, the washing waters and the filtrates were combined and kept in air for evaporation of the solvent until dryness, and the pale-yellow solid residue formed was washed with one 1.0-mL portion of Me₂CO, followed by centrifugation and decantation of washing waters. After that, the pale-yellow powder formed was washed with one 0.2-mL portion of Me₂CO and one 0.2-mL portion of Et₂O, followed by centrifugation and decantation of washing waters, and dried in air at 20–25 °C. The washing waters and the filtrates were combined, and one 5.0-mL portion of Et₂O was added to the pale-yellow solution formed. The released pale-yellow precipitate was centrifuged, washed with one 2.0-mL portion of a Me₂CO:Et₂O = 1:1 mixture and one 2.0-mL portion of Et₂O, followed by centrifugation and decantation of washing waters, and dried in air at 20–25 °C and combined with the first fraction. Yields were as follows: 22 mg, 50% (**4**); 20 mg, 41% (**5**); 28 mg, 58% (**6**).

4·⅓CHCl₃. Anal. Calcd for C₁₉H₂₅N₇Cl₂Pt·⅓CHCl₃: C, 35.33; H, 3.89; N, 14.92. Found: C, 35.12; H, 4.57; N, 14.72. ESI⁺-MS: *m/z* 1199 [2M – Cl]⁺, 1162 [2M – 2HCl]⁺, 1128 [2M – 3Cl]⁺, 582 [M – Cl]⁺. DTA/TG: 141 °C (gradual decomposition). IR (KBr, selected bands, cm^{−1}): 3375 (m), ν(N–H); 3150 (m), ν(N–H and/or C–H from Ar); 3094 (m), 3050 (m), ν(C–H from Ar); 2963 (m), 2925 (m), 2813 (m-w), ν(C–H from NMe₂); 2295 (s), ν(C≡N); 1646 (vs), 1594 (s), ν(C=N and/or C=C from Ar); 756 (m), 694 (m), δ(C–H from Ar). ¹H NMR (CDCl₃, δ): 10.28 (br, H₂N–CN(Ph)), 8.30 (d, 2H), 7.50 (t, 2H), 7.41 (t, 3H), 7.27 (t,

1H), 7.17 (d, 1H) (Ph's), 5.67 (s, Pt–NH=C), 3.04 (s, 6H), 3.01 (s, 0.5H), 2.98 (s, 0.5H), 2.58 (s, 5H) (NMe₂). ¹³C{¹H} NMR (CDCl₃, δ): 157.50, 154.73 (C=N), 144.67, 140.72 (C_{ipso}), 130.07, 129.81, 128.88, 127.81, 127.21, 125.92 (carbons in Ph), 39.90 (HN=CNMe₂), 39.51 (N≡CNMe₂) (carbons in NMe₂).

The washing waters and filtrates were combined and kept in air for evaporation of the solvent until dryness. The pale-yellow solid residue formed was dissolved in one 1.0-mL portion of Me₂CO, whereupon one 5.0-mL portion of Et₂O was added to the pale-yellow solution. The released pale-yellow precipitate was centrifuged, washed with one 2.0-mL portion of a Me₂CO:Et₂O = 1:1 mixture and one 2.0-mL portion of Et₂O, followed by centrifugation and decantation of washing waters, and dried in air. The yield was 9 mg, 20%. The ¹H NMR spectrum for this portion is reported below and indicates that it contains at least two compounds including complex **4**.

¹H NMR (CDCl₃, δ): 11.33 (br), 10.45 (br) (H₂NCN(Ph)), 8.34 (d, 1H), 7.89 (br, 2H, NH), 7.53 (t, 1H), 7.45–7.37 (m, 4H), 7.32–7.24 (m, 2H), 7.17 (t, 2H) (Ph's), 5.90 (s), 5.62 (s) (Pt–NH=C), 3.07 (s, 3H), 3.04 (s, 3H), 3.01 (s, 3H), 2.60 (s, 3H) (NMe₂, the ratio of compounds obtained by ¹H NMR integration of signals corresponding to NMe protons is ca. 1:1). Assignment of the signals will be done by application of ¹H–¹³C HETCOR and 1D NOE NMR experiments.

5. Anal. Calcd for C₂₅H₃₃N₇Cl₂Pt: C, 43.05; H, 4.77; N, 14.06. Found: C, 43.45; H, 5.03; N, 14.29. ESI⁺-MS: *m/z* 662 [M – Cl]⁺. TG curve: mass loss is 11.8% at 131 °C (calcd mass loss for –HNC₅H₁₀ is 12.2%). IR (KBr, selected bands, cm^{–1}): 2937 (m-s), 2856 (m), ν(C–H from NC₅H₁₀); 2285 (s), 2208 (m-w), ν(C≡N); 1639 (vs, br), ν(C=N and C=C from Ar); 748 (m), 697 (m), δ(C–H from Ar). ¹H NMR (CDCl₃, δ): 10.27 (s, br, H₂N–CN(Ph)), 8.35 (d, 2H), 7.53 (t, 2H), 7.46–7.42 (t + t, 3H), 7.28 (t, 1H), 7.21 (d, 2H) (Ph's), 5.71 (s, Pt–NH=C), 3.50 (br), 3.39–3.36 (m), 2.86 (s, 4H), 1.93 (s, 3H), 1.68 (br, m), 1.60 (br, m), 1.43 (br), 1.20 (br) (NCNC₅H₁₀). ¹³C{¹H} NMR (CDCl₃, δ): 157.89, 155.17 (C=N), 145.10, 141.99 (C_{ipso}), 130.38, 130.13, 129.27, 128.15, 128.04, 126.41 (carbons in Ph), 49.66 (α-CH₂), 25.15 (β-CH₂ in HN=CNC₅H₁₀), 24.76 (β-CH₂ in N≡CNC₅H₁₀), 24.00 (γ-CH₂ in HN=CNC₅H₁₀), 22.69 (γ-CH₂ in N≡CNC₅H₁₀) (carbons in NC₅H₁₀).

6·¹/₄CHCl₃. Anal. Calcd for C₂₃H₂₉N₇Cl₂PtO₂·¹/₄CHCl₃: C, 34.24; H, 3.58; N, 11.53. Found: C, 34.83; H, 3.94; N, 11.71. ESI⁺-MS: *m/z* 666 [M – Cl]⁺. DTA/TG: 150 °C (gradual decomposition). IR (KBr, selected bands, cm^{–1}): 3050 (m-w), ν(C–H from Ar); 2963 (m-w), 2919 (m-w), 2906 (m-w), 2850 (m-w), ν(C–H from NC₄H₈O); 2288 (m-w), ν(C≡N); 1638 (s), 1594 (s), 1563 (s), ν(C=N and/or C=C from Ar); 756 (m), 700 (m), δ(C–H from Ar). ¹H NMR (CDCl₃, δ): 8.30 (d, 1H), 7.56 (t, 2H), 7.49–7.43 (t + t or t + d, 4H), 7.38–7.24 (m, 3H) (Ph's), 5.84 (s, br, Pt–NH=C), 3.79 (t, 1H), 3.75 (t, 1H), 3.69 (t, 2H), 3.58 (t, 4H), 3.49 (t, 1H), 3.38 (t, 2H), 3.31 (br, 2H), 3.25 (t, 1H), 2.95 (t, 2H) (NCNC₄H₈O). ¹³C{¹H} NMR (CDCl₃, δ): 157.59, 154.54 (C=N), 144.58, 141.17 (C_{ipso}), 130.28, 130.08, 129.93, 127.97, 127.27, 126.01 (carbons in Ph), 65.52, 65.26 (OCH₂), 47.92, 47.64 (NCH₂) (carbons in NC₄H₈O).

Reaction of *trans*-[PtCl₂(NCNR₂)₂] and 2 equiv of DPG in CHCl₃. *trans*-[PtCl₂(NCNR₂)₂] (R = Me; R₂ = C₅H₁₀, C₄H₈O) (0.09 mmol) and HN=C(NHPh)₂ (0.040 mg, 0.19 mmol) were dissolved in CHCl₃ (1 mL) and left to stand at 20–25 °C for 20 h. The pale-yellow solution was evaporated to dryness, and the pale-yellow solid residue formed was washed with one 1.0-mL portion of Me₂CO (R = Me; R₂ = C₅H₁₀) to form the colorless precipitate, which was filtered off, washed with one 1.0-mL portion of Me₂CO and one 1.0-mL portion of Et₂O (R = Me, R₂ = C₅H₁₀), and dried

in air at 20–25 °C. Slow evaporation of the reaction mixture (R₂ = C₄H₈O) for 48 h at 20–25 °C gave colorless crystals. The colorless crystals formed were separated from the pale-yellow oily residue by washing with one 0.5-mL portion of CHCl₃, followed by decantation, washing with two 0.25-mL portions of CHCl₃, and drying in air at 20–25 °C. Yields were as follows: 12 mg, 17% (**7**); 29 mg, 36% (**8**); 12 mg, 14% (**9**).

Reaction of *trans*-[PtCl₂(NCNR₂)₂] and 2 equiv of DPG in MeNO₂. *trans*-[PtCl₂(NCNR₂)₂] (R = Me; R₂ = C₅H₁₀, C₄H₈O) (0.08 mmol) and HN=C(NHPh)₂ (0.037 mg, 0.17 mmol) were dissolved in MeNO₂ (1 mL) and left to stand at 20–25 °C for 48 h. The colorless precipitate that was formed was separated by filtration, washed with one 1.0-mL portion of MeNO₂ (R = Me; R₂ = C₅H₁₀, C₄H₈O), two 1.0-mL portions of CHCl₃ (R₂ = C₅H₁₀), and one 1.0-mL portion of Et₂O (R = Me; R₂ = C₅H₁₀, C₄H₈O), and dried in air at 20–25 °C. Yields were as follows: 13 mg, 19% (**7**); 23 mg, 32% (**8**); 15 mg, 20% (**9**).

7·³/₄CHCl₃. Anal. Calcd for C₃₂H₃₈N₁₀Cl₂Pt·³/₄CHCl₃: C, 42.84; H, 4.25; N, 15.25. Found: C, 42.81; H, 4.97; N, 15.48. ESI⁺-MS: *m/z* 757 [M – Cl – HCl]⁺. DTA/TG: 201 °C (dec). IR (KBr, selected bands, cm^{–1}): 3421 (m-s), 3265 (m-s), 3107 (m-s), ν(N–H); 1632 (vs), 1585 (s), ν(C=N and C=C from Ar); 752 (m), 698 (m), δ(C–H from Ar). ¹H NMR (CD₃OD, δ): 7.61 (t, 4H), 4.54–7.44 (m, 6H), 7.38 (t, 2H), 7.32 (d, 4H), 7.27 (d, 4H) (Ph's), 2.98 (s, 1H), 2.61 (s, 11H) (NMe₂). ¹³C{¹H} NMR (CD₃OD, δ): 157.89, 156.12 (C=N), 145.58, 141.59 (C_{ipso}), 131.35, 131.10, 130.31, 126.94, 123.98, 122.84 (Ph carbons), 38.98 (NMe₂).

In the case when the reaction is performed in MeNO₂, the washing waters and the filtrates were combined and kept in air at 20–25 °C for slow evaporation of the solvent until dryness. The yellow oily residue formed was dissolved in MeNO₂ (0.25 mL), whereupon Et₂O (2 mL) was added to the yellow solution formed. The released pale-yellow precipitate was centrifuged, washed with one 3.50-mL portion of a MeNO₂:Et₂O = 1.0:6.0 mixture and one 1.0-mL portion of Et₂O, followed by centrifugation and decantation of washing waters, and dried in air at 20–25 °C. The yield was 36 mg, 55%. The ¹H NMR spectrum for this portion is reported below, and it indicates that the mixture contains, besides **7**, at least two more compounds.

¹H NMR (CD₃OD, δ): 7.79 (d, 1H), 7.72 (d, 1H), 7.62 (t, 2H), 7.55–7.45 (m, 9H), 7.41–7.27 (m, 7H) (Ph's), 3.04 (s), 3.02 (s), 3.00 (s), 2.96 (s), 2.89 (s), 2.63 (s) (12H, NMe, the ratio of compounds obtained by ¹H NMR integration of signals corresponding to NMe protons is ca. 1.5:1.0:3.0).

Slow evaporation of the reaction mixture (CHCl₃) to ¹/₃ of the starting volume for 1 day at 20–25 °C gave colorless crystals, which were characterized by X-ray crystallography. These crystals were separated from the pale-yellow solution by decantation, washed with three 0.2-mL portions of CHCl₃, and dried in air at 20–25 °C. The yield was 12 mg, 16%.

When the reaction was performed in CHCl₃, the washing waters and the filtrates were combined and kept in air at 20–25 °C for slow evaporation of the solvent until dryness, the pale-yellow solid residue formed was dissolved in Me₂CO (2 mL), whereupon Et₂O (3 mL) was added to the pale-yellow solution formed. The released colorless precipitate was centrifuged, washed with one 2-mL portion of a Me₂CO:Et₂O = 2:3 mixture, followed by centrifugation and decantation of washing waters, and dried in air at 20–25 °C. The yield was 30 mg, 40%. ¹H and ¹³C{¹H} NMR spectra for this portion are reported below and indicate that it contains, besides **7**, at least two more compounds.

¹H NMR (CD₃OD, δ): 7.77 (d, 1H), 7.70 (d, 1H), 7.60 (t, 2H), 7.56–7.44 (m, 10H), 7.41 (d, 1H), 7.38–7.35 (m, 3H), 7.31 (d,

2H), 7.26 (d, 1H) (Ph's), 3.02 (s), 2.98 (s), 2.61 (s) (12H, NMe, the ratio of compounds obtained by ^1H NMR integration of signals corresponding to NMe protons is ca. 2.0:1.0:2.0). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_3OD , δ): 159.26, 158.72, 158.61, 157.86, 157.23, 156.23 (C=N), 145.32, 142.76, 142.22, 142.17, 137.74, 137.52, 136.38 (C_{ipso}), 131.77, 131.50, 131.34, 131.25, 131.20, 131.19, 131.12, 131.06, 129.57, 129.45, 129.16, 128.62, 128.27, 128.19, 127.78, 126.91, 126.77, 126.27, 125.82, 125.58, 124.89, 124.26, 123.75, 122.89 (carbons in Ph), 39.86, 39.56, 39.29 (NMe_2).

8· $\frac{1}{2}\text{CHCl}_3$. Anal. Calcd for $\text{C}_{38}\text{H}_{46}\text{N}_{10}\text{Cl}_2\text{Pt}\cdot\frac{1}{2}\text{CHCl}_3$: C, 47.69; H, 4.94; N, 14.45. Found: C, 47.71; H, 5.55; N, 14.32. $\text{ESI}^+\text{-MS}$: m/z 837 $[\text{M} - \text{Cl} - \text{HCl}]^+$. $\text{FAB}^+\text{-MS}$: m/z 872 $[\text{M} - \text{HCl}]^+$, 837 $[\text{M} - \text{Cl} - \text{HCl}]^+$. DTA/TG: 168 °C (dec). IR (KBr, selected bands, cm^{-1}): 3625 (m-w), 3365 (m), $\nu(\text{N-H})$; 3100 (m-s), 3059 (m-s), $\nu(\text{N-H}$ and/or C-H from Ar); 2941 (m-s), 2859 (m), $\nu(\text{C-H}$ from NC_5H_{10}); 1634 (s, br), $\nu(\text{C=N}$ and C=C from Ar); 748 (m), 697 (m), $\delta(\text{C-H}$ from Ar). ^1H NMR ($\text{DMSO}-d_6$, δ): 8.96 (s, br) (NH), 7.58 (t, 4H), 7.49 (t, 4H), 7.40 (d, 4H), 7.35 (t, 4H), 7.29 (d, 4H) (20H, Ph's), 3.54 (br), 2.88 (br), 2.73 (br), 2.27 (br), 1.42 (br), 1.27 (br), 0.47 (br) (20H, NC_5H_{10}). ^1H NMR (CD_3OD , δ): 7.64 (t, 4H), 7.55 (t, 4H), 7.49–7.42 (t + t, 8H), 7.37 (d, 4H) (20H, Ph's), 3.47 (br), 2.97 (br), 1.52 (br), 1.38 (br), 1.31 (s), 0.91 (br), 0.73 (br) (20H, NC_5H_{10}). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_3OD , δ): 156.49, 155.27 (C=N), 144.68, 141.27 (C_{ipso}), 130.39, 130.01, 128.14, 127.72, 125.98, 123.84 (carbons in Ph), 48.20 ($\alpha\text{-CH}_2$), 24.78 ($\beta\text{-CH}_2$), 23.59 ($\gamma\text{-CH}_2$) (carbons in NC_5H_{10}).

Slow evaporation of the reaction mixture (CHCl_3) to $\frac{1}{3}$ of the starting volume for 1 day at 20–25 °C gave colorless crystals; the latter were characterized by X-ray crystallography. The colorless crystals formed were separated from the pale-yellow solution by decantation, washed with three 0.2-mL portions of CHCl_3 , and dried in air at 20–25 °C. The yield was 29 mg, 35%.

9. Anal. Calcd for $\text{C}_{36}\text{H}_{42}\text{N}_{10}\text{Cl}_2\text{PtO}_2$: C, 47.37; H, 4.64; N, 15.35. Found: C, 46.71; H, 5.08; N, 15.95. $\text{ESI}^+\text{-MS}$: m/z 876 $[\text{M} - \text{HCl}]^+$, 840 $[\text{M} - 2\text{HCl}]^+$, 764 $[\text{M} - 2\text{Cl} - \text{PhH}]^+$. DTA/TG: 217 °C (dec). IR (KBr, selected bands, cm^{-1}): 3409 (m), 3068 (m), $\nu(\text{N-H}$ and/or C-H from Ar); 2961 (m), 2926 (m), 2849 (m), $\nu(\text{C-H}$ from $\text{NC}_4\text{H}_8\text{O}$); 1637 (vs), 1595 (s), $\nu(\text{C=N}$ and C=C from Ar); 751 (m-s), 695 (m-s), $\delta(\text{C-H}$ from Ar). ^1H NMR (CD_3OD , δ): 7.64 (t, 4H), 7.58 (t, 4H), 7.51–7.43 (m, 8H), 7.38 (d, 4H) (20H, Ph's), 2.98 (br, 16H, $\text{NC}_4\text{H}_8\text{O}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_3OD , δ): 156.78, 155.20 (C=N), 144.58, 140.98 (C_{ipso}), 130.46, 130.23, 128.20, 128.03, 126.04, 123.69 (carbons in Ph), 65.35 (OCH_2), 47.51 (NCH_2) (carbons in $\text{NC}_4\text{H}_8\text{O}$).

When the reaction was performed in chloroform, slow evaporation of the reaction mixture to $\frac{1}{3}$ of the starting volume for 48 h at 20–25 °C gave colorless crystals. These crystals were separated from the pale-yellow oily residue by washing with one 0.5-mL portion of CHCl_3 with decantation and two 0.25-mL portions of CHCl_3 and drying in air at 20–25 °C. The yield was 12 mg, 14%. Complex **9** crystallizes as a **9**·2MeOH solvate from the reaction mixture (CHCl_3) upon the addition of MeOH (0.2 mL).

In the case when the reaction is performed in CHCl_3 , the washing waters were evaporated to dryness, and the pale-yellow solid residue formed was washed with one 1.0-mL portion of a $\text{Me}_2\text{CO}:\text{Et}_2\text{O} = 1:1$ mixture ($\text{R}_2 = \text{C}_4\text{H}_8\text{O}$) to form the colorless precipitate, which was filtered off, washed with three 0.8-mL portions of a $\text{Me}_2\text{CO}:\text{Et}_2\text{O} = 1:1$ mixture ($\text{R}_2 = \text{C}_4\text{H}_8\text{O}$), and dried in air at 20–25 °C. The yield was 46 mg, 56%. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra for this portion are reported below and indicate that it contains, besides **9**, at least two more compounds.

^1H NMR (CD_3OD , δ): 7.92 (d), 7.83 (t), 7.63 (t), 7.59–7.53 (m), 7.51–7.44 (m), 7.41–7.33 (m), 7.27 (t), 7.21–7.11 (m) (20H,

Ph's), 4.58 (s, br), 3.64 (t), 3.59 (br), 3.50 (t), 3.46–3.34 (m), 3.27 (t), 3.15 (br), 2.97 (br), 2.83 (br) (16H, $\text{NC}_4\text{H}_8\text{O}$). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_3OD , δ): 158.49, 158.27, 157.77, 156.93, 156.38, 156.15, 156.06 (C=N), 145.58, 145.55, 143.57, 143.10, 142.51, 142.50, 141.97, 138.36, 137.74, 136.44 (C_{ipso}), 131.46, 131.33, 131.22, 131.20, 131.16, 131.14, 131.05, 130.36, 129.94, 129.17, 129.04, 128.58, 128.28, 127.95, 127.66, 127.04, 126.53, 126.24, 125.28, 124.81, 124.09, 123.54, 123.34 (carbons in Ph), 67.81, 67.55, 66.88, 66.74, 66.44, 66.34 (OCH_2), 46.13, 45.27 (NCH_2).

Synthesis of *cis*-[PtCl₂(NCNC₄H₈O)₂]. A synthetic experiment was performed in accordance with the previously reported method for the preparation of *cis*-[PtCl₂(C₆H₅CH₂CN)₂].⁴⁶ Thus, the clathrate $\text{Pt}_6\text{Cl}_{12}\cdot 0.1\text{C}_2\text{H}_5\text{Cl}\cdot 5.7\text{H}_2\text{O}$ (0.07 mmol) was placed into a 10-mL flask thermostated at 100 °C, and 1 mL (9.9 mmol) of $\text{NCNC}_4\text{H}_8\text{O}$ also heated to 100 °C was added. The mixture was kept at 100 °C for 2 min, whereupon the warm solution was filtered off from some undissolved material. The greenish-yellow filtrate was cooled to 20–25 °C and crystallized under a layer of Et_2O (15 mL) to form the solid beige powder, which was separated by filtration, washed with three 3-mL portions of Et_2O , and dried in air at 20–25 °C. At 100 °C, the complex was released as a mixture of *cis* and *trans* isomers in ca. 2.7:1.0 ratio (by ^1H NMR integration). The pure *cis* isomer was obtained from the *cis*/*trans* mixture by column chromatography on SiO_2 (silica gel 60 F₂₅₄, 0.063–0.200 mm, Merck; eluent $\text{Me}_2\text{CO}:\text{CHCl}_3 = 1:1$, $R_f = 0.47$, second fraction). The yield was 83 mg, 38%.

***cis*-[PtCl₂(NCNC₄H₈O)₂] $\cdot\frac{1}{9}\text{NCNC}_4\text{H}_8\text{O}\cdot\text{H}_2\text{O}$** . Anal. Calcd for $\text{C}_{10}\text{H}_{16}\text{N}_4\text{Cl}_2\text{PtO}_2\cdot\frac{1}{9}\text{NCNC}_4\text{H}_8\text{O}\cdot\text{H}_2\text{O}$: C, 24.37; H, 3.66; N, 11.37. Found: C, 24.33; H, 3.51; N, 11.12. $\text{ESI}^+\text{-MS}$: m/z 508 $[\text{M} + \text{H}_2\text{O}]^+$, 491 $[\text{M} + \text{H}]^+$. TLC: $R_f = 0.47$ (eluent $\text{Me}_2\text{CO}:\text{CHCl}_3 = 1:1$). IR (KBr, selected bands, cm^{-1}): 2968 (m-w), 2927 (m-w), 2858 (m-w), $\nu(\text{C-H}$ from $\text{NC}_4\text{H}_8\text{O}$); 2295 (m-s), $\nu(\text{C}\equiv\text{N})$. ^1H NMR (CDCl_3 , δ): 3.79 (t, 4H, $J = 4.89$ Hz, OCH_2), 3.47 (t, 4H, $J = 4.89$ Hz, NCH_2). Poor solubility of this compound in all common deuterated solvents and rapid solvolysis in $\text{DMSO}-d_6$, where the complex is soluble, precluded $^{13}\text{C}\{^1\text{H}\}$ NMR measurements.

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Supporting Information Available: Description of solution dynamic processes for **1–3**, detailed description of X-ray structures of **1**· CHCl_3 and **2**· CHCl_3 , Tables S2–S4 giving selected bond lengths, total energies, enthalpies, and Gibbs free energies of the calculated structures and reaction energies, Scheme S1 depicting reactions considered theoretically, Figure S7 giving equilibrium geometries of the calculated structures, and Figure S8 giving calculated thermodynamic energy profiles. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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