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Amidrazone Complexes from a Cascade Platinum(II)-Mediated Reaction between Amidoximes and Dialkylcyanamides

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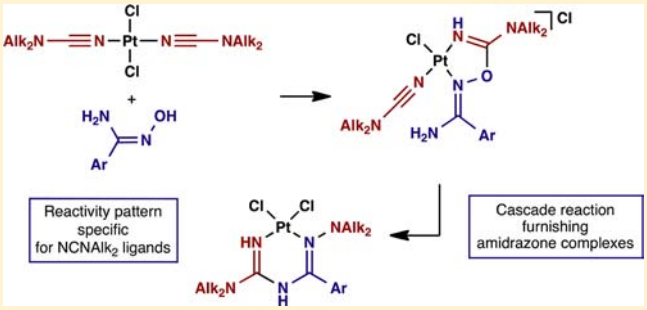
Supporting Information

ABSTRACT: The aryl amidoximes $R'C_6H_4C(NH_2)$═NOH (R′ = Me, **2a**; H, **2b**; CN, **2c**; NO_2, **2d**) react with the dialkylcyanamide platinum(II) complexes *trans*-$[PtCl_2(NCNAlk_2)_2]$ (Alk_2 = Me_2, **1a**; C_5H_{10}, **1b**) in a 1:1 molar ratio in $CHCl_3$ to form chelated *mono*-addition products [**3a**–**h**]Cl, viz. $[PtCl(NCNAlk_2)\{\underline{N}H{=}C(NR_2)O\underline{N}{=}C(C_6H_4R')NH_2\}]Cl$ (Alk_2 = Me_2; R′ = Me, **a**; H, **b**; CN, **c**; NO_2, **d**; Alk_2 = C_5H_{10}; R′ = Me, **e**; H, **f**; CN, **g**; NO_2, **h**). In the solution, these species spontaneously transform to the amidrazone complexes $[PtCl_2\{\underline{N}H{=}C(NR_2)NC(C_6H_4R')\underline{N}NH_2\}]$ (**7a**–**h**; 36–47%); this conversion proceeds more selectively (49–60% after column chromatography) in the presence of the base $(PhCH_2)_3N$. The observed reactivity pattern is specific for $NCNAlk_2$ ligands, and it is not realized for conventional alkyl- and arylnitrile ligands. The mechanism of the cascade reaction was studied by trapping the isocyanate intermediates $[PtCl(NCO)\{\underline{N}H{=}C(NR_2)NC(C_6H_4R')\underline{N}NH_2\}]$ (**5a**–**h**) and also by ESI-MS identification of the ammonia complexes $[PtCl(NH_3)\{\underline{N}H{=}C(NR_2)NC(C_6H_4R')\underline{N}NH_2\}]^+$ ([**6a**–**h**]$^+$) in solution. The complexes [**3a**]Cl, [**3c**–**h**]Cl, **5a**–**h** and **7a**–**h** were characterized by elemental analyses, high resolution ESI-MS, IR, and ^{1}H NMR techniques, while **5b**, **5d**, **5g**, **7b**, and **7e** were also studied using single-crystal X-ray diffraction.



INTRODUCTION

In view of the general interest in ligand reactivity and organic transformations involving metal complexes,[1] we have focused our attention on reactions of metal-activated nitriles. This fascinating area of research has been repeatedly reviewed along the years by some of us[2] and other researchers.[3] In particular, we have observed additions of various ketoximes, aldoximes, *vic*-dioximes, and functionalized oximes to nitriles at Pt^{II}, Pt^{IV}, Pd^{II}, Ni^{II}, Rh^{III}, and Re^{IV} centers (see refs 2b and 4 and references therein). It is worthwhile mentioning that although the addition of oximes to (nitrile)[M] species in the beginning of the project had purely basic interest, later it provided a strong background for practical implications such as facile syntheses of phthalocyanines,[5] efficient Zn^{II}-catalyzed hydration of NCR species,[6] generation of various 1,3,5-triazapentadiene systems,[7] and synthesis of amidines under neutral Co^{II}-mediated conditions.[8]

Despite the wealth of chemistry associated with the nucleophilic addition of the oxime functionality HON═C to the so-called conventional NCR ligands (R = alkyl, aryl), only a few works[4] explored metal-bound dialkylcyanamides, $NCNAlk_2$, as substrates for the addition. These reports indicate substantial distinctions in the reaction rates and the nature of products formed,[4] and it means that these variances were recognized not only at the *quantitative*[9] but also at the *qualitative* level when dialkylcyanamide and conventional nitrile ligands react with the same reagent in absolutely different ways giving and, consequently, different products.[10]

Thus, we recently studied the platinum(IV)-mediated addition of $PhC(NH_2)$═NOH to dimethylcyanamide ligands in complex **A1** (Scheme 1), and observed an unusual conversion of the iminoacylated amidoxime in **B1** giving—after the intermolecular coupling with the nitrile group—chelate **C1** featuring the new tridentate ligand.[4a] As an amplification of that project, we attempted to carry out a similar transformation at a platinum(II) center and, to our surprise, found that the iminoacylated oximes easily convert to metal-bound functionalized amidrazones (IUPAC name:[11] carbamimidoylhydrazonamides; see Scheme 2 later) providing simple synthesis of these species. Insofar as such conversions are not known and, moreover, amidrazones[12] were never obtained by this or any other method that utilizes dialkylcyanamides and amidoximes, we conducted a systematic study uncovering this chemistry, and

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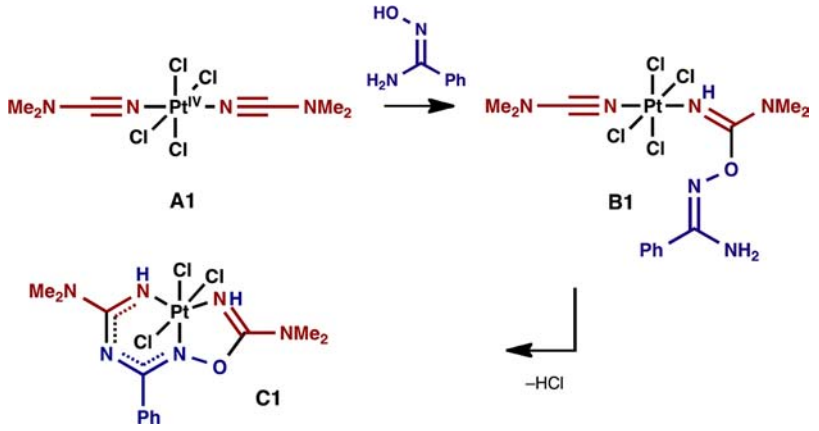
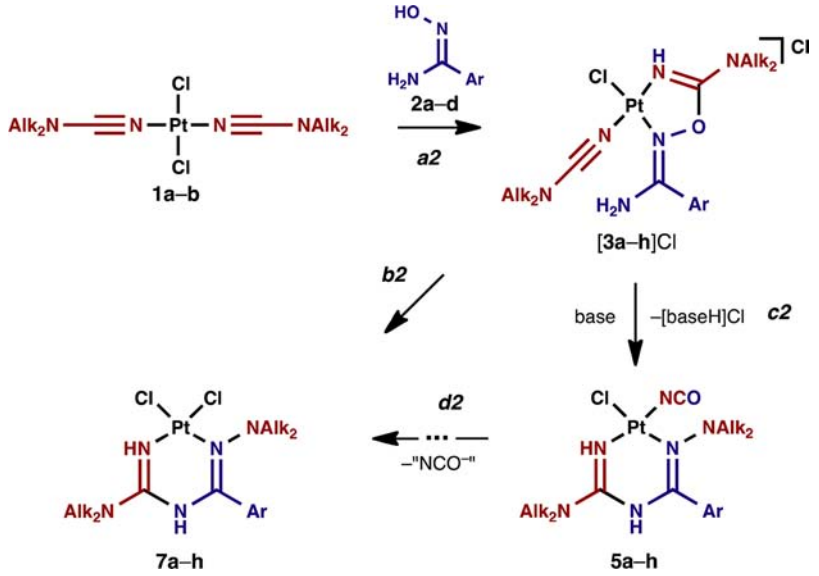
Scheme 1. Transformations of the *mono*-Addition Products of Benzamidoxime−Dimethylcyanamide Coupling



Scheme 2. Nucleophilic Addition of Amidoximes to Nitrile Platinum Complexes and Further Transformations of [3a−h]Cl to Amidrazone Complexes 5a−h and 7a−h



our results are reported in this work. The scenario of our experiments was the following. We, first, extended the Pt^{II}-mediated formation of amidrazone ligands to a different combination of dialkylcyanamides and amidoximes; second, we investigated the reaction pathway by trapping intermediates and proposed the mechanism of the reaction. The description follows these lines.

RESULTS AND DISCUSSION

As the starting materials for studying the platinum(II)-mediated generation of the amidrazones, we addressed, on one hand, the dialkylcyanamide platinum(II) complexes *trans*-[$PtCl_2$-$(NCNAlk_2)_2$] (Alk_2 = Me_2, **1a**; C_5H_{10}, **1b**) and, on the other hand, the amidoximes *p*-R′$C_6H_4C(NH_2)$=NOH (R′ = Me, **2a**; H, **2b**; CN, **2c**; NO_2, **2d**). Reaction between complexes **1a,b** and amidoximes **2a−d** (in all possible combinations) at 40 °C in a 1:1 molar ratio in $CHCl_3$ followed by the addition of 1 equiv of the base $(PhCH_2)_3N$ with the further addition of 1 equiv of an acid (*p*-$MeC_6H_4SO_3H$, abbreviated as PTSA) results in the formation of amidrazone complexes **7a−h** that were isolated in 49−60% yields after column chromatography.

Reaction between the *trans*-(Dialkylcyanamide)Pt^{II} Complexes and 1 equiv of Aryl Amidoximes. Aryl amidoximes **2a−d** react with dialkylcyanamide platinum(II) complexes **1a,b** (in all possible combinations) in a 1:1 molar ratio for 5 min at RT to form chelated *mono*-addition products [**3a−h**]Cl (Scheme 2, ***a2***). The reaction proceeds similarly to that described in our previous work,[4b] and [**3a**]Cl·$2H_2O$ and [**3c−h**]Cl·$2H_2O$ were isolated and characterized by CHN analyses, high-resolution ESI^+-MS, IR, and ^1H NMR. Complex [**3b**]Cl·$2H_2O$ was characterized previously.[4b]

The reaction of complexes **1a,b** with *p*-$Me_2NC_6H_4C(NH_2)$=NOH proceeds differently. Thus, the interplay between these reactants for 10 min at either RT or even at 0 °C leads to a broad spectrum of yet unidentified products. This observation can be explained in terms of the strong *M*+ effect of the dimethylamino group in *p*-$Me_2NC_6H_4C(NH_2)$=NOH, which increases the nucleophilicity of the amidoxime moiety and makes reaction ***a2*** (Scheme 2) less selective.

We found that [**3a−h**]Cl in the solution spontaneously transform to furnish amidrazone complexes **7a−h** (Table 1). This cascade transformation proceeds for 26 h at 40 °C or for 5 days at RT in a chloroform solution to accomplish **7a−h**, and the latter species were isolated in 36−47% yields (Scheme 2, ***b2***) by column chromatography on silica gel. The reaction mixture also contains a broad spectrum of yet unidentified products, and this explains the rather low yields of **7a−h**. The reaction also

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Table 1. Literal Abbreviations for Complexes [3]Cl−7

nos.	Alk_2	Ar
[**3a**]Cl−**7a**	Me_2	C_6H_4Me-*p*
[**3b**]Cl−**7b**	Me_2	C_6H_5
[**3c**]Cl−**7c**	Me_2	C_6H_4CN-*p*
[**3d**]Cl−**7d**	Me_2	$C_6H_4NO_2$-*p*
[**3e**]Cl−**7e**	C_5H_{10}	C_6H_4Me-*p*
[**3f**]Cl−**7f**	C_5H_{10}	C_6H_5
[**3g**]Cl−**7g**	C_5H_{10}	C_6H_4CN-*p*
[**3h**]Cl−**7h**	C_5H_{10}	$C_6H_4NO_2$-*p*

takes place in nitromethane, dichloromethane, and acetone but gives **7a−h** in lower yields than that conducted in chloroform.

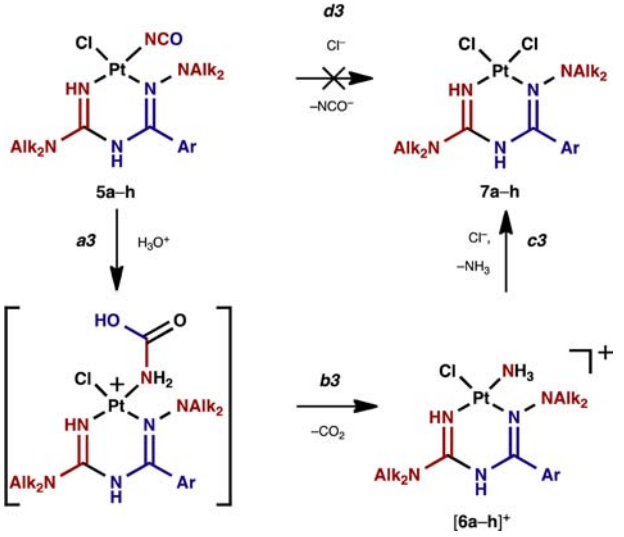
As far as the driving forces of the cascade reaction are concerned, no reaction between any of **2a−d** and dimethylcyanamide in $CDCl_3$ was observed for 7 days at room temperature. These blank experiments suggest that the nucleophilic addition of the amidoximes to the $NCNAlk_2$ and further transformations are Pt^{II}-mediated.

Reaction between [3a−h]Cl and 1 equiv of Base. The addition of 1 equiv of the base $(PhCH_2)_3N$ to a solution of any of [**3a−h**]Cl results in substantial acceleration of the conversion. On the contrary, the addition of 1 equiv of PTSA completely inhibits the transformation of [**3a−h**]Cl. The reaction pathway suggests participation of the *deprotonated amide* moiety in the second nucleophilic addition, and therefore, for this purpose we use base as the promoter. The same reaction without the addition of a base proceeds much slower and less selective. Thus, 1 equiv $(PhCH_2)_3N$ promotes the conversion of [**3a−h**]Cl to **5a−h** by abstraction of HCl (Scheme 2, ***c2***). The reaction proceeds for 1 h at 40 °C accomplishing **5a−h** that were isolated in 74−87% yields. When 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU) was used as the dehydrochlorinating agent, yields of **5a−h** decrease to ca. 45%, and these species are generated along with a broad spectrum of unidentified products. Compounds **5a−h** are stable in the presence of $(PhCH_2)_3N$ but decompose in the presence of acids, e.g. PTSA or acetic acid. Although we did not observe the generation of complexes **4** (see Scheme 5 later), we believe based on our earlier observations, however, that the reaction proceeds via the formation of the tridentate ligand (see Scheme 1 and discussion later).

Acid-Catalyzed Hydrolysis of the Coordinated Cyanate in 5a−h. *Reaction between **5a−h** and 1 equiv of an Acid.* Upon investigation of reaction ***b2*** (Scheme 2) by ESI-MS, in the spectra of the reaction mixtures, we observed the signals of the molecular ions of both cyanate **5a−h** and ammonia $[\mathbf{6a-h}]^+$ (Scheme 3) complexes and suggested that these species are derived from the hydrolysis. Therefore, we decided to obtain the ammonia complexes selectively, by the addition of an acid, and to study their further conversions to get more data supporting the mechanism of the amidrazone generation.

Thus, addition of 1 equiv of PTSA to undried nitromethane−methanol (1:1, v/v) solution of **5a−h** at RT for 10 min leads to the generation of cationic ammonia complexes [**6a−h**]-(*p*-$MeC_6H_4SO_3$) formed via the hydrolysis of the coordinated cyanate (Scheme 3, ***a3*** and ***b3***; see Table 2S in the Supporting Information for characteristic peaks of [**6a−h**](*p*-$MeC_6H_4SO_3$)). The reaction also proceeds with AcOH as an acid, but use of the solid PTSA is more convenient from the synthetic viewpoint. Compounds [**6a−h**](*p*-$MeC_6H_4SO_3$) are rather unstable, and they were detected *in situ* by ESI^+-MS. It is worthwhile mentioning that facile acid-promoted hydrolysis of *N*-bound

Scheme 3. Mechanism of the Cyanate to Chloride Substitution



cyanates is well-known, and it was previously explored at Re^{I},[13] Ru^{II},[14] Ru^{III},[15] Co^{III},[16] Rh^{III},[15,17] and Pt^{II}[18] metal centers. It is generally believed that the hydrolysis proceeds via the protonation of the ligated cyanate followed by the addition of water to the NCO^- ligand,[15] and finally, carbon dioxide eliminates to give the coordinated ammonia (Scheme 3).

*Reaction between [**6a−h**]$^+$ and Chloride.* The addition of a chloroform solution of $[Bu_4N]Cl$ (1.1 equiv) to nitromethane−methanol (1:1, v/v) solution of *in situ* generated $[\mathbf{6a-h}]^+$ followed by keeping the reaction mixture for 90 min at 40 °C leads to **7a−h** (Scheme 3, ***c3***). These compounds were isolated from the reaction mixture by column chromatography.

It should be noticed that no structural changes were detected when **5a−h** and $[Bu_4N]Cl$ (1.1 equiv) were kept at 50 °C for 6 h in a nitromethane−methanol−chloroform solution (Scheme 3, ***d4***). The latter small experiment points out that the direct substitution of the cyanate in **5a−h** with the chloride to give **7a−h** is not possible under the reaction conditions.

Transformations of Methyl Carbamidoxime Derivatives. The reaction between dialkylcyanamide complexes **1a,b** and $MeC(NH_2)$=NOH proceeds differently than those for the aryl amidoximes (see above). This interaction leads to the chelated complexes $[PtCl(NCNAlk_2)\{HN{=}C(NR_2)O{=}C(Me)\text{-}NH_2\}]Cl$ (Alk_2 = Me_2 ([**8a**]Cl), C_5H_{10} ([**8b**]Cl)), which are structurally similar to [**3a−h**]Cl. Compounds [**8a,b**]Cl are less reactive than complexes [**3a−h**]Cl, and no structure transformations were observed for [**8a,b**]Cl for 24 h at 20−40 °C. Furthermore, [**8a,b**]Cl are stable in the presence of 1 equiv of $(PhCH_2)_3N$ for 6 h at 40 °C, while in the presence of 1 equiv of DBU at 40 °C, complexes [**8a,b**]Cl undergo slow unselective degradation (Scheme 4).

Compounds [**8a,b**]Cl transform to the chelated dichloride complexes $[PtCl_2\{HN{=}C(NR_2)O{=}C(Me)NH_2\}]$ (R_2 = Me_2, **9a**; C_5H_{10}, **9b**) for 3 days at 60 °C (76 and 72% isolated yields, respectively). We suggest that the Cl^- in the reaction mixture directs the reaction to dichloride monochelate species **9a,b**. We prepared [**8a,b**](OTf) with the so-called noncoordinated anion, viz. OTf^-, but even in this case we did not observe the nucleophilic addition to the $NCNAlk_2$ ligand. Complexes [**8a**]Cl and **9a** were identified in our previous work,[4b] while [**8b**]Cl was characterized by ESI-MS *in situ* (415.060

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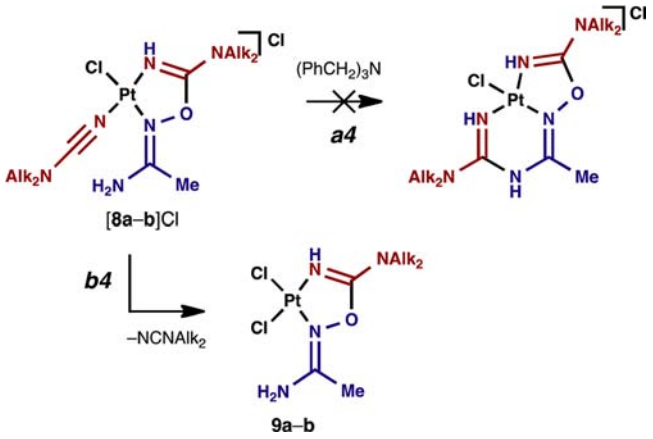
Scheme 4. Transformation of [8a,b]Cl



([M − $NCNC_5H_{10}$ − Cl]$^+$, calcd 415.064), 525.147 ([M − Cl]$^+$, calcd 525.149)). The characterization of **9a** is given in the current work.

The absence of the nucleophilic addition of the amide group of $MeC(NH_2)$=NOH to a coordinated dialkylcyanamide indicates that nucleophilicity of the amide moiety significantly depends on the nature of the substituent in the molecule. On the basis of observation of the effect of the substituent, the nucleophilic attack of the deprotonated form of the amide group to the $NCNAlk_2$ ligand can be postulated. In this case, the aromatic substituent in the amidoxime favors deprotonation due to higher electronegativity of the Ar substituent compared to Alk, which makes the amidoximes bearing the aromatic group more reactive rather than $MeC(NH_2)$=NOH.

Plausible Mechanism for Cascade Generation of the Amidrazone Complexes. Upon the basis of the experimental data disclosed above, we suggest a plausible mechanism for generation of amidrazones **7a–h** from dialkylcyanamide complexes **1a**,**b** and amidoximes **2a–d**. The reactions start as the known[4b] nucleophilic addition of 1 equiv of an amidoxime to a platinum-bound dialkylcyanamide (Scheme 2) to furnish chelates [**3a–h**]Cl (Scheme 5, **A2**). The latter species undergo the intramolecular nucleophilic attack by the NH_2 group to the nitrile C atom to give intermediates **B2** that were not detected, but similar dichelates were previously observed in the platinum(IV) chemistry and X-ray crystallography data indicated the anomalously long [1.520(6) Å] oxime N–O bond.[4a] Most likely, this step is rate determining in the absence of base (26 h, 40 °C), but it dramatically accelerates by the addition of $(PhCH_2)_3N$ (1 h, 40 °C). It is, on the contrary, inhibited by PTSA. On the basis of the observation of the effect of substituents (different for Alk and Ar, see above), the nucleophilic attack of the deprotonated form of the amide group to the $NCNAlk_2$ ligand can be suggested. The aromatic substituent in the amidoxime favors deprotonation due to a greater electron-withdrawing effect of the Ar substituent comparing to Alk.

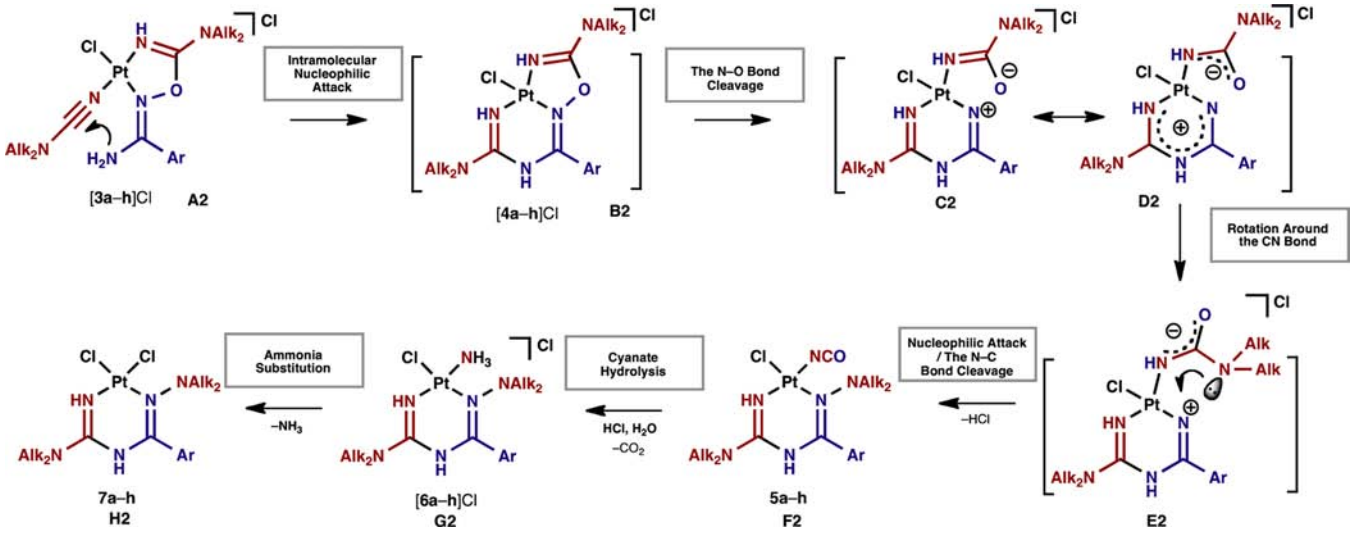
The heterolytic N–O bond cleavage in **B2** gives the zwitterionic intermediate **C2**, where the anionic and the cationic parts are stabilized by the electron delocalization (**D2**). Similar heterolytic splitting of the oxime N–O bond takes place, as generally believed, in Beckmann[19] and Tiemann[20] rearrangements. However, an alternative concerted mechanism of the transformation cannot be ruled out.

In the intermediate, the rotation around the CN bond provides suitable arrangement (**E2**) of the N centers for the N–N bond formation and generation of the isocyanate complexes **F2**; these species were isolated and identified. The transformation of isocyanates to **H2** could not be achieved by the direct substitution with a chloride but easily occurs via the acid-promoted hydrolysis and substitution of the metal-bound ammonia with Cl^-; the NH_3/Cl^- displacements at platinum(II) centers had some precedents in the past.[21]

Analytical and Spectroscopy Data. Complexes [**3a**]-Cl·$2H_2O$, [**3c–h**]Cl·$2H_2O$, **5a–h**, and **7a–h** give satisfactory C, H, and N elemental analyses for the proposed formulas, and they were also characterized by IR, high resolution ESI-MS, ^{1}H NMR spectroscopy, and single-crystal X-ray diffraction (for **5b**, **5d**, **5g**, **7b**, and **7e**).

Several complexes provide cocrystallization of solvent molecules, which are reflected in the results of C, H, and N elemental analyses, and this cocrystallization is typical for the triazapentadiene complexes.[7a,b,22] Thus, various complexes bearing the triazapentadiene moiety are well-known as systems that provide cocrystallization of solvent molecules.[7a] Moreover, these species even serve as convenient models for studying weak molecular interactions involving cocrystallized solvent;[7b,22]

Scheme 5. Plausible Mechanism for a Cascade Generation of the Amidrazone Complexes



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small variation of cocrystallization conditions for the triazapentadiene systems often gives solvates of various composition. All of these explain why the composition of some complexes for microanalyses and for X-ray diffraction studies is different.

In the IR spectra of **5a**–**h** and **7a**–**h**, the Pt^{II}-bound organic ligands exhibit a medium-to-strong band at 3448–3192 cm^{-1}, which can be attributed to the N–H stretches.[23] The spectra also display two C=N absorption bands in the range of 1666–1601 cm^{-1} specific for the metal-bound 1,3,5-triazapentadienes.[7a,b,24] The spectra of **5a**–**h** represent a very strong band in the range of 2270–2217 cm^{-1} specific for the platinum(II)-bound cyanate.[25] In addition, the spectra of **5c**, **5g**, **7c**, and **7g** display medium to medium-to-strong intensity bands in the range of 2226–2243 cm^{-1} assignable to the C≡N stretches from the *p*-substituted benzonitrile.[23]

Positive mode high resolution ESI mass-spectra of nonionic species **5a**–**h** and **7a**–**h** exhibit peaks corresponding to the quasi-ion $[M + H]^+$ and/or ions $[M + Na]^+$, $[M + K]^+$, $[2\ M + H]^+$, $[2\ M + Na]^+$, and $[2\ M + K]^+$ or fragmentation ions, i.e., $[M - Cl]^+$ (**5a**–**h** and **7a**–**h**), $[M - NCO]^+$ (**5a**–**h**), and $[M - NCO - Cl - H]^+$ (**5a**–**h**); the latter fragmentations are typical for platinum(II) chloride complexes.[4a,26] Negative mode high resolution ESI mass-spectra of nonionic species **5a**–**h** and **7a**–**h** display peaks corresponding to the quasi-ion $[M - H]^-$ and/or ions $[2\ M - H]^-$ (**5a**–**h** and **7a**–**h**), $[M - NMe_2]^-$, and $[2\ M - NMe_2]^-$ (**7a**–**d**). The spectra of ionic species [**3a**–**h**]Cl and [**6a**–**h**](*p*-$MeC_6H_4SO_3$) represent peaks from the cation $[M - Cl]^+$ ([**3a**–**h**]$^+$) and $[M - p\text{-}MeC_6H_4SO_3]^+$ ([**6a**–**h**]$^+$) and the fragmentation ions $[M - NCNAlk_2 - Cl]^+$ ([**3a**–**h**]$^+$).

The ^1H NMR spectra of **5a**–**d** and **7a**–**d** display two singlets from the different NMe_2 groups, while the spectra of **5e**–**h** and **7e**–**h** show two multiplets, where the lower-field signal is assignable to the $N(CH_2)_2$ moieties and another peak to carbon chains of the NC_5H_{10} groups. The ^1H NMR spectra of **5a**–**h** and **7a**–**h** exhibit two broad signals from the N–*H* resonances. The low-field signal corresponds to the proton of the amidrazone amide group, while the high-field signal is from the imino-proton with observable (in some cases) $^2J_{PtH}$ constant (34 Hz), which is specific for platinum-bound imines.[4a,27] The signals of the hydrazone NMe_2 moiety in **5a**–**d** are shifted to higher-field relatively to **7a**–**d** at ca. 0.2 ppm, which may be accounted for by the shielding effect of the cyanate ligand.

Characterizations of [**3a**]Cl·$2H_2O$ and [**3c**–**h**]Cl·$2H_2O$ are similar to that described for [**3b**]Cl·$2H_2O$.[4b]

X-Ray Structure Determinations. Molecular structures of **5b**, **5d**, **5g**, **7b**, and **7e** indicate that all coordination polyhedra exhibit a typical square-planar geometry (Figures 1 and 2). All bond angles around the Pt^{II} centers are close to 90°, except the N–Pt–Cl angles in dichloride complexes **7b** and **7h**; N(4)–Pt(1)–Cl(2) for **7b** and N(1)–Pt(1)–Cl(2) for **7h** are 97.22(4) and 96.13(16)°, while N(1)–Pt(1)–Cl(1) for **7b** and N(5)–Pt(1)–Cl(1) for **7h** are equal to 86.30(5) and 85.31(16)°, correspondingly. The Pt–Cl distances (2.3100(5)–2.3301(16) Å) are specific for the Pt^{II}–Cl bonds.[28] The Pt–N_{imine} bond lengths (1.955(5)–1.9844(15) Å) exhibit values characteristic for (imine)Pt^{II} species.[24] The Pt–$N_{hydrazone}$ bond lengths (2.016(2)–2.0271(15) Å) have values characteristic for Pt^{II}–$N(sp^2)$ species,[28] and the Pt–$N_{cyanate}$ bond distances (2.005(2)–2.071(4) Å) are usual for (cyanate)Pt^{II} complexes.[29]

The C–N_{imine} and C–$N_{hydrazone}$ bond lengths are the typical C=N double bonds, ranging from 1.294(2) to 1.300(4) Å and from 1.299(6) to 1.306(3) Å, respectively, while the amide

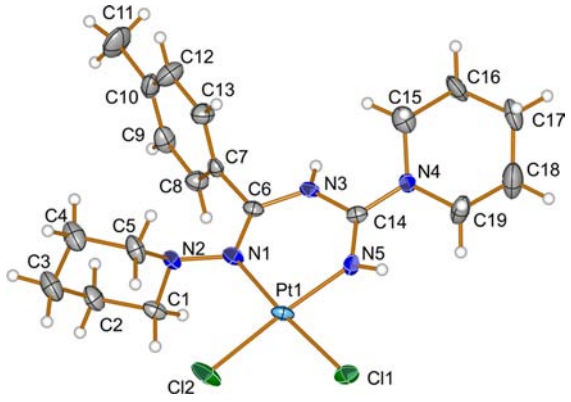

Figure 1. Molecular structure of **7e** with the atomic numbering scheme. Thermal ellipsoids are given at the 50% probability level.

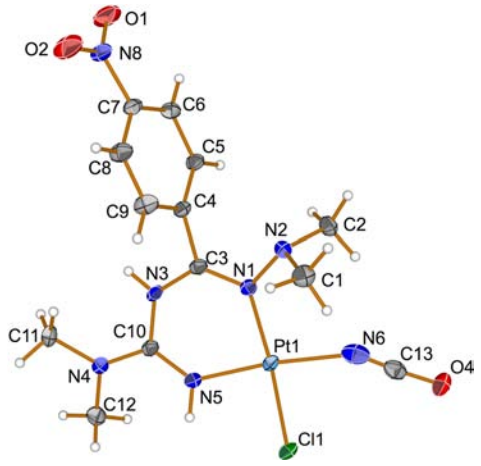

Figure 2. Molecular structure of **5d** with the atomic numbering scheme. Thermal ellipsoids are given at the 50% probability level.

N–$(C{=}N)_{imine}$, N–$(C{=}N)_{hydrazone}$, and C–NR_2 distances are close to the normal single bonds[30] [1.370(8)–1.385(2), 1.363(8)–1.374(6), and 1.340(2)–1.376(8) Å, correspondingly]. In **5g**, the C(13)–N(3) distance (1.143(9) Å) is the normal triple bond.[30] In **5b**, **5d**, and **5g**, the C–N and the C–O distances in the cyanate ligand fall in the intervals 1.070(5)–1.159(4) Å and 1.196(8)–1.219(4) Å, respectively, which are characteristic for *N*-coordinated cyanates.[29,31] The N–N distances [1.426(7)–1.449(2) Å] are specific for the normal single $N(sp^2)$–$N(sp^3)$ bonds.[30]

In the molecular structures of **5b**, **5d**, **5g**, **7b**, and **7e**, the (1,3,5-triazapentadiene)Pt^{II} rings have almost planar geometry. All bond angles in these metallacycles are close to 120°, except the $(N{=}C)_{imine}$–N–$(C{=}N)_{hydrazone}$ angles, which range from 127.95(11) to 130.0(5)°, and the N–Pt–N angles, which are close to 90°. The π-systems of the aromatic rings do not conjugate with the (1,3,5-triazapentadiene)Pt^{II} system that can be inferred from the inspection of the torsion angles, which are in the range 70.00–88.84° between the cycles.

FINAL REMARKS

The results obtained in this work could be considered from at least three perspectives. *First*, the accumulated data in the area of the nitrile chemistry from our[4,10,32] and other groups[33] demonstrate that the reactivity of dialkylcyanamides, $NCNAlk_2$, in many instances is different from that observed for the

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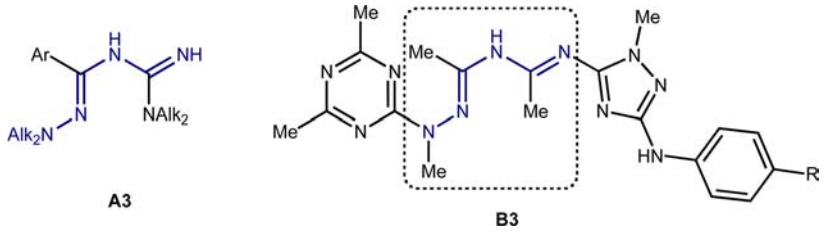


Figure 3. Our (**A3**) and known (**B3**) imidoylamidrazones.

conventional nitrile substrates NCR (R = Alk, Ar). Thus, in this work, we found a novel platinum(II)-mediated cascade reaction between amidoximes and dialkylcyanamides furnishing coordinated amidrazones. This reactivity pattern of dialkylcyanamides $NCNAlk_2$ is not realized for NCR, and the platinum(II)-mediated generation of amidrazones is specific for $NCNAlk_2$ ligands.

Second, we found a novel method for the synthesis of functionalized amidrazones. The most developed methods leading to these species include the reaction of hydrazines with nitriles, iminoesters, imidoylhalides, amides, thioamides, amidines, and their salts; aminolysis of hydrazonoylhalides; and the reduction of formazanes and tetrazolium salts.[12,34]

Third, the acyclic systems with the atom sequence $R^1NC(NR^2R^3)N(R^4)C(R^5)N{-}NR^6R^7$ (Figure 3, **A3**) were not previously reported. It should be noticed that a relevant system picked in dashed lines in Figure 3 (**B3**) was synthesized *via* the metal-free reaction of dicyclohexylcarbodiimide and 1,1,4-trisubstituted thiosemicarbazides.[35]

Furthermore, the obtained ligand system also relates to 1,3,5-trazapentadiene metallacycles,[36] which have been the subject of significant attention for the past decade due to their pH-dependent luminescence properties[24,36,37] and catalytic activity.[36] Additionally, **5a**−**h** and **7a**−**h** represent a new example of platinum complexes having an amidrazone functionality, coordinated via the $N(sp^2)$ hydrazide atom (Figure 4, **A4**).

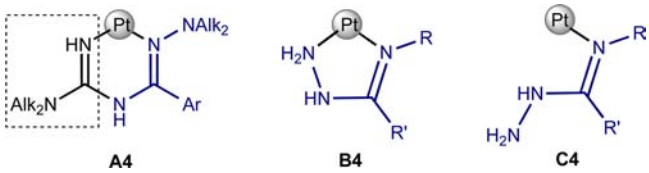


Figure 4. Observed in this work (**A4**) and known (**B4** and **C4**) coordination modes of amidrazones at platinum(II) centers.

The known (amidrazone)Pt^{II} species exhibit other coordination modes (Figure 4, **B4** and **C4**).[38] In our case, the stabilization of the six-membered amidrazone metallacycle is determined by the existence of the carbamimidoyl fragment (picked in dashed lines in Figure 4, **A4**) that provides the chelation.

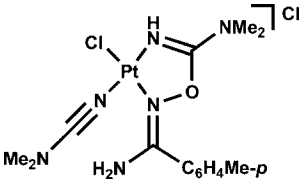
We are currently attempting the extension of the observed reaction to other metal centers and also to other push−pull nitrile systems.

EXPERIMENTAL SECTION

Materials and Instrumentation. Solvents were obtained from commercial sources and used as received. The amidoximes were synthesized according to the literature methods.[39] The complexes $[PtCl_2(NCNAlk_2)_2]$ (R_2 = Me_2, C_5H_{10}) were synthesized in accord with the published procedure;[32] the *cis*- and *trans*-isomers were separated by column chromatography on SiO_2 (Silicagel 60 F_{254}, 0.063−0.200 mm, Merck). Microanalyses were carried out in the analytical laboratory of the University of Eastern Finland. Electrospray ionization mass-spectra were obtained on a Bruker micrOTOF spectrometer equipped with an electrospray ionization (ESI) source. The instrument was operated both in positive and in negative ion mode using a m/z range of 50−3000. The capillary voltage of the ion source was set at −4500 V (ESI^+-MS) and the capillary exit at ±(70−150) V. The nebulizer gas flow was 0.4 bar and the drying gas flow 4.0 L/min. For ESI, species were dissolved in MeOH or a Me_2SO−MeOH mixture. In the isotopic pattern, the most intensive peak is reported. TLC was performed on Silufol UV254 SiO_2 plates. Infrared spectra (4000−400 cm^{-1}) were recorded on a Shimadzu FTIR-8400S instrument in KBr pellets. ^1H NMR spectra were measured on a Bruker DPX 300 spectrometer in Me_2CO-d_6 and Me_2SO-d_6 at ambient temperature; residual solvent signals were used as the internal standard.

X-Ray Structure Determinations. The crystals of complexes **5b**, **5d**, **5g**, **7b**, and **7e** were immersed in cryo-oil, mounted in a Nylon loop, and measured at a temperature of 100 or 120 K. The X-ray diffraction data were collected on a Bruker Kappa Apex II Duo, Bruker Kappa Apex II, or Bruker Smart Apex II diffractometer using Mo Kα radiation (λ = 0.710 73 Å). The APEX2[40] software packages were used for cell refinements and data reductions. The structures were solved by direct methods using the SHELXS-97[41] program with the WinGX[42] graphical user interface. A numerical absorption correction based on crystal faces (SADABS)[43] was applied to all data. Structural refinements were carried out using SHELXL-97.[41] In **5g**, nitromethane of crystallization was disordered and omitted from the final refinement. The contribution of the disordered solvent to the calculated structure factors was taken into account by using a SQUEEZE routine of PLATON.[44] The total residual electron count was found to be 66, and it was equated with two nitromethane molecules. In all structures (except **5g**), the NH, NH_2, and H_2O hydrogen atoms were located from the difference Fourier map but constrained to ride on their parent nitrogen atom with U_{iso} = 1.5U_{eq} (parent atom). Other hydrogens were positioned geometrically and constrained to ride on their parent atoms, with C−H = 0.95−0.99 Å, N−H = 0.88 Å, and U_{iso} = 1.2−1.5U_{eq} (parent atom). The crystallographic details are summarized in Table S2 (Supporting Information).

Synthetic Work. *I. Nucleophilic Addition of 1 equiv of p-R′C$_6$H$_4$C(NH$_2$)=NOH (R′ = Me, H, CN, NO$_2$) to trans-[PtCl$_2$(NCNAlk$_2$)$_2$] (Alk$_2$ = Me$_2$, C$_5$H$_{10}$).* A solution of any of the amidoximes *p*-R′$C_6H_4C(NH_2)$=NOH (**2a**−**d**; 0.10 mmol) in chloroform (3 mL) was added dropwise for 20 min to a stirred solution of *trans*-$[PtCl_2(NCNAlk_2)_2]$ (**1a**,**b**; 0.10 mmol) in chloroform (3 mL). After 20 min, the solvent was evaporated under a vacuum to form oily residues. The residues were washed with three 3-mL portions of dry diethyl ether, crystallized under dry diethyl ether, and dried in the air at RT.



[**3a**]Cl·2H_2O yield: 89%. Anal. Calcd. for $C_{14}H_{22}N_6OCl_2Pt{\cdot}2H_2O$: C, 28.39; H, 4.42; N, 14.19. Found: C, 28.43; H, 4.48; N, 14.14%.

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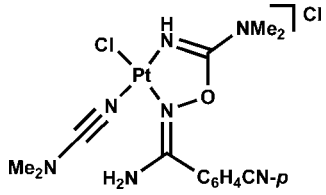
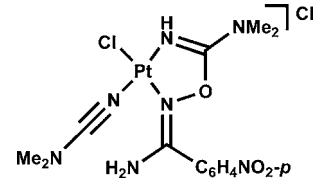
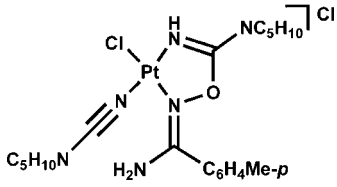
High resolution ESI$^+$-MS (MeOH, m/z): 451.069 ([M − $NCNMe_2$ − Cl]$^+$, calcd 451.061), 521.120 ([M − Cl]$^+$, calcd 521.114). IR (KBr, selected bonds, cm^{-1}): 3419(s), 3363(s) ν(N−H); 3030(vw), 2984(vw), 2952(vw) ν(C−H); 2305 (m) ν(C≡N); 1660(m-s), 1620(m-s) ν(C═N). ^{1}H NMR (DMSO-d_6, δ): 8.84 (s, br, 1H, NH_2), 8.55 (s, br, 1H, NH_2), 7.65 (s, br, 1H, NH), 7.43 (d, $^3J_{HH}$ = 8 Hz, 2H, CH), 7.30 (d, $^3J_{HH}$ = 8 Hz, 2H, CH), 3.10 (s, 6H, $N(CH_3)_2$), 2.71 (s, 6H, $N(CH_3)_2$), 2.35 (s, 3H, $ArCH_3$).



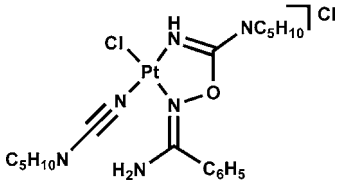
[**3c**]Cl·2H_2O yield: 87%. Anal. Calcd. for $C_{13}H_{19}N_7OCl_2Pt·2H_2O$: C, 27.87; H, 3.84; N, 16.25. Found: C, 27.91; H, 3.83; N, 16.28%. High resolution ESI$^+$-MS (MeOH, m/z): 462.044 ([M − $NCNMe_2$ − Cl]$^+$, calcd 462.040), 532.095 ([M − Cl]$^+$, calcd 532.093). IR (KBr, selected bonds, cm^{-1}): 3424(s), 3360(s) ν(N−H); 3033(vw), 2988(vw), 2952(vw) ν(C−H); 2305(m) and 2247(s) ν(C≡N); 1666(m-s), 1624(m-s) ν(C═N). ^{1}H NMR (DMSO-d_6, δ): 8.88 (s, br, 1H, NH_2), 8.57 (s, br, 1H, NH_2), 7.88 (s, br, 1H, NH), 7.82 (d, $^3J_{HH}$ = 8 Hz, 2H, CH), 7.59 (d, $^3J_{HH}$ = 8 Hz, 2H, CH), 3.15 (s, 6H, $N(CH_3)_2$), 2.76 (s, 6H, $N(CH_3)_2$).



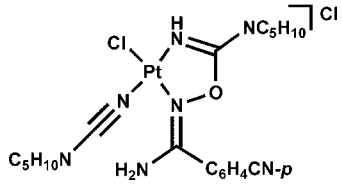
[**3d**]Cl·2H_2O yield: 82%. Anal. Calcd. for $C_{13}H_{19}N_7O_3Cl_2Pt·2H_2O$: C, 25.01; H, 3.87; N, 15.70. Found: C, 25.00; H, 3.76; N, 15.79%. High resolution ESI$^+$-MS (MeOH, m/z): 482.037 ([M − $NCNMe_2$ − Cl]$^+$, calcd 482.030), 552.086 ([M − Cl]$^+$, calcd 552.083). IR (KBr, selected bonds, cm^{-1}): 3421(s), 3360(s) ν(N−H); 3030(vw), 2986(vw), 2952(vw) ν(C−H); 2305 (m) ν(C≡N); 1666(m-s), 1622(m-s) ν(C═N), 1520(s) $\nu(N{=}O)_{as}$, 1342(s) $\nu(N{=}O)_s$. ^{1}H NMR (DMSO-d_6, δ): 8.90 (s, br, 1H, NH_2), 8.59 (s, br, 1H, NH_2), 7.93 (s, br, 1H, NH), 7.82 (d, $^3J_{HH}$ = 8 Hz, 2H, CH), 7.55 (d, $^3J_{HH}$ = 8 Hz, 2H, CH), 3.15 (s, 6H, $N(CH_3)_2$), 2.77 (s, 6H, $N(CH_3)_2$).



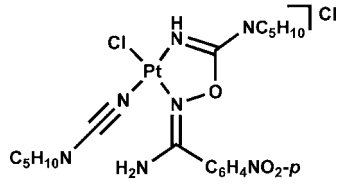
[**3e**]Cl·2H_2O yield: 84%. Anal. Calcd. for $C_{20}H_{30}N_6OCl_2Pt·2H_2O$: C, 35.72; H, 5.10; N, 12.50. Found: C, 35.81; H, 5.12; N, 12.53%. High resolution ESI$^+$-MS (MeOH, m/z): 491.098 ([M − $NCNC_5H_{10}$ − Cl]$^+$, calcd 491.092), 601.181 ([M − Cl]$^+$, calcd 601.176). IR (KBr, selected bonds, cm^{-1}): 3410 (s), 3368 (s) ν(N−H); 3033 (vw), 2992 (vw), 2966 (vw) ν(C−H); 2288 (m) ν(C≡N); 1666 (m-s), 1623 (m-s) ν(C═N). ^{1}H NMR (DMSO-d_6, δ): 8.91 (s, br, 1H, NH_2), 8.55 (s, br, 1H, NH_2), 7.60 (s, br, 1H, NH), 7.42 (d, $^3J_{HH}$ = 8 Hz, 2H, CH), 7.20 (d, $^3J_{HH}$ = 8 Hz, 2H, CH), 3.15−2.98 (m, 8H, NCH_2), 2.33 (s, 3H, $ArCH_3$), 1.62−1.48 (m, 6H, CH_2), 1.22−1.03 (m, 6H, CH_2).



[**3f**]Cl·2H_2O yield: 67%. Anal. Calcd for $C_{19}H_{28}N_6OCl_2Pt·2H_2O$: C, 34.66; H, 4.90; N, 12.76. Found: C, 34.81; H, 4.81; N, 12.64%. High resolution ESI$^+$-MS (MeOH, m/z): 479.092 ([M − Cl − $NCNMe_2$]$^+$, calcd 479.085). IR (KBr, selected bonds, cm^{-1}): 3416(s), 3358(m) ν(N−H); 3045(vw), 2932(w) ν(C−H); 2295(m-s) ν(C≡N); 1666(s), 1626(vs) 1603(m) ν(C═N). ^{1}H NMR (DMSO-d_6, δ): 8.86 (s, br, 1H, NH_2), 8.54 (s, br, 1H, NH_2), 7.75−7.72 (m, 4H, NH + *o*-, *p*-CH), 7.61 (t, 2H, *m*-CH), 1.60−1.48 (m, 6H, CH_2), 1.23−1.03 (m, 6H, CH_2).



[**3g**]Cl·2H_2O yield: 80%. Anal. Calcd. for $C_{20}H_{27}N_7OCl_2Pt·2H_2O$: C, 35.09; H, 4.71; N, 14.32. Found: C, 35.12; H, 4.59; N, 14.47%. High resolution ESI$^+$-MS (MeOH, m/z): 502.073 ([M − $NCNC_5H_{10}$ − Cl]$^+$, calcd 502.072), 612.157 ([M − Cl]$^+$, calcd 612.156). IR (KBr, selected bonds, cm^{-1}): 3410 (s), 3368 (s) ν(N−H); 3038 (vw), 2992 (vw), 2966 (vw) ν(C−H); 2268(m) and 2228(s) ν(C≡N); 1666 (m-s), 1623 (m-s) ν(C═N). ^{1}H NMR (DMSO-d_6, δ): 8.93 (s, br, 1H, NH_2), 8.64 (s, br, 1H, NH_2), 7.70 (s, br, 1H, NH), 7.65 (d, $^3J_{HH}$ = 8 Hz, 2H, CH), 7.32 (d, $^3J_{HH}$ = 8 Hz, 2H, CH)), 3.24−2.95 (m, 8H, NCH_2), 1.66−1.50 (m, 6H, CH_2), 1.30−1.07 (m, 6H, CH_2).



[**3h**]Cl·2H_2O yield: 84%. Anal. Calcd. for $C_{19}H_{27}N_7O_3Cl_2Pt·2H_2O$: C, 32.39; H, 4.58; N, 13.92. Found: C, 32.38; H, 4.49; N, 13.93%. High resolution ESI$^+$-MS (MeOH, m/z): 522.063 ([M − $NCNC_5H_{10}$ − Cl]$^+$, calcd 522.061), 632.147 ([M − Cl]$^+$, calcd 623.146). IR (KBr, selected bonds, cm^{-1}): 3415 (s), 3368 (s) ν(N−H); 3038 (vw), 2992 (vw), 2969 (vw) ν(C−H); 2288 (m) ν(C≡N); 1666 (m-s), 1624 (m-s) ν(C═N), 1520(s) $\nu(N{=}O)_{as}$, 1342(s) $\nu(N{=}O)_s$. ^{1}H NMR (DMSO-d_6, δ): 8.95 (s, br, 1H, NH_2), 8.64 (s, br, 1H, NH_2), 7.72 (s, br, 1H, NH), 7.62 (d, $^3J_{HH}$ = 8 Hz, 2H, CH), 7.34 (d, $^3J_{HH}$ = 8 Hz, 2H, CH), 3.19−2.98 (m, 8H, NCH_2), 1.66−1.52 (m, 6H, CH_2), 1.31−1.12 (m, 6H, CH_2).

ii. Intramolecular Nucleophilic Addition to Cyanamide Ligand Followed by Rearrangement. A solution of freshly prepared [**3**]Cl (see above) in chloroform (2 mL) was kept for 7 min at RT, whereupon a solution of tribenzylamine (0.10 mmol) in chloroform (1 mL) was added. The reaction mixture was kept at 40 °C for 1 h, and then the solution was cooled to RT. A precipitate formed (for **5b**−**d**, **5g**, and **5h**) was filtered off, washed with two 0.5-mL portions of chloroform, and dried in the air at RT, while solutions of **5a**, **5e**, and **5f** were transferred to a short (l = 7 cm, d = 0.7 cm) column filled with silica gel [eluent: chloroform−nitromethane (5:1, v/v, for **5a**) or chloroform (12 mL; for **5e** and **5f**), whereupon elution was performed with chloroform−nitromethane (3:2, v/v) mixture until separation of the first fraction]. The product (**5a**, **5e**, and **5f**) was isolated from the column in the first fraction. The solvent was evaporated *in vacuo* to give cyanate complexes **5a**, **5e**, and **5f** that contain a small amount (ca. 5−10% relatively to the isolated yield of **5**) of corresponding dichloride complex **7a**, **7e**, or **7f**.

5a yield: 58%. TLC (eluent: chloroform/acetone = 2:1, v/v) R_f = 0.47. High resolution ESI$^+$-MS (MeOH, m/z): 441.140 ([M − NCO − Cl − H]$^+$, calcd 441.136), 478.117 ([M − NCO]$^+$, calcd 478.112), 484.147 ([M − Cl]$^+$, calcd 484.142), 521.124 ([M + H]$^+$, calcd 521.118), 543.109 ([M + Na]$^+$, calcd 543.100), 559.079 ([M + K]$^+$, calcd 559.074), 997.223 ([2 M − NCO]$^+$, calcd 997.225), 1003.260

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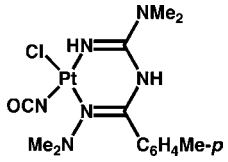
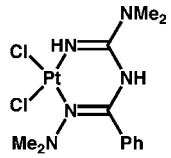
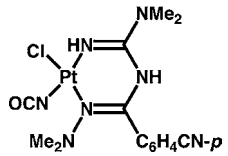


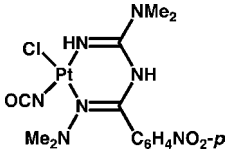
([2 M − Cl]$^+$, calcd 1003.252), 1062.219 ([2 M + Na]$^+$, calcd 1062.210), 1078.195 ([2 M + K]$^+$, calcd 1078.184). High resolution ESI$^-$-MS (MeOH, *m/z*): 519.109 ([M − H]$^-$, calcd 519.102), 1038.225 ([2 M − H]$^-$, calcd 1038.213). IR (KBr, selected bonds, cm^{-1}): 3448(m), 3379(m-s) ν(N−H); 2217(vs) ν(OCN); 1665(vs), 1624(m-s) ν(C═N); 1551(s) δ(N−H). ^{1}H NMR (Me$_2$CO-*d*$_6$, δ): 8.84 (s, br, 1H, N*H*), 7.42 (d, $^3J_{HH}$ = 8 Hz, 2H, C*H*), 7.28 (d, $^3J_{HH}$ = 8 Hz, 2H, C*H*), 5.98 (s+d, $^2J_{PtH}$ = 34 Hz, br, 1H, N*H*), 3.05 (s, 6H, N(CH_3)$_2$), 2.58 (s, 6H, N(CH_3)$_2$), 2.39 (s, 3H, ArCH_3).



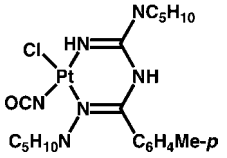
5b yield: 74%. TLC (eluent: chloroform/acetone = 2:1, v/v) R_f = 0.42. Anal. Calcd for $C_{13}H_{19}N_6OClPt\cdot 1/2H_2O$: C, 30.33; H, 3.92; N, 16.32. Found: C, 30.64; H, 3.86; N, 16.10%. High resolution ESI$^+$-MS (MeOH, *m/z*): 464.093 ([M − NCO]$^+$, calcd 464.092), 470.102 ([M − Cl]$^+$, calcd 470.121), 529.081 ([M + Na]$^+$, calcd 529.080), 545.054 ([M + K]$^+$, calcd 545.054), 1034.165 ([2 M + Na]$^+$, calcd 1034.171), 1050.138 ([2 M + K]$^+$, calcd 1050.145). High resolution ESI$^-$-MS (MeOH, *m/z*): 505.086 ([M − H]$^-$, calcd 505.082), 1010.197 ([2 M − H]$^-$, calcd 1010.173). IR (KBr, selected bonds, cm^{-1}): 3382(m), 3245(m), 3221(m) ν(N−H); 2250(vs) ν(OCN); 1666(vs), 1619(m-s) ν(C═N); 1515(s) δ(N−H). ^{1}H NMR (Me$_2$CO-*d*$_6$, δ): 9.03 (s, br, 1H, N*H*), 7.55−7.45 (m, 5H, C*H*), 5.99 (s+d, $^2J_{PtH}$ = 34 Hz, br, 1H, N*H*), 3.04 (s, 6H, NMe_2), 2.57 (s, 6H, NMe_2). Crystals suitable for X-ray study were obtained by slow evaporation of a nitromethane−methanol solution in the air at RT.



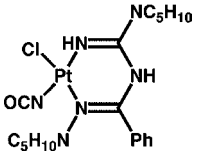
5c yield: 85%. TLC (eluent: chloroform/acetone = 2:1, v/v) R_f = 0.32. Anal. Calcd for $C_{14}H_{18}N_7OClPt\cdot H_2O$: C, 30.63; H, 3.67; N, 17.86. Found: C, 30.58; H, 3.74; N, 17.94%. High resolution ESI$^+$-MS (MeOH, *m/z*): 489.094 ([M − NCO]$^+$, calcd 489.088), 495.121 ([M − Cl]$^+$, calcd 495.117), 554.084 ([M + Na]$^+$, calcd 554.075), 570.060 ([M + K]$^+$, calcd 570.049). High resolution ESI$^-$-MS (MeOH, *m/z*): 530.088 ([M − H]$^-$, calcd 530.078), 1060.179 ([2 M − H]$^-$, calcd 1060.164). IR (KBr, selected bonds, cm^{-1}): 3432(m), 3403(m), 3345(m), 3278(w-m) ν(N−H); 2245(vs) ν(OCN); 2232(m-s) ν(C≡N); 1664(vs), 1648(s) ν(C═N); 1539(s) δ(N−H). ^{1}H NMR (Me$_2$CO-*d*$_6$, δ): 9.02 (s, br, 1H, N*H*), 7.88 (d, $^3J_{HH}$ = 8 Hz, 2H, C*H*), 7.76 (d, $^3J_{HH}$ = 8 Hz, 2H, C*H*), 5.96 (s, br, 1H, N*H*), 3.00 (s, 6H, NMe_2), 2.55 (s, 6H, NMe_2).



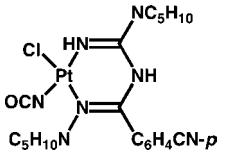
5d yield: 87%. TLC (eluent: chloroform/acetone = 2:1, v/v) R_f = 0.34. Anal. Calcd for $C_{13}H_{18}N_7O_3ClPt\cdot 1/2CHCl_3$: C, 26.56; H, 3.05; N, 16.06. Found: C, 26.50; H, 3.21; N, 15.93%. High resolution ESI$^+$-MS (MeOH, *m/z*): 472.103 ([M − NCO − Cl − H]$^+$, calcd 472.101), 509.087 ([M − NCO]$^+$, calcd 509.077), 515.100 ([M − Cl]$^+$, calcd 515.106), 574.070 ([M + Na]$^+$, calcd 574.065), 590.043 ([M + K]$^+$, calcd 590.039). High resolution ESI$^-$-MS (MeOH, *m/z*): 550.078 ([M − H]$^-$, calcd 550.068), 1100.159 ([2 M − H]$^-$, calcd 1100.143). IR (KBr, selected bonds, cm^{-1}): 3430(m-s), 3390(m-s), 3230(w-m) ν(N−H); 2231(vs) ν(OCN); 1666(vs), 1638(m-s) ν(C═N); 1521(m-s) δ(N−H) and ν(N═O)$_{as}$, 1346(s) ν(N═O)$_s$. ^{1}H NMR (Me$_2$CO-*d*$_6$, δ): 9.05 (s, br, 1H, N*H*), 8.31 (d, $^3J_{HH}$ = 8 Hz, 2H, C*H*), 7.82 (d, $^3J_{HH}$ = 8 Hz, 2H, C*H*), 5.98 (s, br, 1H, N*H*), 3.00 (s, 6H, NMe_2), 2.55 (s, 6H, NMe_2). Crystals suitable for X-ray study were obtained by slow evaporation of a nitromethane−methanol solution in the air at RT.



5e yield: 65%. TLC (eluent: chloroform/acetone = 5:1, v/v) R_f = 0.51. High resolution ESI$^+$-MS (MeOH, *m/z*): 521.200 ([M − NCO − Cl − H] $^+$, calcd 521.199), 558.176 ([M − NCO]$^+$, calcd 558.175), 564.203 ([M − Cl]$^+$, calcd 564.205), 601.182 ([M + H]$^+$, calcd 601.181), 623.164 ([M + Na]$^+$, calcd 623.163), 639.138 ([M + K]$^+$, calcd 639.136), 1157.335 ([2 M − NCO]$^+$, calcd 1157.348), 1163.360 ([2 M − Cl]$^+$, calcd 1163.377), 1200.338 ([M + H]$^+$, calcd 1200.354), 1222.319 ([2 M + Na]$^+$, calcd 1222.336), 1239.293 ([2 M + K]$^+$, calcd 1239.310). High resolution ESI$^-$-MS (MeOH, *m/z*): 599.173 ([M − H]$^-$, calcd 599.165), 1198.342 ([2 M − H]$^-$, calcd 1198.338). IR (KBr, selected bonds, cm^{-1}): 3451(m), 3361(m) ν(N−H); 2938(s), 2852(m-s) ν(C−H); 2266(vs) ν(OCN); 1659(vs), 1621(s) ν(C═N); 1528(m) δ(N−H). ^{1}H NMR (Me$_2$CO-*d* $_6$, δ): 9.28 (s, br, 1H, N*H*), 7.37 (d, $^3J_{HH}$ = 8 Hz, 2H, C*H*), 7.29 (d, $^3J_{HH}$ = 8 Hz, 2H, C*H*), 6.41 (s, br, 1H, N*H*), 3.40−3.20 (m, 8H, NCH_2), 1.65−1.55 (m, 6H, CH_2), 1.20−1.10 (m, 6H, CH_2).



5f yield: 52%. TLC (eluent: chloroform/acetone = 5:1, v/v) R_f = 0.53. High resolution ESI$^+$-MS (MeOH, *m/z*): 507.185 ([M − NCO − Cl − H] $^+$, calcd 507.183), 544.162 ([M − NCO]$^+$, calcd 544.159), 550.191 ([M − Cl]$^+$, calcd 550.189), 609.151 ([M + Na]$^+$, calcd 609.147), 625.123 ([M + K]$^+$, calcd 625.121), 1129.310 ([2 M − NCO]$^+$, calcd 1129.317), 1138.336 ([2 M − Cl]$^+$, calcd 1135.346), 1194.294 ([2 M + Na]$^+$, calcd 1194.307), 1210.265 ([2 M + K]$^+$, calcd 1210.278). High resolution ESI$^-$-MS (MeOH, *m/z*): 585.160 ([M − H]$^-$, calcd 585.149), 1170.321 ([2 M − H]$^-$, calcd 1170.307). IR (KBr, selected bonds, cm^{-1}): 3448(m), 3375(m) ν(N−H); 2932(s), 2853(m-s) ν(C−H); 2269(vs) ν(OCN); 1659(vs), 1624(s) ν(C═N); 1521(m) δ(N−H). ^{1}H NMR (Me$_2$CO-*d* $_6$, δ): 9.37 (s, br, 1H, N*H*), 7.49−7.45 (m, 5H, Ph), 6.44 (s+d, $^2J_{PtH}$ = 34 Hz, br, 1H, N*H*), 3.40−3.20 (m, 8H, NCH_2), 1.65−1.55 (m, 6H, CH_2), 1.20−1.10 (m, 6H, CH_2).



5g yield: 86%. TLC (eluent: chloroform/acetone = 3:1, v/v) R_f = 0.43. Anal. Calcd for $C_{20}H_{26}N_7OClPt\cdot 1/2CHCl_3$: C, 36.71; H, 3.98; N, 14.62. Found: C, 36.70; H, 4.05; N, 14.62%. High resolution ESI$^+$-MS (MeOH, *m/z*): 532.179 ([M − NCO − Cl − H] $^+$, calcd 532.173), 569.155 ([M − NCO]$^+$, calcd 569.150), 575.181 ([M − Cl]$^+$,

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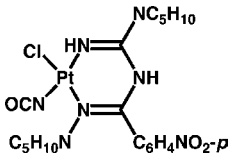
calcd 575.179), 634.142 ([M + Na]$^+$, calcd 634.138), 650.117 ([M + K]$^+$, calcd 650.112), 1243.280 ([2 M + Na]$^+$, calcd 1244.287), 1261.254 ([2 M + K]$^+$, calcd 1261.260). High resolution ESI$^-$-MS (MeOH, *m*/*z*): 610.156 ([M − H]$^-$, calcd 610.140), 1220.309 ([2 M − H]$^-$, calcd 1220.289). IR (KBr, selected bonds, cm^{-1}): 3429(m-s), 3367(m) ν(N−H); 2943(s), 2859(m-s) ν(C−H); 2270(vs) ν(OCN); 2231(m-s) ν(C≡N); 1660(vs), 1631(m-s) ν(C═N); 1526(m) δ(N−H). ^{1}H NMR (Me_2CO-d_6, δ): 9.60 (s, br, 1H, N*H*), 7.91 (d, $^3J_{HH}$ = 8 Hz, 2H, C*H*), 7.77 (d, $^3J_{HH}$ = 8 Hz, 2H, C*H*), 6.45 (s+d, $^2J_{PtH}$ = 34 Hz, br, 1H, N*H*), 3.40−3.20 (m, 8H, NCH_2), 1.70−1.40 (m, 12H, CH_2). Crystals suitable for X-ray study were obtained by slow evaporation of a nitromethane−methanol solution in the air at RT.

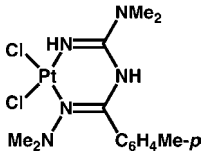


5h yield: 85%. TLC (eluent: chloroform/acetone = 3:1, v/v) R_f = 0.53. Anal. Calcd for $C_{18}H_{26}N_6O_2Cl_2$ Pt·1/2$CHCl_3$: C, 30.40; H, 3.42; N, 12.10. Found: C, 30.43; H, 3.45; N, 12.16%. High resolution ESI$^+$-MS (MeOH, *m*/*z*): 552.169 ([M − NCO − Cl − H] $^+$, calcd 552.163), 589.145 ([M − NCO]$^+$, calcd 589.140), 595.172 ([M − Cl]$^+$, calcd 595.169), 654.133 ([M + Na]$^+$, calcd 654.128), 670.107 ([M + K]$^+$, calcd 670.102), 1284.259 ([2 M + Na]$^+$, calcd 1284.266), 1301.231 ([2 M + K]$^+$, calcd 1301.240). High resolution ESI$^-$-MS (MeOH, *m*/*z*): 630.147 ([M − H]$^-$, calcd 630.130), 1260.280 ([2 M − H]$^-$, calcd 1260.269). IR (KBr, selected bonds, cm^{-1}): 3437(m-s), 3390(m-s) ν(N−H); 2941(s), 2855(m-s) ν(C−H); 2270(vs) ν(OCN); 1651(vs), 1633(m-s) ν(C═N); 1516(m-s) δ(N−H) and $\nu(N{=}O)_{as}$, 1345(s) $\nu(N{=}O)_s$. ^{1}H NMR (Me_2CO- d_6, δ): 9.68 (s, br, 1H, N*H*), 8.35 (d, $^3J_{HH}$ = 9 Hz, 2H, C*H*), 7.85 (d, $^3J_{HH}$ = 9 Hz, 2H, C*H*), 6.43 (s, br, 1H, N *H*), 3.40−3.20 (m, 8H, NCH_2), 1.70−1.40 (m, 12H, CH_2).

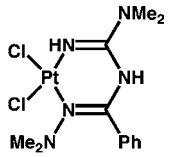
iii. Hydrolysis of the Coordinated Cyanate. A solution of PTSA (0.10 mmol) in acetone (1 mL) was added to a solution of **5** (0.10 mmol) in a nitromethane−methanol (1:1, v/v; 2 mL) mixture, and the solution was kept at RT. After 10 min, a 5-μL aliquot of the homogeneous solution obtained was diluted with methanol (1 mL), and the products were identified by ESI-MS$^+$ without liberation from the reaction mixture. See Table 2S (Supporting Information) for characteristic peaks of [**6a**−**h**](*p*-$MeC_6H_4SO_3$).

*iv. Preparation of **7a**−**h**. Procedure A. One-Pot Preparation from Platinum Complexes **1a,b** and Amidoximes **2a**−**d**.* Powder of aromatic amidoxime **2** (0.1 mmol) was added to a vigorously stirred solution of complex **1** (0.1 mmol) in chloroform (2 mL) at RT. After 5 min, a solution of $(PhCH_2)_3N$ (0.1 mmol) in chloroform (1 mL) was added to the stirred solution, whereupon the mixture was stirred at 40 °C. Then, a solution of PTSA (0.1 mmol) in a nitromethane−methanol (1:1, v/v) mixture (1 mL) was added to the reaction mixture, and it was kept on stirring at 40 °C for an additional 2 h, whereupon the solvent was evaporated *in vacuo* at RT. A residue was completely dissolved in a chloroform−nitromethane (5:1, v/v) mixture (volume varies in the range of 2−5 mL depending on particular complexes), and the solution obtained was transferred to a short (*l* = 7 cm, *d* = 0.7 cm) column and chromatographed on silica gel (eluent: chloroform−nitromethane (5:1, v/v, 12 mL), and then a chloroform−nitromethane (3:2, v/v) mixture until eluation of the first fraction). The product was isolated from the column in the first fraction. The solvent was evaporated *in vacuo* at RT to give pure amidrazone complex **7**.

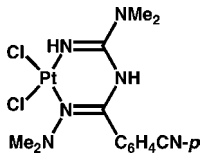
*Procedure B. Substitution of the Ammonia with the Chloride in [**6**]$^+$.* A solution of tetrabuthylammonium chloride (0.15 mmol) in chloroform (0.5 mL) was added to the solution (3 mL) of [**6**](*p*-$MeC_6H_4SO_3$) right after its preparation, and the reaction mixture was kept at 40 °C for 2 h, whereupon the solvent was evaporated *in vacuo* at RT to dryness. The residue was dissolved in a chloroform−nitromethane (2:1, v/v; 2 mL) mixture. The resulting solution was transferred to a short column (*l* = 7 cm, *d* = 0,7 cm) and chromatographed on silica gel (eluent: chloroform−nitromethane (5:1, v/v; 12 mL) mixture, then a chloroform−nitromethane (3:2, v/v) mixture). The solvent was evaporated *in vacuo* at RT to give pure amidrazone complex **7** in ca. 50% yield (based on **5**). Below we give the yields of **7a**−**h** for more convenient procedure A, which provides ca. 5% higher yields.



7a yield: 51%. TLC (eluent: chloroform/acetone = 2:1, v/v) R_f = 0.49. Anal. Calcd for $C_{13}H_{21}N_5Cl_2Pt{\cdot}H_2O$: C, 29.38; H, 4.36; N, 13.18. Found: C, 29.47; H, 4.18; N, 13.01%. High resolution ESI$^+$-MS (MeOH, *m*/*z*): 478.110 ([M − Cl]$^+$, calcd 478.108), 536.069 ([M + Na]$^+$, calcd 536.067), 552.042 ([M + K]$^+$, calcd 552.040), 991.182 ([2 M − Cl]$^+$, calcd 991.185), 1027.158 ([2 M + H]$^+$, calcd 1027.162), 1049.138 ([2 M + Na]$^+$, calcd 1049.144), 1065.112 ([2 M + K]$^+$, calcd 1065.118). High resolution ESI$^-$-MS (MeOH, *m*/*z*): 469.025 ([M − NMe_2]$^-$, calcd 469.027), 512.061 ([M − H]$^-$, calcd 512.069), 1025.137 ([2 M − H]$^-$, calcd 1025.146). IR (KBr, selected bonds, cm^{-1}): 3300(m), 3246(w-m) ν(N−H); 1659(vs), 1614(m-s) ν(C═N); 1506(m-s) δ(N−H). ^{1}H NMR (Me_2CO- d_6, δ): 8.79 (s, br, 1H, N*H*), 7.40 (d, $^2J_{HH}$ = 8 Hz, 2H, C*H*), 7.27 (d, $^2J_{HH}$ = 8 Hz, 2H, C*H*), 6.06 (s, br, 1H, N*H*), 3.05 (s, 6H, $N(CH_3)_2$), 2.72 (s, 6H, $N(CH_3)_2$), 2.38 (s, 3H, $ArCH_3$).



7b yield: 59%. TLC (eluent: chloroform/acetone = 2:1, v/v) R_f = 0.38. Anal. Calcd for $C_{12}H_{19}N_5Cl_2Pt$: C, 28.87; H, 3.84; N, 14.03. Found: C, 29.03; H, 3.76; N, 14.17%. High resolution ESI$^+$-MS (MeOH, *m*/*z*): 464.101 ([M − Cl]$^+$, calcd 464.092), 522.060 ([M + Na]$^+$, calcd 522.051), 538.034 ([M + K]$^+$, calcd 538.025), 963.161 ([2 M − Cl]$^+$, calcd 963.154), 1021.119 ([2 M + Na]$^+$, calcd 1021.113), 1037.092 ([2 M + K]$^+$, calcd 1037.087). High resolution ESI$^-$-MS (MeOH, *m*/*z*): 455.004 ([M − NMe_2]$^-$, calcd 455.011), 498.046 ([M − H]$^-$, calcd 498.053), 954.063 ([2 M − NMe_2]$^-$, calcd 954.073), 997.105 ([2 M − H]$^-$, calcd 997.115). IR (KBr, selected bonds, cm^{-1}): 3308(m), 3227(m) ν(N−H); 1664(vs), 1616(m-s) ν(C═N); 1516(m-s) δ(N−H). ^{1}H NMR (Me_2CO-d_6, δ): 8.90 (s, br, 1H, N*H*), 7.53−7.45 (m, 5H, Ph), 6.08 (s, br, 1H, N*H*), 3.04 (s, 6H, $N(CH_3)_2$), 2.72 (s, 6H, $N(CH_3)_2$). Crystals suitable for X-ray study were obtained by slow evaporation of a nitromethane solution in the air at RT.



7c yield: 60%. TLC (eluent: chloroform/acetone = 2:1, v/v) R_f = 0.33. Anal. Calcd for $C_{13}H_{18}N_6Cl_2$ Pt·1/4H $_2$O: C, 29.53; H, 3.53; N, 15.89. Found: C, 29.36; H, 3.66; N, 16.05%. High resolution ESI$^+$-MS (MeOH, *m*/*z*): 547.046 ([M + Na]$^+$, calcd 547.046), 563.026 ([M + K]$^+$, calcd 563.020). High resolution ESI$^-$-MS (MeOH, *m*/*z*): 509.034 ([M − Me]$^-$, calcd 509.033), 523.050 ([M − H]$^-$, calcd 523.049). IR (KBr, selected bonds, cm^{-1}): 3371(m), 3217(m) ν(N−H); 2243(m) ν(C≡N); 1666(vs), 1624(m-s) ν(C═N); 1528(m-s) δ(N−H). ^{1}H NMR (Me_2CO-d_6, δ): 9.13 (s, br, 1H, N*H*), 7.91 (d, $^2J_{HH}$ = 9 Hz, 2H, C*H*), 7.79 (d, $^2J_{HH}$ = 9 Hz, 2H, C *H*), 6.13 (s, br, 1H, N*H*), 3.02 (s, 6H, $N(CH_3)_2$), 2.70 (s, 6H, $N(CH_3)_2$).

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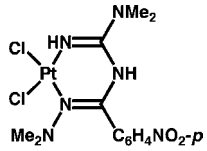
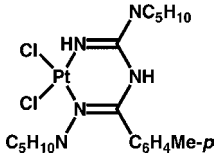
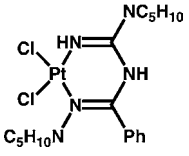


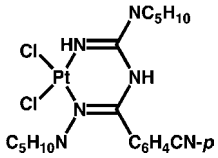
7d yield: 55%. TLC (eluent: chloroform/acetone = 2:1, v/v) R_f = 0.37. Anal. Calcd for $C_{12}H_{18}N_6O_2Cl_2Pt{\cdot}H_2O$: C, 25.63; H, 3.58; N, 14.95. Found: C, 25.51; H, 3.53; N, 14.79%. High resolution ESI$^+$-MS (MeOH, *m*/*z*): 509.079 ([M − Cl]$^+$, calcd 509.077), 567.037 ([M + Na]$^+$, calcd 567.036), 583.008 ([M + K]$^+$, calcd 583.010), 1111.079 ([2 M + Na]$^+$, calcd 1111.083). High resolution ESI$^-$-MS (MeOH, *m*/*z*): 543.031 ([M − H]$^-$, calcd 543.038), 1088.086 ([2 M − H]$^-$, calcd 1088.093). IR (KBr, selected bonds, cm^{-1}): 3381(m), 3358(m-s) ν(N−H); 1659(vs), 1637(m-s) ν(C═N); 1518(s) ν(N═O)$_{as}$; 1348(s) ν(N═O)$_s$. ^{1}H NMR (Me$_2$CO-d_6, δ): 9.06 (s, br, 1H, N*H*), 8.32 (d, $^2J_{HH}$ = 9 Hz, 2H, C*H*), 7.84 (d, $^2J_{HH}$ = 9 Hz, 2H, C*H*), 6.08 (s, br, 1H, N*H*), 3.01 (s, 6H, N(CH_3)$_2$), 2.70 (s, 6H, N(CH_3)$_2$).



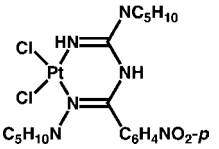
7e yield: 54%. TLC (eluent: chloroform/acetone = 5:1, v/v) R_f = 0.53. Anal. Calcd for $C_{19}H_{29}N_5Cl_2Pt{\cdot}H_2O$: C, 37.32; H, 5.11; N, 11.45. Found: C, 37.49; H, 5.20; N, 11.45%. High resolution ESI$^+$-MS (MeOH, *m*/*z*): 558.178 ([M − Cl]$^+$, calcd 558.171), 616.132 ([M + Na]$^+$, calcd 616.129), 1209.278 ([2 M + Na]$^+$, calcd 1209.269). High resolution ESI$^-$-MS (MeOH, *m*/*z*): 592.134 ([M − H]$^-$, calcd 592.132), 1185.279 ([2 M − H]$^-$, calcd 1185.271). IR (KBr, selected bonds, cm^{-1}): 3364(m), 3269(w-m) ν(N−H); 2932(s), 2854(m-s) ν(C−H); 1649(vs), 1616(m-s) ν(C═N); 1516(m-s) δ(N−H). ^{1}H NMR (Me$_2$CO-d_6, δ): 9.21 (s, br, 1H, N*H*), 7.33 (d, $^2J_{HH}$ = 8 Hz, 2H, C*H*), 7.26 (d, $^2J_{HH}$ = 8 Hz, 2H, C*H*), 6.41 (s, br, 1H, N*H*), 3.45−3.20 (m, 8H, NCH_2), 2.39 (s, 3H, ArCH_3), 1.65−1.50 (m, 6H, CH_2), 1.20−1.00 (m, 6H, CH_2). Crystals suitable for X-ray study were obtained by slow evaporation of a nitromethane solution in the air at RT.



7f yield: 49%. TLC (eluent: chloroform/acetone = 5:1, v/v) R_f = 0.46. Anal. Calcd for $C_{18}H_{27}N_5Cl_2Pt{\cdot}H_2O$: C, 36.19; H, 4.89; N, 11.72. Found: C, 36.40; H, 4.99; N, 11.66%. High resolution ESI$^+$-MS (MeOH, *m*/*z*): 544.160 ([M − Cl]$^+$, calcd 544.155), 602.117 ([M + Na]$^+$, calcd 602.113), 618.092 ([M + K]$^+$, calcd 618.087), 1123.287 ([2 M − Cl]$^+$, calcd 1123.279), 1181.250 ([2 M + Na]$^+$, calcd 1181.238), 1197.236 ([2 M + K]$^+$, calcd 1197.212). High resolution ESI$^-$-MS (MeOH, *m*/*z*): 578.107 ([M − H]$^-$, calcd 578.116), 1157.224 ([2 M − H]$^-$, calcd 1157.240). IR (KBr, selected bonds, cm^{-1}): 3366(m), 3279(m) ν(N−H); 2932(s), 2853(m-s) ν(C−H); 1657(vs), 1618(m-s) ν(C═N); 1518(m-s) δ(N−H). ^{1}H NMR (Me$_2$CO-d_6, δ): 9.33 (s, br, 1H, N*H*), 7.46 (m, 5H, Ph), 6.48 (s, br, 1H, N*H*), 3.45−3.20 (m, 8H, NCH_2), 1.65−1.50 (m, 6H, CH_2), 1.20−1.00 (m, 6H, CH_2).

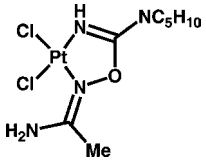


7g yield: 53%. TLC (eluent: chloroform/acetone = 3:1, v/v) R_f = 0.57. Anal. Calcd for $C_{19}H_{26}N_6Cl_2Pt{\cdot}H_2O$: C, 36.66; H, 4.53; N, 13.50. Found: C, 36.47; H, 4.44; N, 13.49%. High resolution ESI$^+$-MS (MeOH, *m*/*z*): 569.154 ([M − Cl]$^+$, calcd 569.150), 627.110 ([M + Na]$^+$, calcd 627.109). High resolution ESI$^-$-MS (MeOH, *m*/*z*): 603.119 ([M − H]$^-$, calcd 603.111), 1207.242 ([2 M − H]$^-$, calcd 1207.231). IR (KBr, selected bonds, cm^{-1}): 3366(m-s) ν(N−H); 2943(s), 2856(m-s) ν(C−H); 2226(m) ν(C≡N); 1655(vs), 1620(m-s) ν(C═N); 1524(m) δ(N−H). ^{1}H NMR (Me$_2$SO-d_6, δ): 10.48 (s, br, 1H, N*H*), 7.94 (d, $^2J_{HH}$ = 9 Hz, 2H, C*H*), 7.68 (d, $^2J_{HH}$ = 9 Hz, 2H, C*H*), 6.62 (s, br, 1H, N*H*), 3.35−3.25 (m, 4H, NCH_2), 3.17−3.05 (m, 4H, NCH_2), 1.60−1.40 (m, 8H, CH_2), 1.10−0.95 (m, 4H, CH_2).



7h yield: 52%. TLC (eluent: chloroform/acetone = 2:1, v/v) R_f = 0.67. Anal. Calcd for $C_{18}H_{26}N_6O_2Cl_2Pt{\cdot}11/2H_2O$: C, 33.19; H, 4.49; N, 12.90. Found: C, 33.26; H, 4.42; N, 12.79%. High resolution ESI$^+$-MS (MeOH, *m*/*z*): 589.146 ([M − Cl]$^+$, calcd 589.140), 647.106 ([M + Na]$^+$, calcd 647.099), 663.076 ([M + K]$^+$, calcd 663.073). High resolution ESI$^-$-MS (MeOH, *m*/*z*): 623.111 ([M − H]$^-$, calcd 623.101). IR (KBr, selected bonds, cm^{-1}): 3375(m), 3192(m-s) ν(N−H); 2939(s), 2856(m-s) ν(C−H); 1655(vs), 1623(m-s) ν(C═N); 1518(s) ν(N═O)$_{as}$; 1346(s) ν(N═O)$_s$. ^{1}H NMR (Me$_2$CO-d_6, δ): 9.03 (s, br, 1H, N*H*), 8.46 (d, $^2J_{HH}$ = 9 Hz, 2H, C*H*), 8.08 (d, $^2J_{HH}$ = 9 Hz, 2H, C*H*), 6.11 (s, br, 1H, N*H*), 3.40−3.20 (m, 8H, NCH_2), 1.70−1.40 (m, 12H, CH_2).

v. Preparation of Complexes 9a,b. A solution of MeC(NH$_2$)═NOH (0.1 mmol) in nitromethane (2 mL) was added dropwise to a vigorously stirred solution of **1** in nitromethane (2 mL) at RT, and the reaction mixture was then stirred at 60 °C for 3 days. The solvent was evaporated *in vacuo* at RT, and a residue obtained was dissolved in a chloroform−nitromethane (3:1, v/v) mixture (2 mL). The solution was transferred to a short (*l* = 5 cm, *d* = 0.7 cm) column and chromatographed on silica gel (eluent: chloroform/nitromethane 2:1, v/v). The first fraction was collected, whereupon the solvent was evaporated *in vacuo* to give pure **9a** (early characterized,[4b] yield 76%) and **9b** (yield 72%).



9b yield: 72%. Anal. Calcd for $C_8H_{16}N_4Cl_2OPt$: C, 21.34; H, 3.58; N, 12.44. Found: C, 21.25; H, 3.51; N, 12.38%. High resolution ESI$^-$-MS (MeOH, *m*/*z*): 449.029 ([M − H]$^-$, calcd 449.022), 485.006 ([M + Cl]$^-$, calcd 484.998), 935.038 ([2 M + Cl]$^-$, calcd 935.028). IR (KBr, selected bonds, cm^{-1}): 3439(m), 3373(s) ν(N−H); 2928(s), 2858(m) ν(C−H); 1645(vs) ν(C═N). TLC (eluent: chloroform/acetone = 2:1, v/v) R_f = 0.57. ^{1}H NMR (Me$_2$CO- d_6, δ): 8.47 (s, br, 1H, NH_2), 6.99 (s, br, 1H, NH_2), 6.58 (s, br, 1H, N*H*), 3.64−3.56 (m, 4H, NCH_2), 2.28 (s, 3H, CH_3), 1.66−1.58 (m, 6H, CH_2).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Characteristic ESI$^+$-MS peaks of [**6a**−**h**](*p*-MeC$_6$H$_4$SO$_3$). Molecular structure of **7b** with the atomic numbering scheme. Thermal ellipsoids are given at the 50% probability level. Molecular structure of **5b** with the atomic numbering scheme. Thermal ellipsoids are given at the 50% probability level. Molecular structure of **5g** with the atomic numbering scheme. Thermal ellipsoids are given at the 50% probability level. Crystal data. Crystallographic information file. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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