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Pt^{II}-Mediated Imine−Nitrile Coupling Leading to Symmetrical (1,3,5,7,9-Pentaazanona-1,3,6,8-tetraenato)Pt(II) Complexes Containing the Incorporated 1,3-Diiminoisoindoline Moiety

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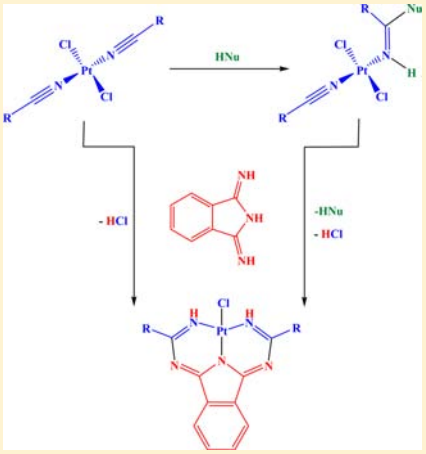
Supporting Information

ABSTRACT: Treatment of *trans*-$[PtCl_2(NCR)_2]$ (**1**; R = Et (**1a**), Ph (**1b**)) with 1,3-diiminoisoindoline (**2**) gives access to the corresponding symmetrical (1,3,5,7,9-pentaazanona-1,3,6,8-tetraenato)Pt(II) complexes $[PtCl\{\underline{N}H{=}C(R)N{=}C(C_6H_4)\text{-}\underline{N}C{=}NC(R){=}\underline{N}H\}]$ (**3**). The reactions of **1** with one equivalent of 1,1,3,3-tetramethylguanidine (**4**), 1,3-diphenylguanidine (**6**), or acetone oxime (**8**) leads to the formation of mixed asymmetrical Pt(II) complexes *trans*-$[PtCl_2\{NH{=}C(R)N{=}C(NMe_2)_2\}(NCR)]$ (**5**), $[PtCl\{\underline{N}H{=}C(R)NC(NHPh){=}\underline{N}Ph\}(NCR)]$ (**7**), or *trans*-$[PtCl_2\{NH{=}C(Ph)ON{=}CMe_2\}(NCPh)]$ (**9**), respectively, as a result of nucleophilic addition to one of the nitrile ligands in **1**. Treatment of **5**, **7**, and **9** with one equivalent of **2** leads to complexes **3**. The complexes were characterized by IR, ^1H, $^{13}C\{^1H\}$, and ^{195}Pt NMR (for **3**) spectroscopies, ESI^+-MS, elemental analyses, and X-ray diffraction (for **3**). Complex **3a** has an asymmetric unit with five independent Pt molecules of the same chemical composition and two molecules of water, resulting in a total of 40 molecules of the complex and sixteen guest water molecules per unit cell. Theoretical calculations revealed that the most plausible mechanism of formation of complexes **3** includes stepwise nucleophilic addition of **2** to one of the nitrile ligands in **1**, a first cyclization upon formation of the Pt−N bond and elimination of HCl, and a second nucleophilic addition/cyclization.



INTRODUCTION

Nucleophilic addition reactions on metal coordinated nitriles have long been used to prepare a variety of useful organic compounds.[1] The formation of C−N or C−O bonds using this methodology has been achieved using different types of nucleophiles[2,3] or 1,3-dipole reagents.[4] 1,3-Diiminoisoindoline, a cyclic diimine and a potential sp^2-nitrogen nucleophile, is well-known for its use in the preparation of metallopthalocyanines[5] and other macrocycles, such as expanded hemiporphyrazine,[6] and is an important ingredient in the pigment industry. The iminoisoindoline-1-one, from which 1,3-diiminoisoindoline is derived, has already been studied by our group as a nucleophile toward activated nitriles and isonitriles.[7] The iminoisoindoline-1-one can act as a nucleophile through its imine group toward such substrates resulting in the formation of triazapentadienato or iminocarbene complexes, respectively. Nevertheless, 1,3-diiminoisoindoline has a potential to employ both its imine groups for nucleophilic attacks on metal-bound organonitriles, thus leading to symmetrical triazapentadienato-type complexes. Unlike β-diimines, triazapentadiene bears one additional N donor site, and DFT calculations[8] indicate that they possess an even greater ability for sequestering metal centers than β-diimines. However, the coordination chemistry of triazapendienes is much less described, at least in part, because of the low stability of triazapentadienes, in particular the unsubstituted ones,[9] which hampers direct syntheses of their complexes. For the preparation of triazapentadiene complexes, a direct one-pot template synthesis with nitriles has been investigated when the nitrile is activated by an electron-withdrawing group.[10] A novel route to (imidoylamidine)Ni(II) complexes has been discovered by us using oximes and Ni(II) ions in combination with nitriles,[11] and this methodology has been extended to prepare (1,3,5-triazapentadienato)Pd(II) complexes as well.[12] Very recently, symmetrical and asymmetrical (alkoxy-1,3,5-triazapentadienato)Cu(II) complexes have been also prepared by us using a template synthesis.[13]

In this work, we have studied the nucleophilic addition of a sp^2-nitrogen nucleophile, 1,3-diiminoisoindoline, to Pt(II)-bound organonitriles like propionitrile and benzonitrile. We have thus observed the formation of symmetrical (1,3,5,7,9-pentaazanona-1,3,6,8-tetraenato)Pt(II) complexes **3a** and **3b**, respectively. These may be regarded as extended triazapentadienato complexes as the

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newly formed ligands can be viewed as two such coupled units bearing one common nitrogen.

On attempting to obtain asymmetrical products from the reactions with 1,3-diiminoisoindoline, this species was reacted with the asymmetrical imine-Pt(II) complexes which have been obtained from nucleophilic addition of 1,1,3,3-tetramethylguanidine, 1,3-diphenylguanidine, or acetone oxime to one of the nitrile ligands of Pt(II)-bound bis(nitrile). It was found that in all cases the above complexes **3a** or **3b** were also formed as a result of substitution of the starting nucleophilic fragment from the respective complexes **5**, **7**, and **9** by 1,3-diiminoisoindoline **2** (see below). Nevertheless, nitrone monocycloaddition product **11** did not respond to such type of reaction. The plausible mechanisms of the formation of **3** from 1,3-diiminoisoindoline **2** and bis(nitrile)-Pt(II) complexes *trans*-$[PtCl_2(NCR)_2]$ (**1**) were studied in detail using theoretical DFT calculations.

RESULTS AND DISCUSSION

Reactions of 1,3-Diiminoisoindoline with Symmetrical Organonitrile Pt(II) Complexes. Following our ongoing project on metal-mediated activation of small molecules (i.e., nitriles[1,2,4] and isonitriles[14]), we have recently discovered that iminoisoindolin-1-ones, which represent a family of stable aromatic imines, exhibit nucleophilic properties toward metal-bound organonitriles and isonitriles. Iminoisoindolin-1-ones bear an endocyclic auxiliary amide functionality, which upon deprotonation may be involved in complexation forming relatively stable *chelated* metallacycles (Figure 1). Thus, the

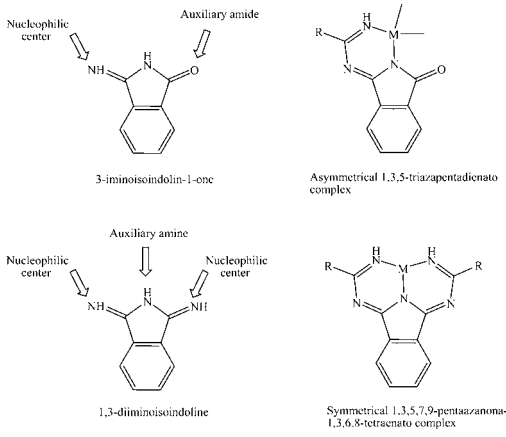


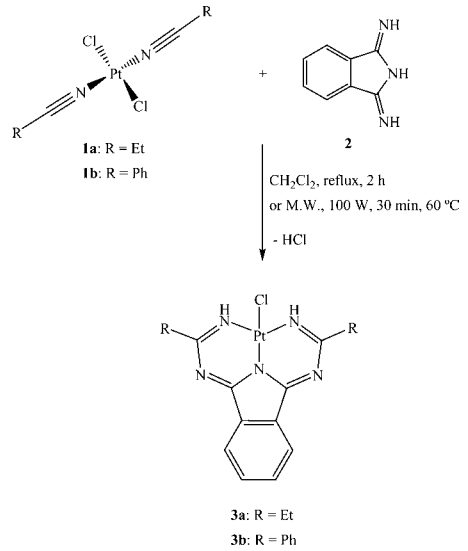
Figure 1.

reaction between iminoisoindolin-1-ones and metal-bound organonitriles or isonitriles leads to the formation of asymmetrical (1,3,5-triazapentadienato)[M] complexes [M = Ni(II),[7a] Cu(II),[7b] Pd(II),[7c] and Pt(II)[7c]].

These observations on the stability of the imine (i.e., iminoisoindolin-1-one) and of the products of its addition to nitriles (chelated 1,3,5-triazapentadienato species[7a,b]) prompted us to widen this type of chemistry to the commercially available 1,3-diiminoisoindoline (Figure 1) (bearing two nucleophilic sp^2–N centers and one endocyclic auxiliary amine functionality, which upon deprotonation might coordinate to the metal forming relatively stable *chelated* fused metallacycles). We employed this nucleophile for coupling with Pt(II)-bound organonitriles.

In the first part of this work, we report the selective synthesis of new symmetrical (1,3,5,7,9-pentaazanona-1,3,6,8-tetraenato)-Pt(II) complexes by using bis(propionitrile) and bis(benzonitrile) as starting dinitrile Pt(II) complexes, and 1,3-diiminoisoindoline as the reacting sp^2-nitrogen nucleophile (Scheme 1).

Scheme 1



Hence, treatment of *trans*-$[PtCl_2(NCR)_2]$ (**1**) (R = Et (**1a**), Ph (**1b**)) with one equivalent of 1,3-diiminoisoindoline HN═CC$_6$H$_4$C(NH)═NH (**2**), in refluxing CH_2Cl_2 for 2 h, gives access to the corresponding symmetrical (1,3,5,7,9-pentaazanona-1,3,6,8-tetraenato)Pt(II) complexes [PtCl{NH═C(R)N═C(C$_6$H$_4$)NC═NC(R)═NH}] (**3**) (R= Et (**3a**), Ph (**3b**)) in good yields (65−70%). The reactions are accelerated by focused microwave irradiation (30 min) giving the same products **3** in comparable yields (∼70%) (Scheme 1).

In a blank experiment, a prolonged reflux (48 h) of a mixture of 1 equiv. of propionitrile and 2 equiv. of 1,3-diiminoisoindoline **2** in CH_2Cl_2 showed no addition to nitrile and only the starting materials were recovered, indicating the Pt(II)-mediated character of the coupling.

The obtained complexes **3**, whose formation was monitored by TLC, were purified by column chromatography on silica gel and characterized by IR, ^{1}H, ^{13}C{^{1}H}, and ^{195}Pt NMR spectroscopies, ESI$^+$-MS, elemental analyses and also by X-ray diffraction.

The IR spectra of complexes **3** do not exhibit the typical υ(N≡C) values (2350−2300 cm^{-1} range), while new bands due to υ(NH) and υ(C═N) are observed at ∼3255 and ∼1648 cm^{-1}, respectively. For example, in the ^{1}H NMR spectrum of complex [PtCl{NH═C(Et)N═C(C$_6$H$_4$)NC═NC(Et)═NH}] (**3a**), the signals of the phenyl ring appear at δ 7.75 and 8.26, and the N*H* protons are exhibited at δ 9.77. The ^{13}C{^{1}H} NMR spectrum of **3a** shows the characteristic signals of the imine groups at δ 153.2 and 163.8, and the absence of the N≡C resonance at ∼116 ppm confirms that the nucleophilic addition of 1,3-diiminoisoindoline **2** occurs to both propionitrile ligands in **1a**.

X-ray Structure Crystallography. The structural parameters for complexes **3a** and **3b** are given in Table 1, representative diagrams are given in Figures 2 and 3 and selected bond distances and angles are provided in the respective legends. Other relevant features of the structures are given as Supporting Information.

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Table 1. Crystal Data, Experimental Parameters, and Selected Details of the Refinement Calculations of Compounds 3a and 3b

	3a·2H$_2$O	3b
formula	$C_{70}H_{84}Cl_5N_{25}O_2Pt_5$	$C_{22}H_{14}ClN_5Pt$
formula weight	2460.32	578.92
crystal system	monoclinic	monoclinic
space group	*C*2/*c*	*Cc*
a (Å)	55.400(2)	13.3847(6)
b (Å)	12.4426(5)	23.6077(10)
c (Å)	25.4089(11)	6.9904(3)
β (deg)	115.2820(10)	120.469(2)
V (Å^3)	15837.1(11)	1903.81(14)
Z	8	4
ρ_{calcd} (g/cm^3)	2.064	2.020
μ(Mo−Kα) (mm^{-1})	9.032	7.530
reflns collected	50855	11008
reflns unique	14378	5581
R_{int}	0.0559	0.0349
R_1,[a] wR2[b] ($I \geq 2\sigma$)	0.0351, 0.0652	0.0305, 0.0548
R_1, wR2 (all data)	0.0605, 0.0704	0.0400, 0.0581
GOF on F^2	1.006	0.954

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

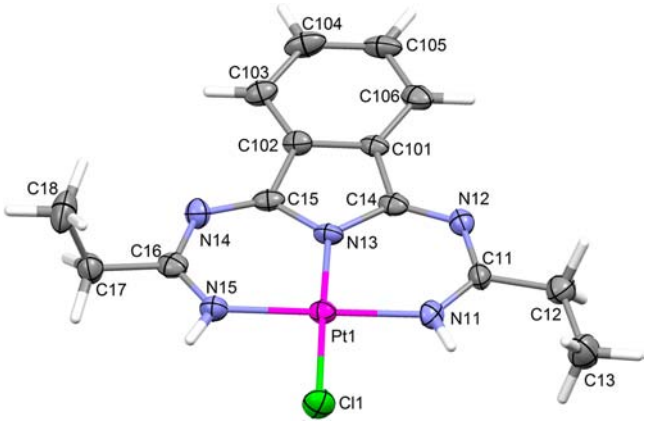

Figure 2. Crystal structure of one of the molecules of complex **3a** with the respective atomic numbering scheme (ellipsoid probability level of 50%). Selected bond distances (Å) and angles (deg): Cl1−Pt1 2.3250(17), N11−Pt1 1.974(5), N13−Pt1 1.942(5), N15−Pt1 1.972(5), C11−N11 1.299(8), C11−N12 1.368(8), C14−N12 1.305(8), C14−N13 1.381(8), C15−N14 1.317(8), C15−N13 1.384(8), C16−N15 1.316(9), C16−N14 1.372(8); N11−C11−N12 124.2(6), N12−C14−N13 128.9(6), N14−C15−N13 128.2(6), N15−C16−N14 125.9(7), N13−Pt1−N15 89.7(2), N13−Pt1−N11 88.9(2), N13−Pt1−Cl1 178.28(16), N15−Pt1−Cl1 91.67(17).

The geometry around the Pt ions in complexes **3a** and **3b** is of square planar type, comprising two fused six-membered metallacycles. Bond distances and angles involving equivalent moieties in both structures do not differ noticeably, but relevant features are described as follows.

Complex **3a** has a relatively simple molecular structure, but it forms a very complex crystal structure in the centrosymmetric *C*2/*c* space group with five independent Pt molecules of the same chemical composition and two molecules of water in the asymmetric unit; therefore, a total of 40 complex molecules and sixteen guest water molecules can be found in the unit cell (Supporting Information Figures S1 and S2). A representative molecular geometry of a single metal complex (the Pt1 molecule)

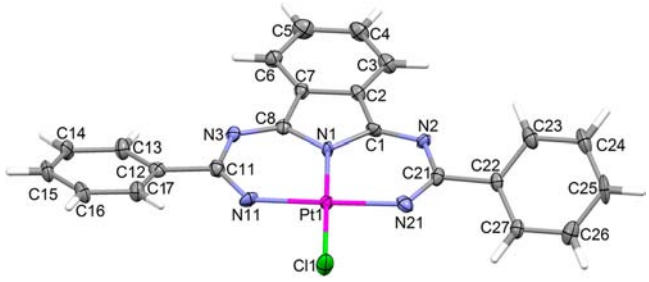

Figure 3. Crystal structure of complex **3b** with atomic numbering scheme (ellipsoid probability level of 50%). Selected bond distances (Å) and angles (deg): N1−Pt1 1.948(4), N11−Pt1 1.948(4), N21−Pt1 1.962(4), Cl1−Pt1 2.3087(16), C21−N21 1.306(7), C21−N2 1.368(6), C1−N2 1.311(6), C1−N1 1.389(6), C8−N3 1.304(6), C8−N1 1.370(7), C11−N11 1.313(6), C11−N3 1.360(6), C8−N1−C1 110.6(4), C1−N2−C21 122.8(4), C8−N3−C11 123.6(5), C11−N11−Pt1 128.8(4), N1−Pt1−N11 89.35(17), N1−Pt1−N21 90.10(18), N11−Pt1−N21 178.86(18), N1−Pt1−Cl1 179.25(13).

is shown in Figure 2. A quaternion fit[15] of the five crystallographically independent Pt complex molecules (hereafter denoted as Pt1−Pt5) was attempted via the program Platon AutoMolFit[16] (Figure S3) which showed that they can be related by pseudoglide planes and pseudorotation symmetries (hydrogen atoms and water molecules were excluded). While Pt1 and Pt2 are related by a pseudo-*c* glide plane [lattice vector of (−0.547, 0.298, 1.000) with a shift of 10.586 Å], the former is related with Pt3 and Pt4 by pseudorotation; a pseudo-*b* glide plane interconnect the Pt3 and Pt4 [lattice vector of (0.632, −1.000, −0.949) with a shift of 7.462 Å]. The overall root-mean square (rms) deviations for fittings of Pt1, Pt2, Pt3 and Pt4 range from 0.084 (for the fitting of Pt3 and Pt4) to 0.220 Å (for the fitting of Pt1 and Pt3). The same method for fitting the Pt5 molecule with any of the other Pt molecules gave rms deviations in the 1.474−1.841 Å range. The shortest Pt···Pt distances were found to be between 4.0880(4) and 4.4616(5) Å.

Multiple molecules in the asymmetric unit is a matter of considerable debate,[17−20] and the phenomena is believed to be the result of a compromise of several factors such as, among others, the size and shape of a molecule and intermolecular interactions.[17,21−23] In the present case, only a few hydrogen bond interactions could be found in the structure (Table S1) and, therefore, other features may be responsible for the high number of metal complex molecules in the asymmetric unit of **3a**. Indeed, the five independent metal complexes and the two water molecules form unique intermolecular hydrogen bonds, of which two represent $D_{water}\cdots A_{Pt}$ interactions with distances of 2.849(7) and 2.950(7) Å, and one represents a $D_{Pt}\cdots A_{water}$ contact (3.021(7) Å) which, in conjunction with contacts between the water molecules, lead to one-dimensional (1D) chains along the crystallographic *c* direction. The remaining hydrogen bonds pertain mainly to $D_{Pt}\cdots A_{Cl}$ contacts in the 3.369(7)−3.514(6) Å range with typical D−H···A angles between 157.9 and 165.6°. Some primary parameters were selected (Supporting Information Table S2) that might have also contributed to the uncommon number of formula units in the structure: (i) the folding of the complex molecules, as expressed by the distance of the Pt atom to the plane of the phenyl ring; in only one of the Pt molecules (Pt5) the metal atom lies on the plane of the phenyl ring, all the others lying below that plane. (ii) The two $(CC)_{Et}CN_{Pt}$ torsion angles

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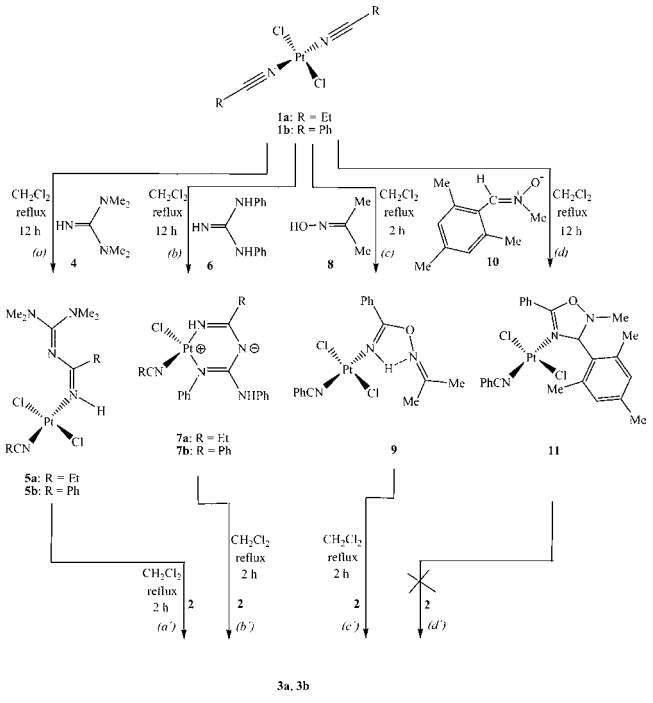
(Table S2) involving the ethyl groups, since in each molecule one of these groups is nearly in the plane of the coordination sphere of the metal while the other is markedly twisted out of that plane; moreover, only in Pt1 and Pt5 molecules both torsion angles have the same sign. Additionally, the molecules are also strongly associated through $\pi\cdots\pi$ interactions involving both the metallacycles and the phenyl rings, in offset parallel displacements (Supporting Information Figure S1), whose centroid···centroid distances range from 3.452(5) to 3.687(5) Å.

The most striking feature of the molecule of **3b** is the relative tilting of the phenyl rings, relative to the plane defined by the coordination atoms; while for the ring (C12−C17) that angle is of 16.79°, for the ring (C22−C27) it widens to 32.02°. Such distortions enables C−H···π strong interactions in the 2.62−2.99 Å range, which should play considerable role in the formation, stabilization, and crystallization of the compound. The shortest metal···metal distance is of 3.7717(3) Å, quite below that found for compound **3a** (see above).

Reactions of 1,3-Diiminoisoindoline with Mixed Asymmetrical Pt(II) Complexes. In the second part of this work, we studied the reactions of 1,3-diiminoisoindoline with asymmetrical Pt(II) complexes derived from the above bis(nitrile) Pt(II) compounds, expecting to obtain asymmetrical final products. For such a purpose, we started with 1,1,3,3-tetramethylguanidine, 1,3-diphenylguanidine, acetone oxime, and acyclic nitrone as the first reacting sp^2-nitrogen nucleophiles, and 1,3-dipole reagents, respectively.

Hence, treatment of *trans*-$[PtCl_2(NCR)_2]$ (**1**) (R = Et (**1a**), Ph (**1b**)) with one equivalent of 1,1,3,3-tetramethylguanidine $HN{=}C(NMe_2)_2$ (**4**), in refluxing CH_2Cl_2 for 12 h, gives access to the corresponding asymmetrical Pt(II) complexes *trans*-$[PtCl_2\{NH{=}C(R)N{=}C(NMe_2)_2\}(NCR)]$ (**5**) (R= Et (**5a**), Ph (**5b**)), containing both N-bound monodentate 1,3-diaza-1,3-diene and nitrile ligands, in good yields (65−67%) (Scheme 2, reaction *a*).

Scheme 2



Complexes **5** are formed by nucleophilic attack of the imine N atom to one nitrile ligand of **1**, since 1,1,3,3-tetramethylguanidine does not react with free NCR (R = Et, Ph) under the coupling conditions, implying that the nitrile-guanidine coupling is Pt(II)-mediated.

Complexes **5a** and **5b** have been characterized by elemental analyses, ESI^+−MS, IR, ^1H, and $^{13}C\{^1H\}$ NMR spectroscopies. The compounds give satisfactory C, H and N elemental analyses for the proposed formulation. In the ESI^+ mass spectra, **5a** and **5b** give the expected molecular ion $[M + 1]^+$.

The IR spectroscopic data additionally confirm the nucleophilic addition of tetramethylguanidine to one NCR ligand and rule out the possibility of displacement of nitriles by the guanidine. Thus, comparison of the IR spectra of **5a** and **5b** with those of the starting complexes shows the presence of intense stretching bands υ(C═N) at ∼1636 cm^{-1}. In addition, the bands because of υ(NH) and υ(N≡C) are observed at ∼3445 and ∼2228 cm^{-1}, respectively.

In the ^1H NMR spectra of **5a** and **5b**, the signal of the proton from the imino group C═N*H* (δ 6.61 and 6.13),[24] is shifted upfield compared to those observed in NMR spectra of other Pt imine complexes (δ 8−9).[2a−c] In the latter, the hydrogen bonding involving the imine C═N*H* proton was unambiguously recognized, while in our case the position of the signal at such a high field gives indirect evidence that the proton of the C═N*H* group is not involved in the hydrogen bonding in solution.[24] The $^{13}C\{^1H\}$ NMR spectra show the signals of the C═N bonds in the 163.3−178.3 ppm range, which corresponds to the characteristic *C*═N resonances in Pt imine complexes.[2,4,24] Moreover, the N≡C resonances are observed at 120.3 and 115.8 ppm, for **5a** and **5b**, respectively.

Treatment of the asymmetrical Pt(II) complexes *trans*-$[PtCl_2\{NH{=}C(R)N{=}C(NMe_2)_2\}(NCR)]$ (**5**) (R= Et (**5a**), Ph (**5b**)) with one equivalent of 1,3-diiminoisoindoline HN═$\underline{C}C_6H_4C(\underline{N}H)$═NH (**2**), in refluxing CH_2Cl_2 for 2 h, gives access to the corresponding above-mentioned symmetrical (1,3,5,7,9-pentaazanona-1,3,6,8-tetraenato) Pt(II) complexes $[PtCl\{\underline{N}H{=}C(R)N{=}C(C_6H_4)\underline{N}C{=}NC(R){=}\underline{N}H\}]$ (**3**) (R= Et (**3a**), Ph (**3b**)) in good yields (65−70%), respectively, as a result of displacement of the tetramethylguanidine moiety (in complex **5**) by 1,3-diiminoisoindoline **2** and elimination of HCl with attack at the nitrile ligand (Scheme 2, reaction *a*′).

Treatment of *trans*-$[PtCl_2(NCR)_2]$ (**1**) (R = Et (**1a**), Ph (**1b**)) with one equivalent of 1,3-diphenylguanidine HN═$C(NHPh)_2$ (**6**), in refluxing CH_2Cl_2 for 12 h, resulted in formation of the known[25] complexes $[PtCl\{\underline{N}H{=}C(R)NC(NHPh){=}\underline{N}Ph\}(NCR)]$ (**7**) (R= Et (**7a**), Ph (**7b**)) (containing both bidentate 1,3,5-triazapentadienato and nitrile ligands), which were isolated in 50 and 60% yields, respectively (Scheme 2, reaction *b*). Complexes **7a**−**7b** are formed as products of the nucleophilic addition of 1,3-diphenylguanidine to one nitrile carbon atom, followed by ring closure of the formed 1,3,5-triazapentadienato ligand and elimination of HCl.

Treatment of the asymmetrical bidentate (1,3,5-triazapentadienate)Pt(II) complexes $[PtCl\{\underline{N}H{=}C(R)NC(NHPh){=}\underline{N}Ph\}(NCR)]$ (**7**) (R= Et (**7a**), Ph (**7b**)) with one equiv of 1,3-diiminoisoindoline **2**, in refluxing CH_2Cl_2 for 2 h, gives access to the corresponding above-mentioned symmetrical (1,3,5,7,9-pentaazanona-1,3,6,8-tetraenato)Pt(II) complexes $[PtCl\{\underline{N}H{=}C(R)N{=}C(C_6H_4)\underline{N}C{=}NC(R){=}\underline{N}H\}]$ (**3**) (R= Et (**3a**), Ph (**3b**)) in good yields (65−70%), respectively, as a result of displacement of diphenylguanidine moiety

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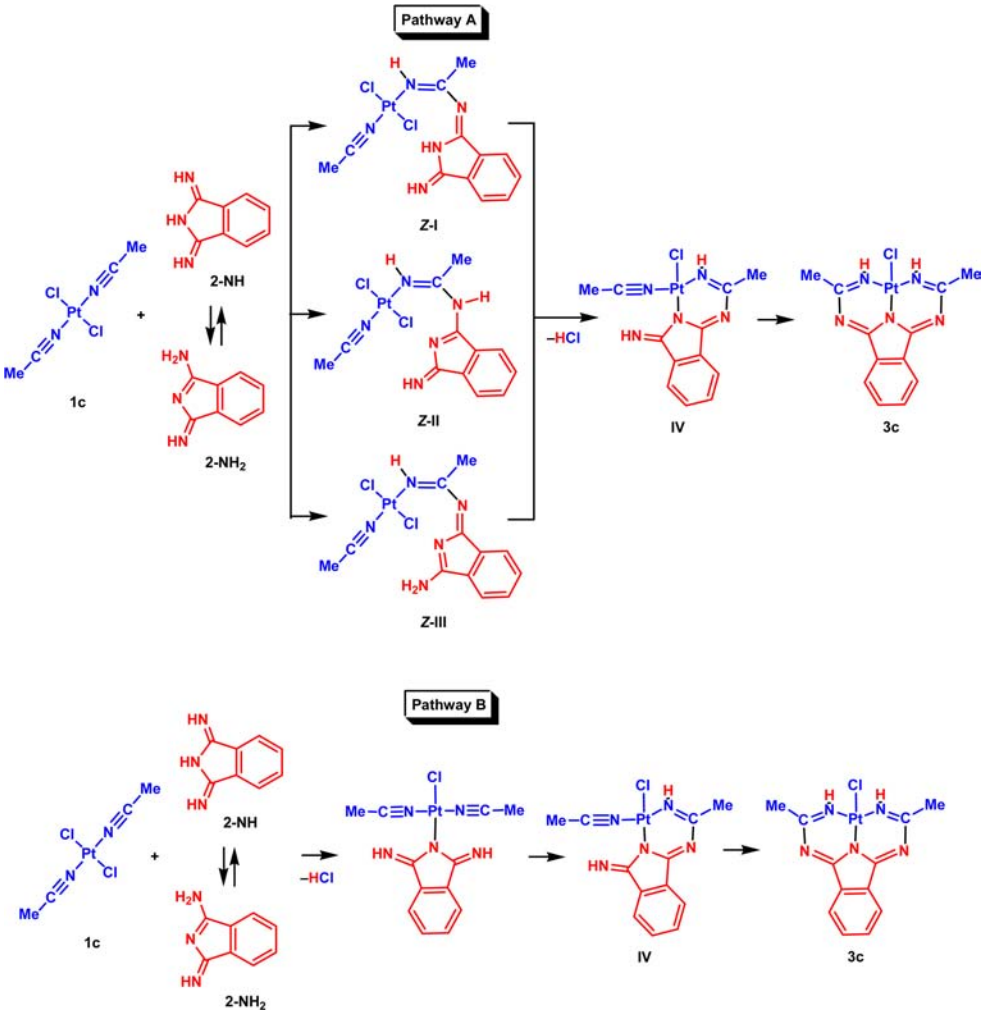
Scheme 3. Two Possible Pathways of the Formation of 3c from 1c and 2



(in complex **7**) by 1,3-diiminoisoindoline **2** and elimination of HCl with attack at the ligated nitrile (Scheme 2, reaction *b*′).

On the other hand, treatment of *trans*-[$PtCl_2(NCPh)_2$] (**1b**) with the acetone oxime HO-N=CMe_2 (**8**), in refluxing CH_2Cl_2 for 2 h, gives access to the known[2a,b] monoimine *trans*-[$PtCl_2${NH=C(Ph)ON=CMe_2}(NCPh)] (**9**) complex in moderate yield (~55%) (Scheme 2, reaction c).

Similarly, treatment of **9** with one equivalent of 1,3-diiminoisoindoline **2**, in refluxing CH_2Cl_2 for 2 h, leads to the corresponding above symmetrical complex [PtCl{NH=C(Ph)N=C(C_6H_4)NC=NC(Ph)=NH}] (**3b**) in good yield (~68%), as a result of displacement of acetone oxime moiety (in complex **9**) by 1,3-diiminoisoindoline **2** and elimination of HCl with attack at the ligated NCPh (Scheme 2, reaction *c*′).

On the other hand, in the reaction of *trans*-[$PtCl_2(NCPh)_2$] (**1b**) with one equivalent of the acyclic nitrone $^{-}O^{+}N(Me)$=C(H)($C_6H_2Me_3$-2,4,6) (**10**), the system was refluxed in CH_2Cl_2 for 12 h, to give the mono-oxadiazoline complex *trans*-[$PtCl_2${N=C(Ph)ON(Me)C(H)($C_6H_2Me_3$-2,4,6)}-(NCPh)] (**11**) as the exclusive product (~67% yield) (Scheme 2, reaction d).

Complex **11** has been characterized by elemental analysis, ESI^+-MS, IR, ^1H, and $^{13}C\{^1H\}$ NMR spectroscopies. The compound gives satisfactory C, H and N elemental analysis for the proposed formulation. In the ESI^+ mass spectrum, **11** gives the expected molecular ion $[M+1]^+$. Its IR spectrum exhibits υ(N≡C) at 2287 cm^{-1} that is identical to that of the starting complex **1b** (2286 cm^{-1}). The N=C stretching vibration (1634 cm^{-1}) is also comparable with those of the corresponding bis-imine[2a−c] or bis-oxadiazoline complexes.[4j] The ^1H and $^{13}C\{^1H\}$ NMR spectra of **11** show that the compound contains both an oxadiazoline and a nitrile ligand. In the ^1H NMR spectrum, the N−C*H*−N resonance is detected at 6.41 ppm, and, in the $^{13}C\{^1H\}$ NMR spectrum, the N−*C*H−N resonance appears at 91.9 ppm, while the N≡*C* signal occurs at 116.3 ppm.

Once the first cycloaddition has taken place, the second nitrile ligand still present in the molecule exhibits a lower reactivity because of the different electronic properties of the oxadiazoline in trans-position, in comparison with the nitrile in **1b**. On the other hand, no reaction between the mono-oxadiazoline complex **11** and the 1,3-diiminoisoindoline **2** has been observed, and only the starting material was recovered (Scheme 2, reaction d′). Refluxing the reaction mixture for a prolonged time (24 h) affords a number of uncharacterized products.

Theoretical Mechanistic Studies. In this part, the plausible mechanisms of the formation of complexes **3** (methyl derivative **3c**) are discussed. Taking into account the previous experimental[1b,2f,26] and theoretical[27] data on the reactions of addition of various protic nucleophiles (H_2O, ROH, NH_3, RNH_2, RR′NH, NR_2OH, RR′C=NOH, etc.) to metal-bound

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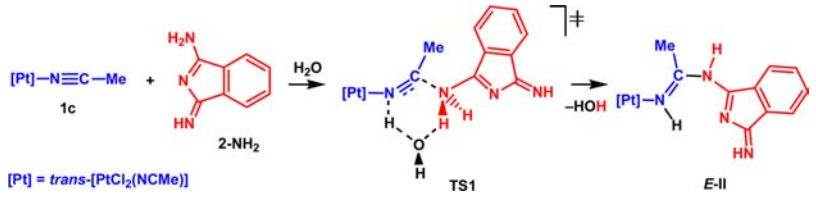
Scheme 4. Concerted Mechanism of the Nucleophilic Addition of 2-NH_2 to 1c by the NH_2 Group

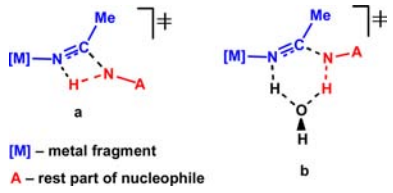


nitriles, it seems to be a good assumption that the reaction starts with the nucleophilic addition (NA) of 1,3-diiminoisoindoline **2** to one of the nitrile ligands of complex *trans*-$[PtCl_2(NCR)_2]$ to give imino-complexes **I**–**III** followed by the first cyclization to **IV** (with HCl elimination) and then by the second nucleophilic addition/cyclization affording the final product **3** (Scheme 3, Pathway A). Alternatively, the coordination of the 1,3-diiminoisoindoline **2** to the Pt atom accompanied by the elimination of HCl may occur on the first step, and then two consecutive NAs of imino groups to the nitrile ligands should afford the final product **3** (Scheme 3, Pathway B). However, the calculations indicate that the Pathway B is much less favorable than the Pathway A (see Supporting Information for details).

Tautomeric Equilibrium of ***2***. 1,3-Diiminoisoindoline **2** may exist in two possible tautomeric forms, that is, diimino form **2-NH** and imino-amino form **2-NH_2** (Scheme 3), which can convert to each other upon an intramolecular H-transfer. Such tautomeric equilibrium was proved for related amidines HN═C(R)–NHR′ ⇄ H_2N–C(R)═NR′ by a series of chemical and physicochemical experiments.[28] Our calculations indicate that both forms **2-NH** and **2-NH_2** have very similar stabilities in both gas phase and solution, the symmetrical form **2-NH** being only by 0.5 kcal/mol more stable in CH_2Cl_2 solution than **2-NH_2**. Hence, the mechanisms of reaction of both **2-NH** and **2-NH_2** forms with *trans*-$[PtCl_2(NCMe)_2]$ (**1c**) are discussed in the following sections.

Nucleophilic Addition of ***2*** *to Coordinated Nitrile. Concerted Mechanism.* For the NAs to metal-coordinated nitriles, three general types of the mechanisms are usually considered, that is, concerted, dissociative, and associative. The first one combines the formation of a new CN bond and the H-transfer from the imino (amino) nitrogen to the nitrile nitrogen in a single step, and it includes the generation of one cyclic transition state (TS) (Scheme 4). This transition state may be 4-membered (type **a**, Chart 1) or 6-membered (type **b**, Chart 1).

Chart 1



In the latter case, a solvent molecule participates in the formation of TS and plays the role of the H-transfer promoter. Previous theoretical studies of NAs of NH_3 and amines to *trans*-$[PtCl_2(NCMe)_2]$ (**1c**)[27c] showed that the solvent (water)-assisted mechanism via the 6-membered TS is much more energetically favorable than the pathway via the 4-membered TS due to a higher stability of 6-membered cyclic structures, and namely this route is discussed in the present work. Taking into account that there is a significant amount of water in nondried CH_2Cl_2 used in the experimental part (see Experimental Section), H_2O was considered as solvent–H-transfer promoter in TSs.

Type **b** transition state of the concerted mechanism, **TS1**, was found for the nucleophilic addition of **2-NH_2** to **1c** by the NH_2 group (Scheme 4). The activation barrier in CH_2Cl_2 solution calculated for this route is 41.1 kcal/mol (in terms of $\Delta G_s^{\ddagger}$) being unacceptably high for an effective realization of this route. This value is even higher than the activation energy estimated previously for the diphenylamine addition to **1c** (32.8 kcal/mol[27c]). Structurally similar transition states (**TS2** and **TS3**) were also found for the reactions of **2-NH** and **2-NH_2** (by NH-group) with **1c**. However, the analysis of the nature of these TSs indicates that they correspond to the associative stepwise rather than concerted mechanism (see the next section and also Supporting Information for more detailed discussion). Thus, the concerted mechanism of the formation of products **I**–**III** may be ruled out.

Associative Mechanism. The associative mechanism involves the addition of nucleophile to the nitrile carbon atom followed by the proton transfer to the nitrile nitrogen atom via one-step H-shift or via deprotonation/protonation steps (Schemes 5 and 6). This mechanism was found for the NAs of **2-NH** and **2-NH_2** (by NH group) to **1c** and it starts with the formation of **TS4** and **TS5**, respectively, leading to intermediates **INT1** and **INT2**, each of them having two isomers with different position of substituents and the lone electron pair relative to the C═N bond. The activation energies of the formation of **INT1a** and **INT2b** are very similar ($\Delta G_s^{\ddagger}$ are 20.0 and 19.3 kcal/mol, respectively), and those of the formation of **INT1b** and **INT2a** are only slightly higher ($\Delta G_s^{\ddagger}$ are 22.9 and 22.6 kcal/mol, respectively). The intermediates **INT1a**, **INT2a**, and **INT2b** have similar thermodynamic stabilities (ΔG_s values of formation are in the range of 11.8–12.5 kcal/mol), whereas **INT1b** is by 4.8–5.5 kcal/mol less stable.

In contrast, no intermediate of the **INT1** or **INT2** type was found for the NA of **2-NH_2** by the NH_2 group. All attempts to locate it resulted in a decomposition of initial structures and moving the *trans*-$[PtCl_2(NCMe)_2]$ and **2-NH_2** molecules away from each other. Thus, the associative stepwise mechanism for the addition of **2-NH_2** by amino-group can be excluded.

The generated intermediates **INT1a** and **INT2a** can be transformed to the nucleophilic addition products *E*-**I** and *E*-**III**, respectively, via transition states **TS2** and **TS3** of the type **b** (Chart 1). The calculated activation barrier of the reaction **INT1a** → **TS2** → *E*-**I** is 7.3 kcal/mol while that of the reaction **INT2a** → **TS3** → *E*-**III** is only 1.0 kcal/mol.

Alternatively, the **INT1** → **I**, **INT1** → **II**, **INT2** → **II**, and **INT2** → **III** transformations could occur in a stepwise manner via the sequential deprotonation/protonation steps. The deprotonation of **INT1** or **INT2** by water molecule in CH_2Cl_2 solution (Schemes 5 and 6, B = H_2O) is very

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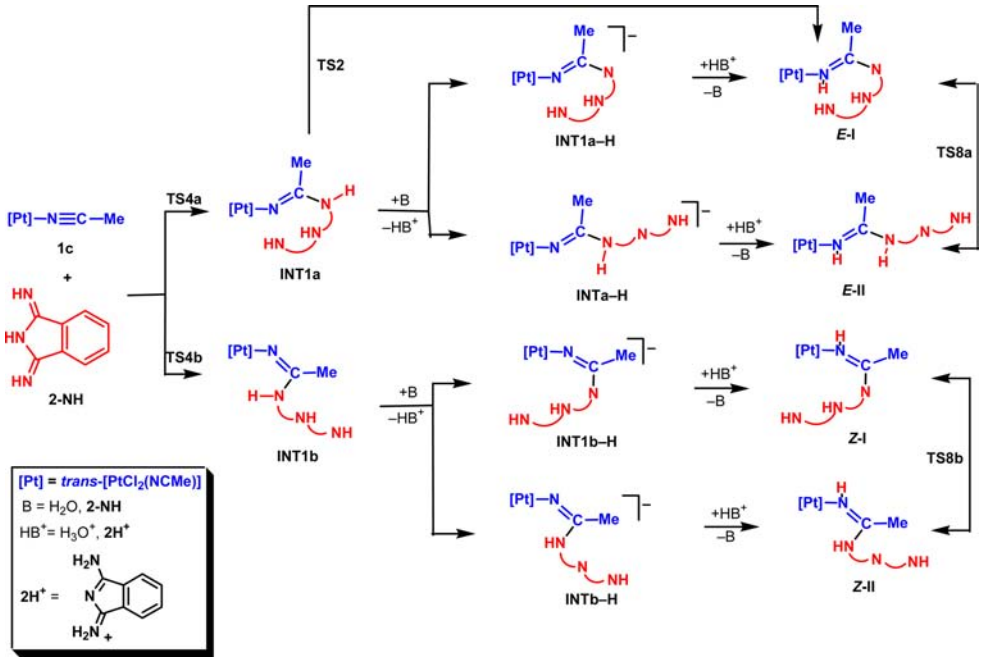
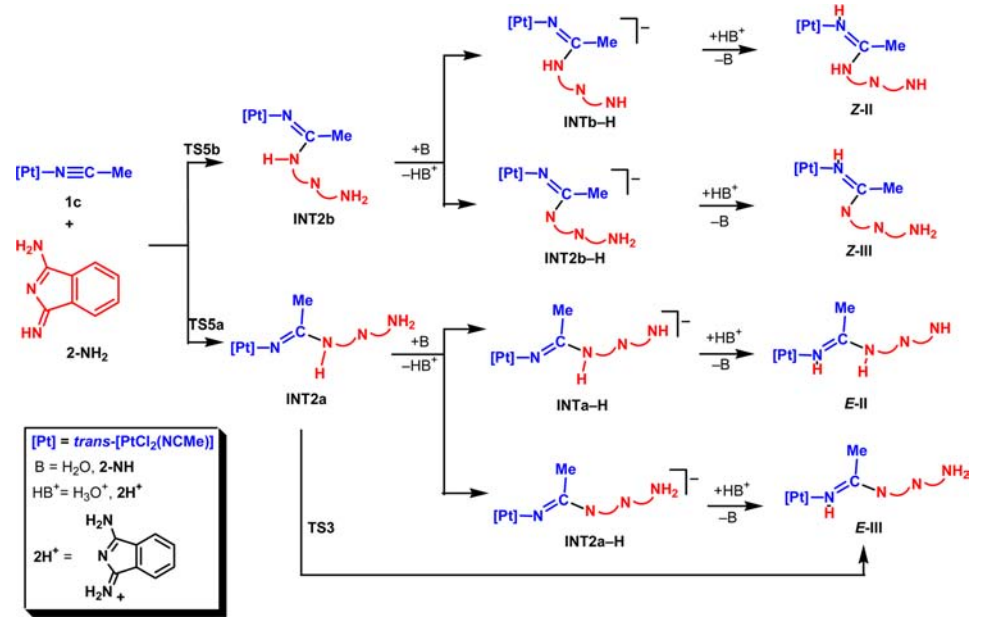
Scheme 5. Stepwise Associative Mechanisms of the Nucleophilic Addition of 2-NH to 1c



Scheme 6. Stepwise Associative Mechanisms of the Nucleophilic Addition of 2-NH_2 to 1c



endoergonic (by 40.1−54.5 kcal/mol, Table S4). However, if **2** plays the role of base (Schemes 5 and 6, B = 2-NH) the deprotoation energies appear to be significantly lower (4.2−18.5 kcal/mol, Tables 2 and S4). The lowest ΔG_s values of deprotonation were found for the reactions **INT1b** + **2-NH** → **INTb-H** + $2H^+$ (4.2 kcal/mol), **INT1b** + **2-NH** → **INT1b-H** + $2H^+$ (6.8 kcal/mol), and **INT1a** + **2-NH** → **INT1a-H** + $2H^+$ (7.5 kcal/mol), all of these processes being quite competitive with the **INT1a** → **TS2** → *E*-**I** route ($\Delta G_s^{\ddagger}$ = 7.3 kcal/mol).

Dissociative Mechanism. The dissociative mechanism includes the initial deprotonation of the nucleophile (by a solvent molecule or autoionization), subsequent addition of the deprotonated fragment to the nitrile carbon atom and protonation of the nitrile nitrogen atom (Scheme 7). However, as was found previously for the nucleophilic addition of oximes[27a] and amines,[27b,c] this mechanism is more energetically demanding compared to the concerted or associative pathways. Indeed, the calculated ΔG_s values of the reactions **2-NH** + B → **2-NH-H** + HB^+, **2-NH_2** + B → **2-NH_2-Ha** + HB^+, and **2-NH_2** + B → **2-NH_2-Hb** + HB^+ in CH_2Cl_2 solution with B = H_2O are 84.8, 70.1, and 98.8 kcal/mol, respectively, and those with B = **2-NH** are 48.9, 34.1, and 62.8 kcal/mol, correspondingly. Additionally, in accord with the experimental kinetic studies of the NA of hydroxylamines R_2NOH to Pt(II) and Pt(IV) nitrile complexes,[29] the activation entropy of these processes has a clearly negative value (−9.8 ± 2.4 cal/mol·K and −11.2 ± 5.5 cal/mol·K, respectively) indicating that the mechanism is of associative or concerted type.

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Table 2. Calculated Energetic Characteristics (in kcal/mol) of the Reactions Discussed in the Text

reaction		$\Delta H_s^{\ddagger}$	$\Delta G_s^{\ddagger}$	ΔH_s	ΔG_s
2-NH → **2-NH$_2$**				0.7	0.5
1c + **2-NH$_2$** → *E*-**II**	via **TS1**	23.5	41.1	−14.9	−4.8
1c + **2-NH** → **INT1a**	via **TS4a**	10.1	20.0	1.6	11.8
1c + **2-NH** → **INT1b**	via **TS4b**	13.1	22.9	6.9	17.3
1c + **2-NH$_2$** → **INT2a**	via **TS5a**	13.9	22.6	3.6	12.5
1c + **2-NH$_2$** → **INT2b**	via **TS5b**	9.5	19.3	1.8	11.9
INT1a → *E*-**I**	via **TS2**	−0.7	7.3	−17.3	−16.9
INT2a → *E*-**III**	via **TS3**	−8.0	1.0	−21.8	−21.3
INT1a + **2-NH** → **INT1a-H** + 2H$^+$				8.0	7.5
INT1b + **2-NH** → **INTb-H** + 2H$^+$				5.2	4.2
INT1b + **2-NH** → **INT1b-H** + 2H$^+$				6.7	6.8
INT2b + **2-NH** → **INTb-H** + 2H$^+$				9.6	9.0
INT1a-H + 2H$^+$ → *E*-**I** + **2-NH**				−25.3	−24.4
INT1b-H + 2H$^+$ → *Z*-**I** + **2-NH**				−29.5	−29.5
INTb-H + 2H$^+$ → *Z*-**II** + **2-NH**				−27.0	−25.8
2-NH + **2-NH** → **2-NH-H** + 2H$^+$				49.6	48.9
2-NH$_2$ + **2-NH** → **2-NH$_2$-Ha** + 2H$^+$				33.8	34.1
2-NH$_2$ + **2-NH** → **2-NH$_2$-Hb** + 2H$^+$				63.0	62.8
INT1a → *E*-**II**	via **TS7**	−1.6	−1.3	−15.8	−16.0
E-**II** → *E*-**I**	via **TS8a**	10.8	19.3	−1.5	−0.9
Z-**II** → *Z*-**I**	via **TS8b**	11.1	19.1	−1.0	−1.0
E-**I** → *E*-**III**	via **TS9a**	6.4	13.8	−1.8	−3.2
Z-**I** → *Z*-**III**	via **TS9b**	11.4	19.5	3.7	2.5
Z-**I** → **IV**	via **TS10**	24.8	26.5	7.8	2.5
Z-**II** → **IV**	via **TS11**	26.5	27.8	6.8	1.5
Z-**III** → **IV**	via **TS12**	13.3	16.2	4.1	0.0
IV → **V**	via **TS13**	5.7	8.3	−6.0	−3.0
V + **2-NH** → **V−H** + 2H$^+$				9.8	9.6
V-H + 2H$^+$ → **3c** + **2-NH**				−34.2	−33.9

Mechanisms Involving the Central NH Group. The presence of the central imino group in the **2-NH** form of the nucleophile opens the possibility of other routes which involve directly this imino group (Scheme 8). The first such route might be a direct one-step addition of **2-NH** to **1c** via **TS6** including the simultaneous formation of the CN bond and H-transfer from the central NH group of **2-NH** to the nitrile nitrogen. However, a search of the potential energy surface for **TS6** showed that there is no transition state of this type. The second possibility is the stepwise mechanism which starts with the formation of **INT1a** (via **TS4a**) and followed by the H-transfer via **TS7** to give the NA product *E*-**II** [route (1)]. The rate limiting step of this mechanism is the first step ($\Delta G_s^{\ddagger}$ = 20.0 kcal/mol, Table 2) while the second step is barrierless in terms of ΔG_s ($\Delta G_s^{\ddagger}$ = −1.3 kcal/mol).

2-NH + **1c** → **TS4a** → **INT1a** → **TS7** → *E*-**II** (1)

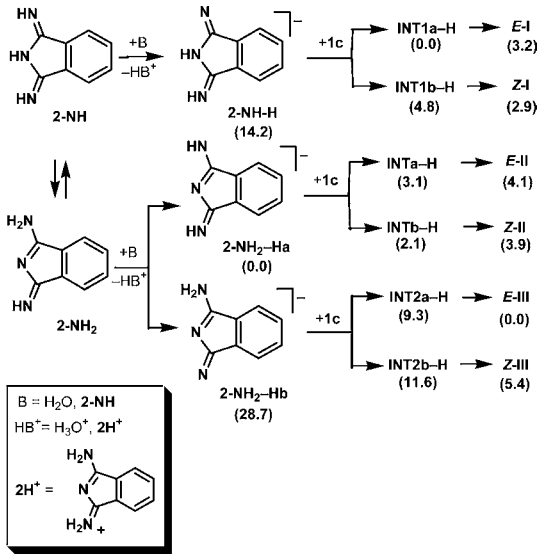
2-NH + **1c** → **TS4a** → **INT1a** → **TS2** → **E-I** (2)

2-NH + **1c** → **TS4a** → **INT1a**(+ 2) → **INT1a-H**(+ 2H$^+$) → *E*-**I** (3)

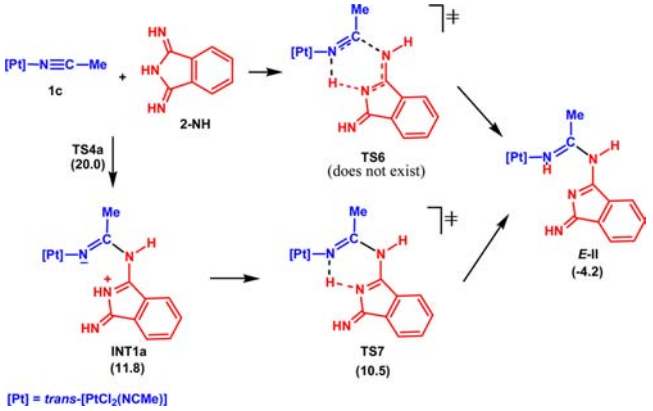
2-NH$_2$ + **1c** → **TS5b** → **INT2b**(+ 2) → **INTb-H**(+ 2H$^+$) → *Z*-**II** (4)

The analysis of the energy profiles of all pathways discussed above indicates that three of the most favorable routes, that is, 1−3, have the same rate limiting step (formation of **INT1a**) and, hence, the same overall activation barrier of 20.0 kcal/mol. The lowest-energy route leading to the formation of a *Z*-isomer (*Z*-**II**) [route 4] requires only 1.5 kcal/mol higher energy than

Scheme 7. Stepwise Dissociative Mechanism of the Nucleophilic Addition of 2 to 1c (Relative Gibbs Free Energies in Solution Are Indicated in Parentheses in kcal/mol)



Scheme 8. Mechanisms of the Nucleophilic Addition of 2-NH to 1c Involving the Central NH Group (Gibbs Free Energies Relative to Reactants 1c + 2-NH are Indicated in Parentheses in kcal/mol)



routes 1−3 and thus it may effectively operate concurrently. The second step of the route 4 is rate limiting: the energy of the deprotonated complex **INTb-H** relative to **1c** + **2-NH** is 21.5 kcal/mol vs the energy of **TS5b** of 19.8 kcal/mol. The activation barriers of the routes 1−4 (20.0 and 21.5 kcal/mol) are close to the experimentally determined Gibbs free energy of activation for the NA of hydroxylamine HON(p-$CH_2C_6H_4Cl$)$_2$ to the Pt(II) complex [$PtCl_3$(NCEt)]$^-$ (20.6 kcal/mol).[29,30]

Nucleophilic Addition Products. The NA products *E*/*Z*-**I**−*E*/*Z*-**III** (Schemes 5 and 6) have rather similar thermodynamic stabilities, the ΔG_s values of their formation from **1c** and **2-NH** being in the range of (−2.9)−(−8.3) kcal/mol. The isomers *E*-**III** and *Z*-**I** are the most stable ones followed by *E*-**I**, *Z*-**II**, *E*-**II**, and *Z*-**III**. Note that according to the experimental X-ray data, both *E*- and *Z*-configurations are known for the products of nucleophilic addition of various amines and imines to nitriles.[24,31] As discussed above, the isomers *E*-**I**, *E*-**II**, and *Z*-**II** are directly accessible upon the reaction of **2** with **1c**. However all isomers **I**−**III** are in equilibrium with each other via

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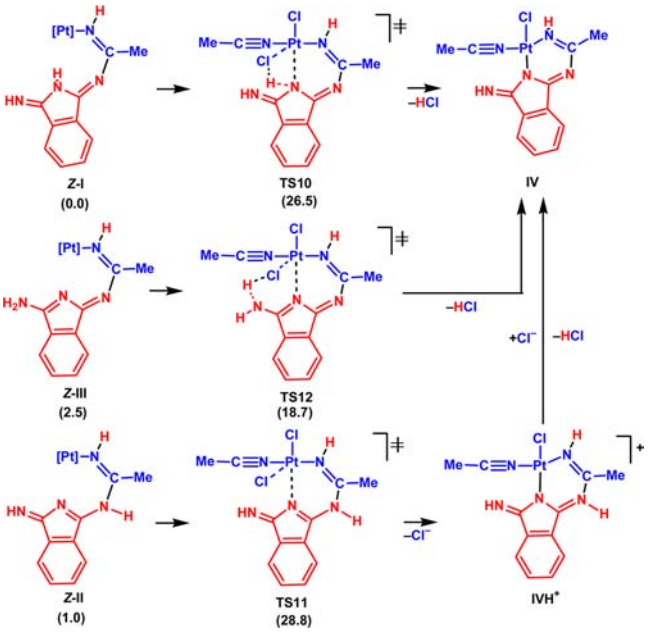
water-assisted H-transfers involving **TS8a,b** and **TS9a,b** (Scheme 5). The activation barriers of the *E*-**II** → *E*-**I**, *Z*-**II** → *Z*-**I**, *E*-**I** → *E*-**III**, and *Z*-**I** → *Z*-**III** transformations are 19.3, 19.1, 13.8, and 19.5 kcal/mol.

First Cyclization. The *Z*-isomers of the NA products formed at the first stage can undergo cyclization to give intermediate **IV** (Scheme 9). Transition states were found for the cyclizations of

Scheme 9. Mechanisms of the First Cyclization Step[a]



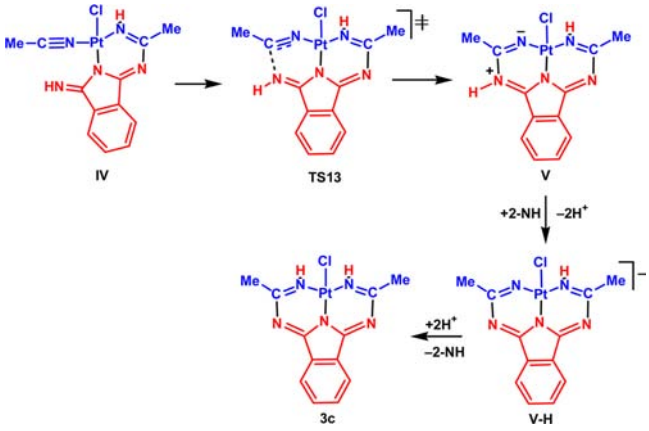
[a]Gibbs free energies relative to *Z*-**I** are indicated in parentheses in kcal/mol.

all three complexes *Z*-**I**–*Z*-**III** (**TS10**–**TS12**). **TS10** and **TS12** correspond to the concerted formation of the Pt–N bond and elimination of the HCl molecule whereas **TS11** is associated with the elimination of the Cl^- ion which, on the next step, abstracts the proton from the N atom. The activation barrier of the reaction *Z*-**III** → **TS12** → **IV** is rather low (16.2 kcal/mol) but those of the reactions *Z*-**I** → **TS10** → **IV** and *Z*-**II** → **TS11** → **IVH**$^+$ (+ Cl^-) → **IV** + (HCl) are significantly higher (26.5 and 27.8 kcal/mol, respectively). Thus, two latter processes are not favorable. Complex **IV** whose formation is by 2.9 kcal/mol exoergonic relative to the initial reactants **2-NH** and **1c** is the precursor for the second cyclization.

Second Nucleophilic Addition/Cyclization. For the last stage of the formation of **3c**, several plausible mechanisms have been examined (see Supporting Information for details). The calculations indicated that the most favorable mechanism of this stage includes the formation of the bicyclic structure **V** via **TS13** and proton migration in a stepwise manner **V** (+ **2**) → **V–H** (+ **2H**$^+$) → **3c** (Scheme 10). The activation barrier of the first step of this route is 8.3 kcal/mol and the energy of deprotonation of **V** is only 9.6 kcal/mol.

In summary, the most plausible mechanism of the formation of **3c** from **1c** and **2** is depicted in Scheme 11, the energy profile is shown in Figure 4. The first nucleophilic addition step of this process is the rate-limiting one and the apparent Gibbs free energy of activation was calculated to be 21.5 kcal/mol, a value quite comparable with the experimental one obtained for the reaction of HON(*p*-$CH_2C_6H_4Cl)_2$ with $[PtCl_3(NCEt)]^-$ (20.6 kcal/mol).[29]

Scheme 10. Most Plausible Mechanisms of the Second Cyclization/Nucleophilic Addition Step



FINAL REMARKS

The results of the experimental part of this work can be summarized under three perspectives. First, the reaction between two *trans*-ligated RCN species (in **1**) and 1,3-diiminoisoindoline (**2**) leads to the formation of symmetrical (1,3,5,7,9-pentaazanona-1,3,6,8-tetraenato)Pt(II) complexes (**3**), and the system represents a novel reactivity mode which has never been reported for any nitrile at a Pt metal center. The developed synthetic method operates under mild conditions, affords pure (1,3,5,7,9-pentaazanona-1,3,6,8-tetraenato)Pt(II) complexes in good yields, and, in contrast to the preparation of asymmetrical (1,3,5-triazapentadienato)Ni(II) complexes,[7a] does not require the addition of a base. The reactions are accelerated by focused microwave irradiation giving the same products in comparable yields.

Second, the asymmetrical imine-Pt(II) complexes obtained by nucleophilic additions to one nitrile ligand of the starting dinitrile Pt(II) compounds react with 1,3-diiminoisoindoline to give the same final (1,3,5,7,9-pentaazanona-1,3,6,8-tetraenato)-Pt(II) complexes **3**.

Third, the obtained products **3** can be viewed as fused tetracyclic *chelates* and represent a novel type of symmetrical pentaazanonatetraene complexes and themselves, bearing two potential coordinating metallacycle-imine groups, can be used as metallaligands, leading to heteronuclear complexes with different molecular architectures. Work focusing on the latter topic is underway in our laboratory.

Theoretical mechanistic studies of the formation of **3** from **1** and **2** reveal that the most plausible pathway of this process includes the stepwise nucleophilic addition of **2** (in imino-amino form **2-NH$_2$**) to one of the nitrile ligands of **1**, a first cyclization accompanying the formation of the Pt–N bond and elimination of HCl, and a second stepwise nucleophilic addition/cyclization. The rate limiting step of the whole process is the first nucleophilic addition, and the calculated apparent Gibbs free energy of activation is 21.5 kcal/mol.

EXPERIMENTAL SECTION

Material and Instrumentation. Solvents and reagents were obtained from commercial sources (Aldrich) and used as received. For TLC, Merck Silica gel $60F_{254}$ plates have been used. C, H, and N elemental analyses were carried out by the Microanalytical Service of the Instituto Superior Técnico. ^1H and $^{13}C\{^1H\}$ spectra (in $CDCl_3$) were measured on Bruker Avance II 300 and 400 MHz (UltraShield Magnet) spectrometers at ambient temperature. ^1H and $^{13}C\{^1H\}$ chemical shifts (δ) are expressed in ppm relative to $Si(Me)_4$, and ^{195}Pt

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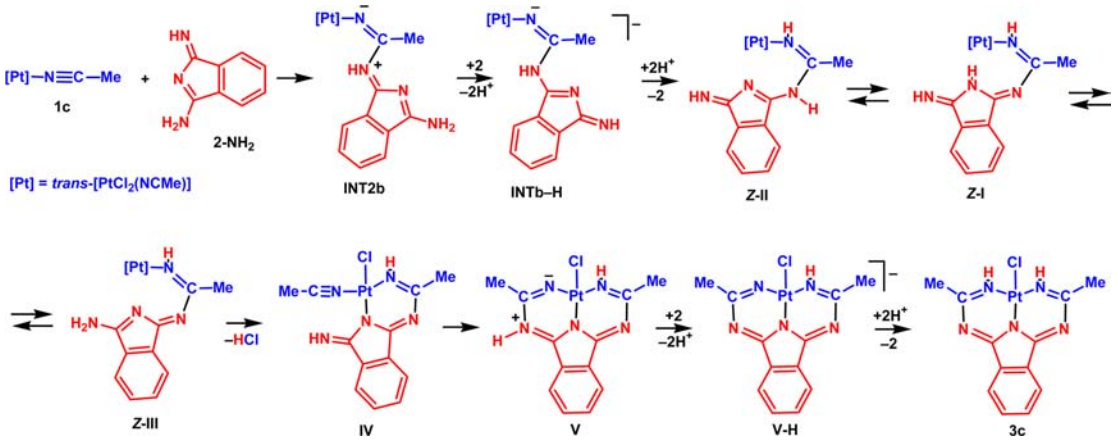
Scheme 11. Most Plausible Mechanism of the Reaction between 2 and 1c Leading to 3c



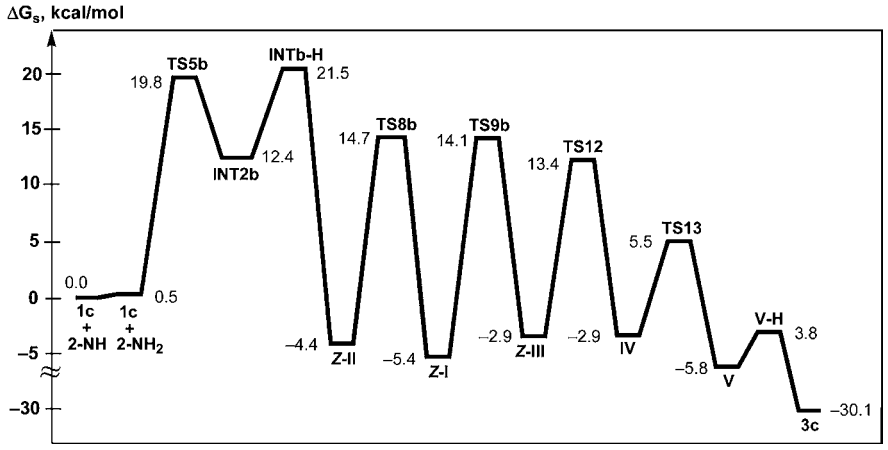


Figure 4. Energy profile of the most plausible mechanism of the reaction between **2** and **1c** leading to **3c**.

chemical shifts are relative to $Na_2[PtCl_6]$ (by using aqueous $K_2[PtCl_4]$, δ = −1630 ppm, as a standard). J values are in Hz. Infrared spectra (4000−400 cm^{-1}) were recorded on a Bio-Rad FTS 3000MX instrument in KBr pellets and the wavenumbers are in cm^{-1}. Electrospray mass spectra were carried out with an ion-trap instrument (Varian 500-MS LC Ion Trap Mass Spectrometer) equipped with an electrospray (ESI) ion source. The solutions in methanol were continuously introduced into the mass spectrometer source with a syringe pump at a flow rate of 10 μL/min. The drying gas temperature was maintained at 350 °C and dinitrogen was used as nebulizer gas at a pressure of 35 psi. Scanning was performed from m/z = 50 to 1500. The microwave irradiation experiments were undertaken in a focused microwave CEM Discover reactor (10 mL, 13 mm diameter, 300 W maximum power), which is fitted with a rotational system and an IR detector of temperature.

*Reactions of the Organonitrile Pt(II) Complexes trans-[$PtCl_2$(NCR)$_2$] [R = Et (**1a**), Ph (**1b**)] with 1,3-Diiminoisoindoline (**2**). By the Conventional Method.* A solution of **1a** (200 mg, 0.532 mmol) or **1b** (200 mg, 0.423 mmol) in CH_2Cl_2 (4 mL) was added at room temperature to 1,3-diiminoisoindoline (**2**) (1 equiv), and the mixture was refluxed for 2 h whereupon the solvent was removed in vacuo. The crude residue was purified by column chromatography on silica (CH_2Cl_2 as the eluent), followed by evaporation of the solvent in vacuo to give the final **3a** or **3b** products.

By Focused Microwave Irradiation. In this method, identical amounts of the reagents described above were added to a cylindrical Pyrex tube, which was then placed in the focused microwave reactor. The system was left under irradiation (100 W) for 30 min at 60 °C. After evaporation of the solvent in vacuo to dryness, the crude residue was purified as indicated in the By the Conventional Method section.

Crystals of **3a** and **3b** suitable for X-ray analysis were obtained by slow evaporation of a chloroform solution.

*Complex **3a**.* Method i, 65% yield; method ii, 68% yield. TLC on SiO_2: R_f = 0.81 (eluent CH_2Cl_2). IR (cm^{-1}): 3255 (NH), 1648 (C═N). ^{1}H NMR ($CDCl_3$), δ: 1.47 (t, J_{HH} 7.5 Hz, 6H, CH_3CH_2), 2.82 (q, J_{HH} 7.5 Hz, 4H, CH_3CH_2), 7.75 (dd, J_{HH} 3.0 and 5.4 Hz, 2H, $CH_{aromatic}$), 8.26 (dd, J_{HH} 3.0 and 5.4 Hz, 2H, $CH_{aromatic}$), 9.77 (s, br, 2H, NH). ^{13}C{^{1}H} NMR ($CDCl_3$), δ: 11.0 (CH_3), 35.1 (CH_2), 123.2, 132.1, 137.9 ($C_{aromatic}$), 153.2 and 163.8 (C═N). ^{195}Pt NMR ($CDCl_3$), δ: −2233. ESI$^+$-MS, m/z: 486.2 [M + 1]$^+$. Anal. Calcd for $C_{14}H_{16}N_5ClPt$ (484.84): C, 34.68; H, 3.33; N, 14.44. Found: C, 34.74; H, 3.25; N, 14.33.

*Complex **3b**.* Method i, 70% yield; method ii, 69% yield. TLC on SiO_2: R_f = 0.83 (eluent CH_2Cl_2). IR (cm^{-1}): 3454 (NH), 1641 (C═N). ^{1}H NMR ($CDCl_3$), δ: 7.56−7.60 (m, 4H, $CH_{aromatic}$), 7.68 (t, J_{HH} 7.6 Hz, 2H, $CH_{aromatic}$), 7.80 (q, J_{HH} 2.8 Hz, 2H, $CH_{aromatic}$), 8.27−8.30 (m, 4H, $CH_{aromatic}$), 8.38 (q, J_{HH} 2.8 Hz, 2H, $CH_{aromatic}$), 10.38 (s, br, 2H, NH). ^{13}C{^{1}H} NMR ($CDCl_3$), δ: 123.4, 127.5, 129.2, 131.6, 132.2, 136.7, 138.1 ($C_{aromatic}$), 153.8 and 156.3 (C═N). ^{195}Pt NMR ($CDCl_3$), δ: −2163. ESI$^+$-MS, m/z: 581.3 [M + 1]$^+$. Anal. Calcd for $C_{22}H_{16}N_5ClPt$ (580.93): C, 45.49; H, 2.78; N, 12.06. Found: C, 45.68; H, 2.55; N, 12.21.

*Reactions of the Organonitrile Pt(II) Complexes trans-[$PtCl_2$(NCR)$_2$] [R = Et (**1a**), Ph (**1b**)] with 1,1,3,3-Tetramethylguanidine (**4**).* A solution of **1a** (200 mg, 0.532 mmol) or **1b** (200 mg, 0.423 mmol) in CH_2Cl_2 (4 mL) was added at room temperature to 1,1,3,3-tetramethylguanidine (**4**) (1 equiv), and the mixture was refluxed for 12 h whereupon the solvent was removed in vacuo. The crude residue was purified by column chromatography on silica (acetone as the eluent), followed by evaporation of the solvent in vacuo to give the final **5a** or **5b** products.

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Complex ***5a***. Yield: 65%. TLC on SiO_2: R_f = 0.67 (eluent acetone). IR (cm^{-1}): 3442 (NH), 2229 (N≡C), 1637 (C=N). ^1H NMR ($CDCl_3$), δ: 1.12−1.39 (m, 6H, CH_3CH_2), 2.83−2.88 (m, 4H, CH_3CH_2), 2.97 (s, 6H, CH_3N), 3.06 (s, 6H, CH_3N), 6.61 (s, br, 1H, NH). $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ: 9.5, 9.6, 12.1, and 13.3 (CH_3CH_2), 29.1, 29.3, 29.9, and 30.8 (CH_2CH_3), 39.9, 40.1, 40.2, and 40.3 ($C(NMe_2)_2$), 119.1 and 120.3 (N≡C), 163.3, 164.2, 175.1, and 178.3 (C=N). ESI^+-MS, m/z: 491.9 $[M + 1]^+$. Anal. Calcd for $C_{11}H_{23}N_5Cl_2Pt$ (491.3): C, 26.89; H, 4.72; N, 14.25. Found: C, 26.75; H, 4.55; N, 14.43.

Complex ***5b***. Yield: 67%. TLC on SiO_2: R_f = 0.69 (eluent acetone). IR (cm^{-1}): 3449 (NH), 2227 (N≡C), 1635 (C=N). ^1H NMR ($CDCl_3$), δ: 3.14 (s, 12H, CH_3N), 6.13 (s, br, 1H, NH), 7.36−7.42 (m, 3H, $CH_{aromatic}$), 7.49−7.52 (m, 2H, $CH_{aromatic}$), 7.57−7.72 (m, 5H, $CH_{aromatic}$). $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ: 40.4 (Me groups), 110.4 (C_{ipso}, N≡C*Ph*), 115.8 (N≡C), 126.8, 128.4, 129.2, 130.5, 133.3, 134.3, and 138.2 ($C_{aromatic}$), 163.6 and 170.1 (*C*=N). ESI^+-MS, m/z: 587.9 $[M + 1]^+$. Anal. Calcd for $C_{19}H_{23}N_5Cl_2Pt$ (587.4): C, 38.85; H, 3.95; N, 11.92. Found: C, 38.66; H, 3.65; N, 11.73.

*Reactions of the Organonitrile Pt(II) Complexes trans-[$PtCl_2(NCR)_2$] [R = Et (**1a**), Ph (**1b**)] with 1,3-Diphenylguanidine (**6**).* A solution of **1a** (200 mg, 0.532 mmol) or **1b** (200 mg, 0.423 mmol) in CH_2Cl_2 (4 mL) was added at room temperature to 1,3-diphenylguanidine **6** (1 equiv), and the mixture was refluxed for 12 h whereupon the solvent was removed in vacuo. The crude residue was purified by column chromatography on silica (CH_2Cl_2 or CH_2Cl_2/Et_2O as the eluent, respectively), followed by evaporation of the solvent in vacuo to give the final **7a** or **7b** products. All the analytical data are identical to those already reported.[25a]

*Reaction of the Organonitrile Pt(II) Complex trans-[$PtCl_2(NCPh)_2$] (**1b**) with Acetone Oxime (**8**).* A solution of **1b** (200 mg, 0.423 mmol) in CH_2Cl_2 (4 mL) was added at room temperature to acetone oxime **8** (30.9 mg, 0.423 mmol), and the mixture was refluxed for 2 h whereupon the solvent was removed in vacuo. The crude residue was purified by column chromatography on silica (CH_2Cl_2 as the eluent), followed by evaporation of the solvent in vacuo to give the final product **9**. All the analytical data are identical to those already reported.[2a,b]

*Reaction of the Organonitrile Pt(II) Complex trans-[$PtCl_2(NCPh)_2$] (**1b**) with the Acyclic Nitrone $^-O^+N(Me)$=C(H)(2,4,6-$Me_3C_6H_4$) (**10**).* A solution of **1b** (200 mg, 0.423 mmol) in CH_2Cl_2 (4 mL) was added at room temperature to acyclic nitrone **10** (74.9 mg, 0.423 mmol), and the mixture was refluxed for 12 h whereupon the solvent was removed in vacuo. The crude residue was purified by column chromatography on silica (CH_2Cl_2 as the eluent), followed by evaporation of the solvent in vacuo to give the final product **11**.

Complex ***11***. Yield: 67%. TLC on SiO_2: R_f = 0.56 (eluent CH_2Cl_2). IR (cm^{-1}): 2287 (N≡C), 1634 (C=N). ^1H NMR ($CDCl_3$), δ: 2.32, 2.49, and 2.82 (three s, 3H each, CH_3Ph), 3.09 (s, 3H, CH_3N), 6.41 (s, 1H, N−C*H*−N), 6.96 (d, J_{HH} 8.1 Hz, 2H, $CH_{aromatic}$), 7.48−7.72 (m, 8H, $CH_{aromatic}$), 9.00 (d, J_{HH} 8.1 Hz, 2H, $CH_{aromatic}$). $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ: 20.1, 20.9, and 21.1 (CH_3Ph), 47.4 (CH_3N), 91.9 (N−*C*H−N), 109.8 (C_{ipso}, N≡C*Ph*), 116.3 (N≡C), 122.2, 128.2, 128.5, 129.1, 129.5, 130.3, 131.6, 133.4, 133.7, 134.6, 137.9, 139.3, and 140.3 ($C_{aromatic}$), 163.7 (C(O)=N). ESI^+-MS, m/z: 650.6 $[M + 1]^+$. Anal. Calcd for $C_{25}H_{25}N_3Cl_2OPt$ (649.5): C, 46.23; H, 3.88; N, 6.47. Found: C, 46.34; H, 3.69; N, 6.56.

*Reaction of the Pt(II) Complexes trans-[$PtCl_2${NH=C(R)N=C(NMe_2)$_2$}(NCR)] [R = Et (**5a**), Ph (**5b**)], [PtCl{NH=C(R)NC(NHPh)=NPh}(NCR)] [R = Et (**7a**), Ph (**7b**)] and trans-[$PtCl_2${NH=C(Ph)ON=CMe_2}(NCPh)] (**9**) with 1,3-Diiminoisoindoline (**2**).* A solution of **5a** (200 mg, 0.407 mmol) or **5b** (200 mg, 0.340 mmol) or **7a** (200 mg, 0.363 mmol) or **7b** (200 mg, 0.309 mmol) or **9** (200 mg, 0.367 mmol) in CH_2Cl_2 (4 mL) was added at room temperature to 1,3-diiminoisoindoline **2** (1 equiv), and the mixture was refluxed for 2 h whereupon the solvent was removed in vacuo. The crude residue was purified by column chromatography on silica (CH_2Cl_2 as the eluent), followed by evaporation of the solvent in vacuo to give the final **3a** or **3b** products.

X-ray Structure Determinations. The X-ray quality single crystals of complexes **3a** and **3b** were immersed in cryo-oil, mounted in a Nylon loop and measured at a temperature of 150 K. Intensity data were collected using a Bruker AXS-KAPPA APEX II diffractometer with graphite monochromated Mo−Kα (λ 0.71073) radiation. Data were collected using omega scans of 0.5° per frame and full sphere of data were obtained. Cell parameters were retrieved using Bruker SMART software and refined using Bruker SAINT[32] on all the observed reflections. Absorption corrections were applied using SADABS.[32] Structures were solved by direct methods by using the SHELXS−97 package[33] and refined with SHELXL−97.[33] Calculations were performed using the WinGX System−Version 1.80.03.[34] All hydrogen atoms were inserted in calculated positions. Least square refinements with anisotropic thermal motion parameters for all the non-hydrogen atoms and isotropic for the remaining atoms were employed. CCDC 884882 and 884883 contain the supplementary crystallographic data for **3a** and **3b**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Computational Details. The full geometry optimization of all structures and transition states (TS) has been carried out at the DFT/HF hybrid level of theory using Becke's three-parameter hybrid exchange functional in combination with the gradient-corrected correlation functional of Lee, Yang and Parr (B3LYP)[35,36] with the help of the Gaussian-03[37] program package. No symmetry operations have been applied. The geometry optimization was carried out using a quasi-relativistic Stuttgart pseudopotential that described 60 core electrons and the appropriate contracted basis set (8s7p6d)/[6s5p3d][38] for the Pt atom and the 6-31G(d) basis set for other atoms. Then, single-point calculations were performed on the basis of the equilibrium geometries found using the 6-311+G(d,p) basis set for nonmetal atoms. The Hessian matrix was calculated analytically for the optimized structures in order to prove the location of correct minima (no imaginary frequencies) or saddle points (only one negative frequency), and to estimate the thermodynamic parameters, the latter being calculated at 25 °C. The nature of all transition states was investigated by the analysis of vectors associated with the imaginary frequency and, in some cases, by the calculations of the intrinsic reaction coordinates (IRC) using the Gonzalez-Schlegel method.[39,40]

Total energies corrected for solvent effects (E_s) were estimated at the single-point calculations on the basis of gas-phase geometries at the CPCM-B3LYP/6-311+G(d,p)//gas-B3LYP/6-31G(d) level of theory using the polarizable continuum model in the CPCM version[41,42] with CH_2Cl_2 as solvent. The UAKS model was applied for the molecular cavity. The entropic term in CH_2Cl_2 solution (S_s) was calculated according to the procedure described by Wertz[43] and Cooper and Ziegler[44] using eqs 1−4

$$\Delta S_1 = R \ln V^s_{m,liq}/V_{m,gas} \quad (1)$$

$$\Delta S_2 = R \ln V^\circ_m/V^s_{m,liq} \quad (2)$$

$$\alpha = \frac{S^{\circ,s}_{liq} - (S^{\circ,s}_{gas} + R \ln V^s_{m,liq}/V_{m,gas})}{S^{\circ,s}_{gas} + R \ln V^s_{m,liq}/V_{m,gas}} \quad (3)$$

$$\begin{aligned} S_s &= S_g + \Delta S_{sol} = S_g + [\Delta S_1 + \alpha(S_g + \Delta S_1) + \Delta S_2] \\ &= S_g + [(-11.80 \text{ cal/mol·K}) - 0.21(S_g - 11.80 \text{ cal/mol·K}) \\ &\quad + 5.45 \text{ cal/mol·K}] \end{aligned} \quad (4)$$

where S_g = gas-phase entropy of solute, ΔS_{sol} = solvation entropy, $S^{\circ,s}_{liq}$, $S^{\circ,s}_{gas}$, and $V^s_{m,liq}$ = standard entropies and molar volume of the solvent in liquid or gas phases (173.84 and 270.28 J/mol·K and 64.15 mL/mol, respectively, for CH_2Cl_2), $V_{m,gas}$ = molar volume of the ideal gas at 25 °C (24450 mL/mol), V°_m = molar volume of the solution corresponding to the standard conditions (1000 mL/mol). The enthalpies and Gibbs free energies in solution (H_s and G_s) were estimated using

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the expressions 5 and 6

$$H_s = E_s(\text{6-311+G(d, p)}) - E_g(\text{6-311+G(d, p)}) + H_g(\text{6-31G(d)}) \quad (5)$$

$$G_s = H_s - TS_s \quad (6)$$

where E_s, E_g, and H_g are the total energies in solution and in gas phase and gas-phase enthalpy calculated at the corresponding level.

■ ASSOCIATED CONTENT

Supporting Information

X-ray crystallographic data for complexes **3a** and **3b** in CIF format, X-ray structure, hydrogen bond distances and angles, and selected bonding parameter of complex **3a**, discussion of the mechanistic details of the nucleophilic addition of **2** to **1**, and tables with calculated energies and atomic coordinates. 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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