

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

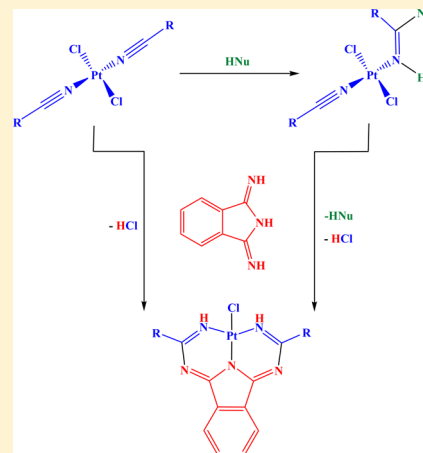
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S Supporting Information

ABSTRACT: Treatment of *trans*-[PtCl₂(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{NH=C(R)N=C(C₆H₄)-NC=NC(R)=NH}] (**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*-[PtCl₂{NH=C(R)N=C(NMe₂)₂}(NCR)] (**5**), [PtCl{NH=C(R)NC(NHPh)=NPh}(NCR)] (**7**), or *trans*-[PtCl₂{NH=C(Ph)ON=CMe₂}(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, ¹³C{¹H}, and ¹⁹⁵Pt 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 sp²-nitrogen nucleophile, is well-known for its use in the preparation of metallophthalocyanines⁵ and other macrocycles, such as expanded hemiporphyrine,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 calculations⁸ indicate that they possess an even greater ability for sequestering metal centers than β -diimines. However, the coordination chemistry

of triazapentadienes 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 (imidoylamidene)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 sp²-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

Received: June 2, 2012

Published: September 21, 2012

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-diiminoisindoline, 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-diiminoisindoline **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-diiminoisindoline **2** and bis(nitrile)-Pt(II) complexes *trans*-[PtCl₂(NCR)₂] (**1**) were studied in detail using theoretical DFT calculations.

RESULTS AND DISCUSSION

Reactions of 1,3-Diiminoisindoline with Symmetrical Organonitrile Pt(II) Complexes. Following our ongoing project on metal-mediated activation of small molecules (i.e., nitriles^{1,2,4} and isonitriles¹⁴), we have recently discovered that iminoisindolin-1-ones, which represent a family of stable aromatic imines, exhibit nucleophilic properties toward metal-bound organonitriles and isonitriles. Iminoisindolin-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

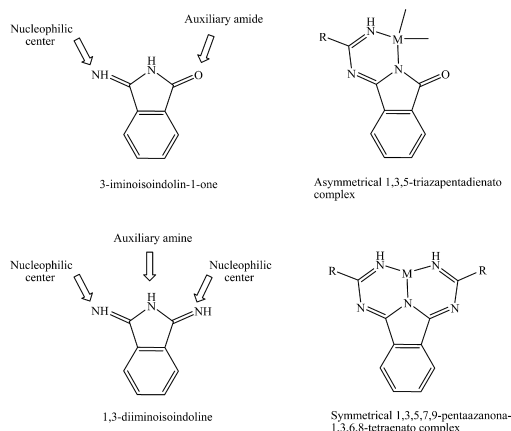


Figure 1.

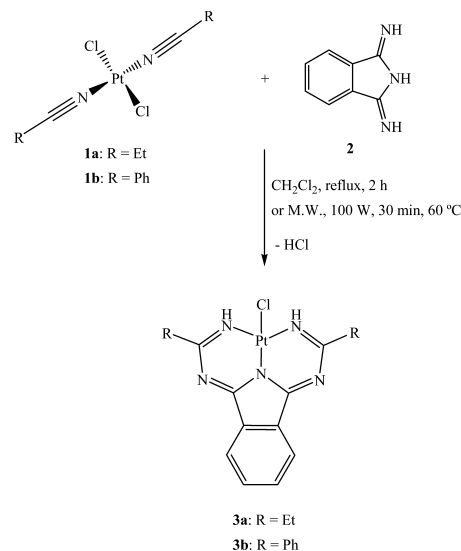
reaction between iminoisindolin-1-ones and metal-bound organonitriles or isonitriles leads to the formation of asymmetrical (1,3,5-triazapentadienato)[M] complexes [M = Ni(II),^{7a} Cu(II),^{7b} Pd(II),^{7c} and Pt(II)^{7c}].

These observations on the stability of the imine (i.e., iminoisindolin-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-diiminoisindoline (Figure 1) (bearing two nucleophilic sp²-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-pentaazaanona-1,3,6,8-tetraenato)-

Pt(II) complexes by using bis(propionitrile) and bis(benzonitrile) as starting dinitrile Pt(II) complexes, and 1,3-diiminoisindoline as the reacting sp²-nitrogen nucleophile (Scheme 1).

Scheme 1



Hence, treatment of *trans*-[PtCl₂(NCR)₂] (**1**) (R = Et (**1a**), Ph (**1b**)) with one equivalent of 1,3-diiminoisindoline HN=C(C₆H₄C(NH)=NH) (**2**), in refluxing CH₂Cl₂ for 2 h, gives access to the corresponding symmetrical (1,3,5,7,9-pentaazaanona-1,3,6,8-tetraenato)Pt(II) complexes [PtCl{NH=C(R)N=C(C₆H₄)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-diiminoisindoline **2** in CH₂Cl₂ 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, ¹H, ¹³C{¹H}, and ¹⁹⁵Pt NMR spectroscopies, ESI⁺-MS, elemental analyses and also by X-ray diffraction.

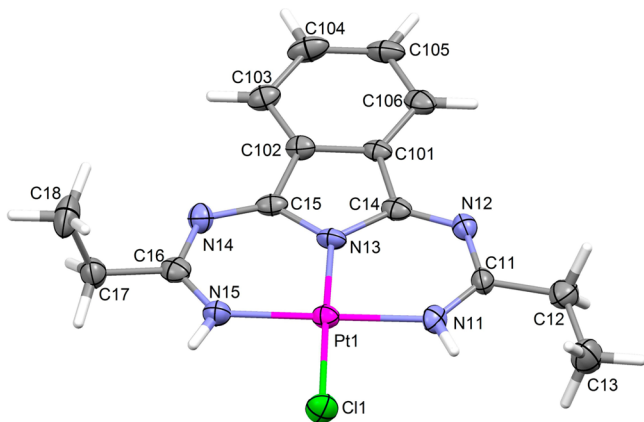
The IR spectra of complexes **3** do not exhibit the typical ν(N≡C) values (2350–2300 cm⁻¹ range), while new bands due to ν(NH) and ν(C=N) are observed at ~3255 and ~1648 cm⁻¹, respectively. For example, in the ¹H NMR spectrum of complex [PtCl{NH=C(Et)N=C(C₆H₄)NC=NC(Et)=NH}] (**3a**), the signals of the phenyl ring appear at δ 7.75 and 8.26, and the NH protons are exhibited at δ 9.77. The ¹³C{¹H} 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-diiminoisindoline **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.

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

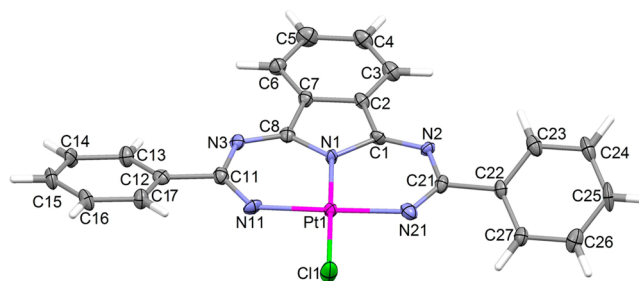
	3a ·2H ₂ O	3b
formula	C ₇₀ H ₈₄ Cl ₅ N ₂₅ O ₂ Pt ₅	C ₂₂ H ₁₄ ClN ₃ Pt
formula weight	2460.32	578.92
crystal system	monoclinic	monoclinic
space group	C2/c	Cc
<i>a</i> (Å)	55.400(2)	13.3847(6)
<i>b</i> (Å)	12.4426(5)	23.6077(10)
<i>c</i> (Å)	25.4089(11)	6.9904(3)
β (deg)	115.2820(10)	120.469(2)
<i>V</i> (Å ³)	15837.1(11)	1903.81(14)
<i>Z</i>	8	4
ρ_{calcd} (g/cm ³)	2.064	2.020
$\mu(\text{Mo-K}\alpha)$ (mm ⁻¹)	9.032	7.530
reflns collected	50855	11008
reflns unique	14378	5581
<i>R</i> _{int}	0.0559	0.0349
<i>R</i> ₁ , ^a <i>wR</i> ₂ ^b (<i>I</i> ≥ 2σ)	0.0351, 0.0652	0.0305, 0.0548
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0605, 0.0704	0.0400, 0.0581
GOF on <i>F</i> ²	1.006	0.954

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}.$$

**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 C2/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 fit¹⁵ of the five crystallographically independent Pt complex molecules (hereafter denoted as Pt1–Pt5) was attempted via the program Platon AutoMolFit¹⁶ (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}···A_{Pt} interactions with distances of 2.849(7) and 2.950(7) Å, and one represents a D_{Pt}···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}···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

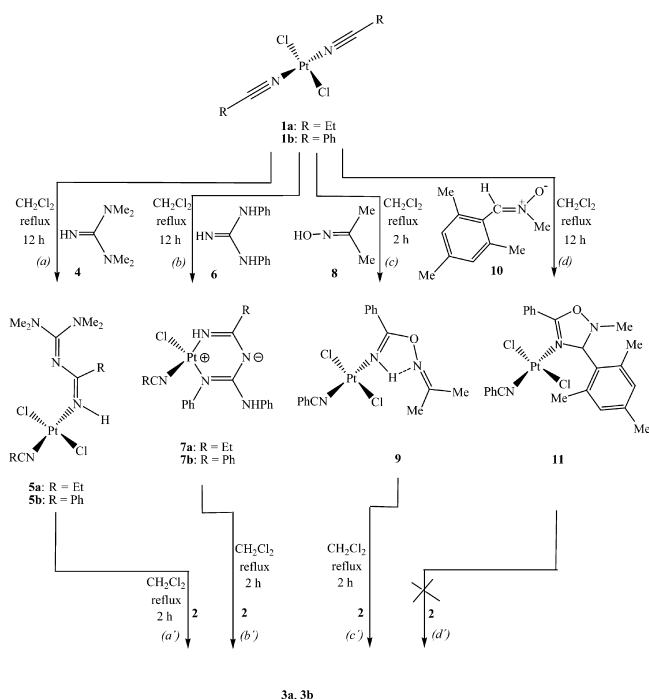
(Table S2) involving the ethyl groups, since in each molecule one of these groups is nearly in the plane of the coordination sphere of the metal while the other is markedly twisted out of that plane; moreover, only in Pt1 and Pt5 molecules both torsion angles have the same sign. Additionally, the molecules 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 $\cdots$ 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 $\cdots\pi$ 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 $\cdots$ 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*-[PtCl₂(NCR)₂] (**1**) (R = Et (**1a**), Ph (**1b**)) with one equivalent of 1,1,3,3-tetramethylguanidine HN=C(NMe₂)₂ (**4**), in refluxing CH₂Cl₂ for 12 h, gives access to the corresponding asymmetrical Pt(II) complexes *trans*-[PtCl₂{NH=C(R)N=C(NMe₂)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 ¹³C{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 ν (C=N) at ~ 1636 cm⁻¹. In addition, the bands because of ν (NH) and ν (N≡C) are observed at ~ 3445 and ~ 2228 cm⁻¹, respectively.

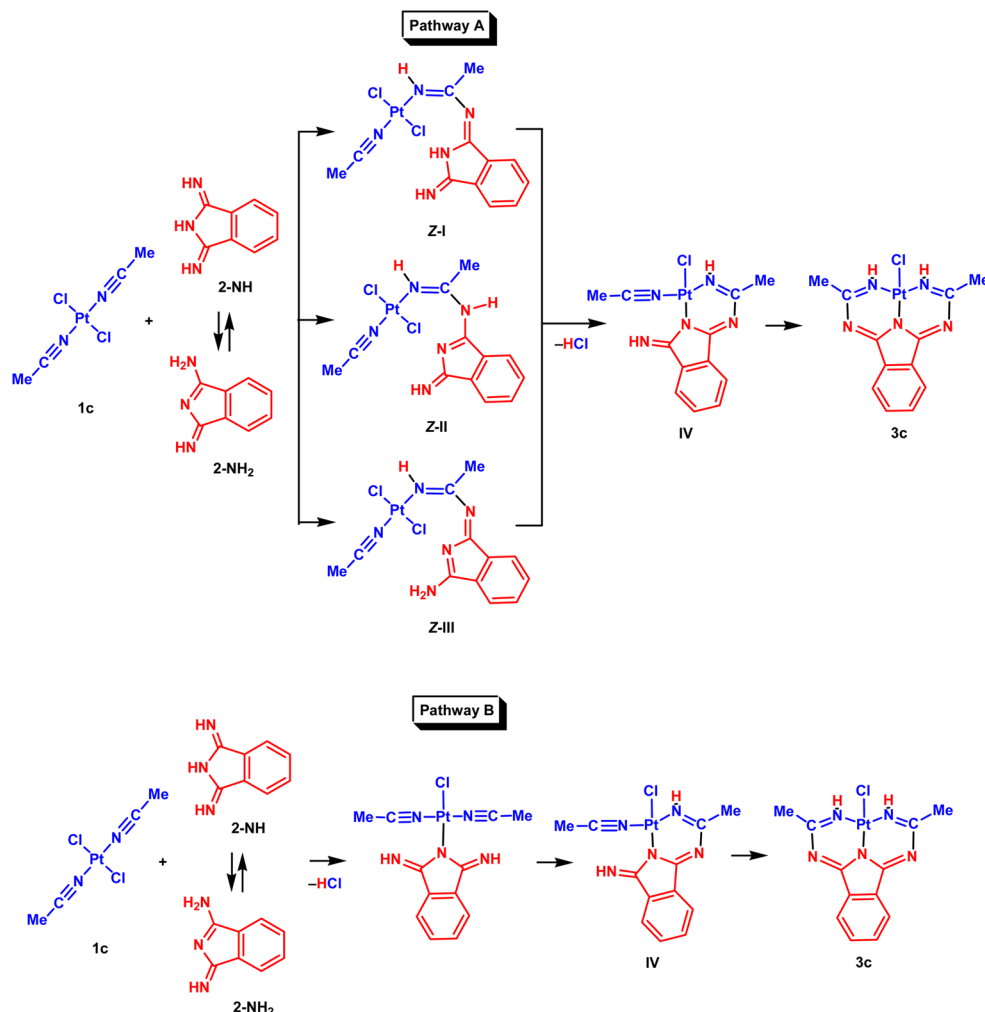
In the ¹H NMR spectra of **5a** and **5b**, the signal of the proton from the imino group C=NH (δ 6.61 and 6.13),²⁴ is shifted upfield compared to those observed in NMR spectra of other Pt imine complexes (δ 8–9).^{2a–c} In the latter, the hydrogen bonding involving the imine C=NH proton was unambiguously recognized, while in our case the position of the signal at such a high field gives indirect evidence that the proton of the C=NH group is not involved in the hydrogen bonding in solution.²⁴ The ¹³C{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*-[PtCl₂{NH=C(R)N=C(NMe₂)₂}(NCR)] (**5**) (R = Et (**5a**), Ph (**5b**)) with one equivalent of 1,3-diiminoisoindoline HN=C(C₆H₄)C(NH)=NH (**2**), in refluxing CH₂Cl₂ for 2 h, gives access to the corresponding above-mentioned symmetrical (1,3,5,7,9-pentaaza-1,3,6,8-tetraenato) Pt(II) complexes [PtCl₂{NH=C(R)N=C(C₆H₄)NC=NC(R)=NH}] (**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*-[PtCl₂(NCR)₂] (**1**) (R = Et (**1a**), Ph (**1b**)) with one equivalent of 1,3-diphenylguanidine HN=C(NHPh)₂ (**6**), in refluxing CH₂Cl₂ for 12 h, resulted in formation of the known²⁵ complexes [PtCl₂{NH=C(R)NC(NHPh)=NPh}(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-triazapentadienato)Pt(II) complexes [PtCl₂{NH=C(R)NC(NHPh)=NPh}(NCR)] (**7**) (R = Et (**7a**), Ph (**7b**)) with one equiv of 1,3-diiminoisoindoline **2**, in refluxing CH₂Cl₂ for 2 h, gives access to the corresponding above-mentioned symmetrical (1,3,5,7,9-pentaaza-1,3,6,8-tetraenato)Pt(II) complexes [PtCl₂{NH=C(R)N=C(C₆H₄)NC=NC(R)=NH}] (**3**) (R = Et (**3a**), Ph (**3b**)) in good yields (65–70%), respectively, as a result of displacement of diphenylguanidine moiety

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*-[PtCl₂(NPh)₂] (1b) with the acetone oxime HO-N=CMe₂ (8), in refluxing CH₂Cl₂ for 2 h, gives access to the known^{2a,b} monoimine *trans*-[PtCl₂{NH=C(Ph)ON=CMe₂}(NPh)] (9) complex in moderate yield (~55%) (Scheme 2, reaction *c*).

Similarly, treatment of 9 with one equivalent of 1,3-diiminoisoindoline 2, in refluxing CH₂Cl₂ for 2 h, leads to the corresponding above symmetrical complex [PtCl₂{NH=C(Ph)N=C(C₆H₄)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 NPh (Scheme 2, reaction *c'*).

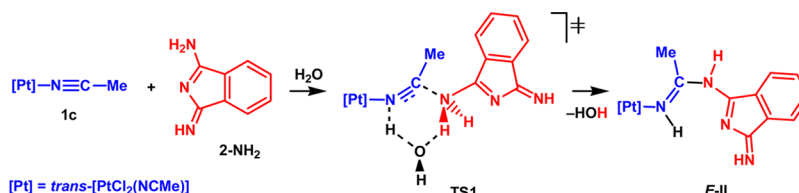
On the other hand, in the reaction of *trans*-[PtCl₂(NPh)₂] (1b) with one equivalent of the acyclic nitron ⁻O⁺N(Me)=C(H)(C₆H₂Me₃-2,4,6) (10), the system was refluxed in CH₂Cl₂ for 12 h, to give the mono-oxadiazoline complex *trans*-[PtCl₂{N=C(Ph)ON(Me)C(H)(C₆H₂Me₃-2,4,6)}(NPh)] (11) as the exclusive product (~67% yield) (Scheme 2, reaction *d*).

Complex 11 has been characterized by elemental analysis, ESI⁺-MS, IR, ¹H, and ¹³C{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

$\nu(\text{N}\equiv\text{C})$ 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 ¹³C{¹H} NMR spectra of 11 show that the compound contains both an oxadiazoline and a nitrile ligand. In the ¹H NMR spectrum, the N-CH-N resonance is detected at 6.41 ppm, and, in the ¹³C{¹H} NMR spectrum, the N-CH-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 theoretical²⁷ data on the reactions of addition of various protic nucleophiles (H₂O, ROH, NH₃, RNH₂, RR'NH, NR₂OH, RR'C=NOH, etc.) to metal-bound

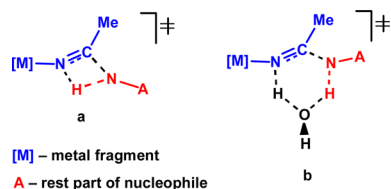
Scheme 4. Concerted Mechanism of the Nucleophilic Addition of 2-NH₂ to 1c by the NH₂ Group

nitriles, it seems to be a good assumption that the reaction starts with the nucleophilic addition (NA) of 1,3-diiminoisindoline 2 to one of the nitrile ligands of complex *trans*-[PtCl₂(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-diiminoisindoline 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-Diiminoisindoline 2 may exist in two possible tautomeric forms, that is, diimino form 2-NH and imino-amino form 2-NH₂ (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' ⇌ H₂N–C(R)=NR' by a series of chemical and physicochemical experiments.²⁸ Our calculations indicate that both forms 2-NH and 2-NH₂ 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 CH₂Cl₂ solution than 2-NH₂. Hence, the mechanisms of reaction of both 2-NH and 2-NH₂ forms with *trans*-[PtCl₂(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 NH₃ and amines to *trans*-[PtCl₂(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 CH₂Cl₂ used in the experimental part (see Experimental Section), H₂O 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-NH₂ to 1c by the NH₂ group (Scheme 4). The activation barrier in CH₂Cl₂ solution calculated for this route is 41.1 kcal/mol (in terms of ΔG_s[‡]) 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-NH₂ (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.

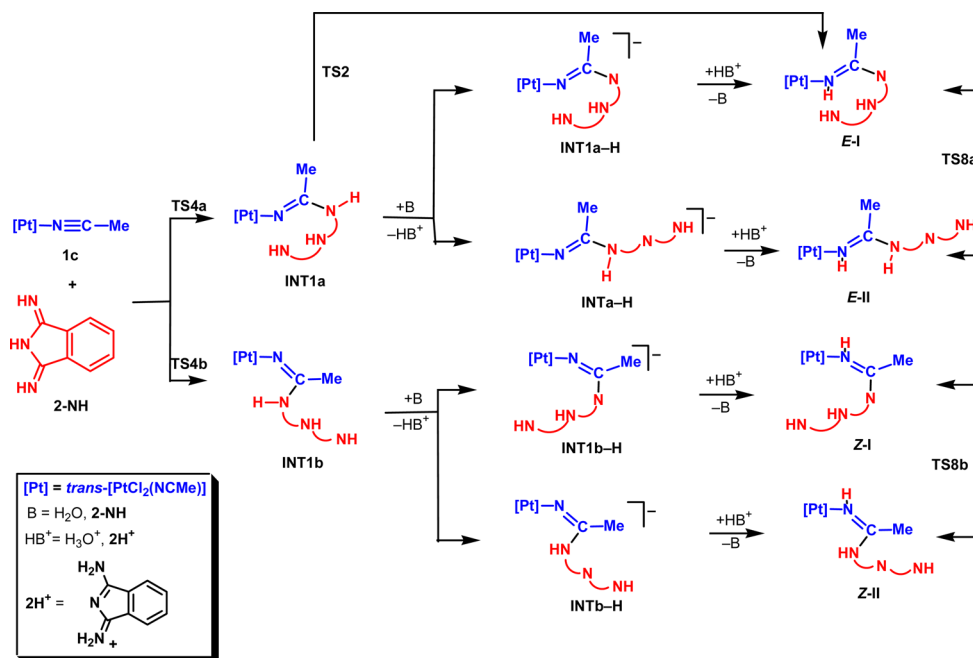
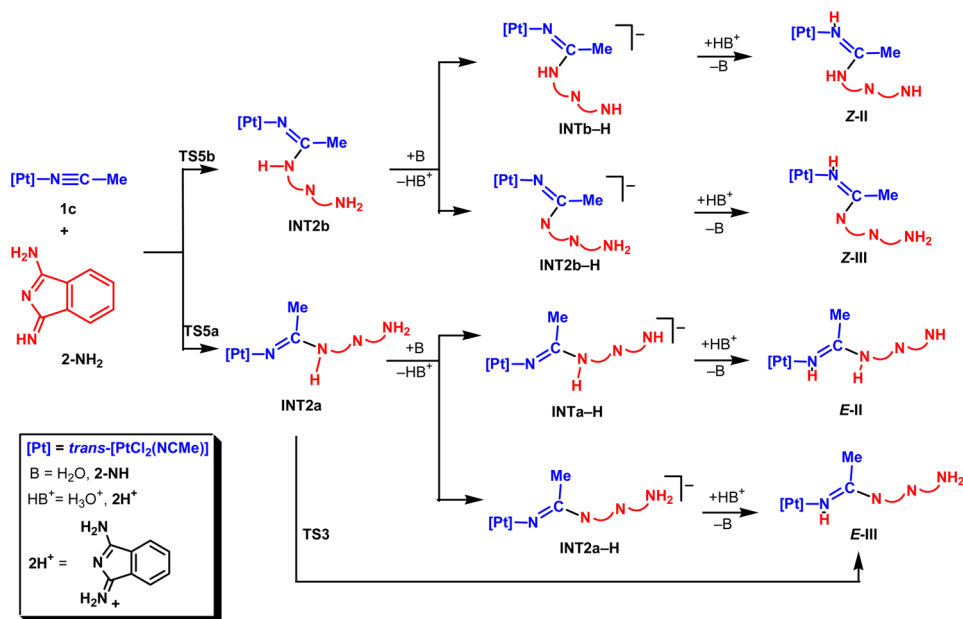
Associative Mechanism. The associative mechanism involves the addition of nucleophile to the nitrile carbon atom followed by the proton transfer to the nitrile nitrogen atom via one-step H-shift or via deprotonation/protonation steps (Schemes 5 and 6). This mechanism was found for the NAs of 2-NH and 2-NH₂ (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 (ΔG_s[‡] are 20.0 and 19.3 kcal/mol, respectively), and those of the formation of INT1b and INT2a are only slightly higher (ΔG_s[‡] 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-NH₂ by the NH₂ group. All attempts to locate it resulted in a decomposition of initial structures and moving the *trans*-[PtCl₂(NCMe)₂] and 2-NH₂ molecules away from each other. Thus, the associative stepwise mechanism for the addition of 2-NH₂ 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 CH₂Cl₂ solution (Schemes 5 and 6, B = H₂O) is very

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-NH₂ 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 deprotonation 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 $\text{INT1b} + 2\text{-NH} \rightarrow \text{INTb-H} + 2\text{H}^+$ (4.2 kcal/mol), $\text{INT1b} + 2\text{-NH} \rightarrow \text{INT1b-H} + 2\text{H}^+$ (6.8 kcal/mol), and $\text{INT1a} + 2\text{-NH} \rightarrow \text{INT1a-H} + 2\text{H}^+$ (7.5 kcal/mol), all of these processes being quite competitive with the $\text{INT1a} \rightarrow \text{TS2} \rightarrow \text{E-I}$ route ($\Delta G_s^\ddagger = 7.3$ kcal/mol).

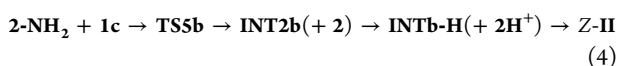
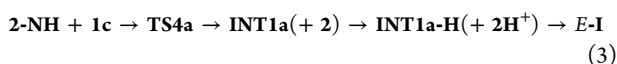
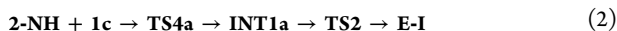
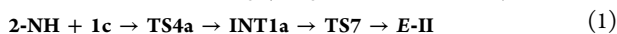
Dissociative Mechanism. The dissociative mechanism includes the initial deprotonation of the nucleophile (by a solvent molecule or autoionization), subsequent addition of the deprotonated fragment to the nitrile carbon atom and protonation of the nitrile nitrogen atom (Scheme 7). However, as was found 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 $2\text{-NH} + \text{B} \rightarrow 2\text{-NH-H} + \text{HB}^+$, $2\text{-NH}_2 + \text{B} \rightarrow 2\text{-NH}_2\text{-Ha} + \text{HB}^+$, and $2\text{-NH}_2 + \text{B} \rightarrow 2\text{-NH}_2\text{-Hb} + \text{HB}^+$ in CH₂Cl₂ solution with B = H₂O 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 R₂NOH 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.

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

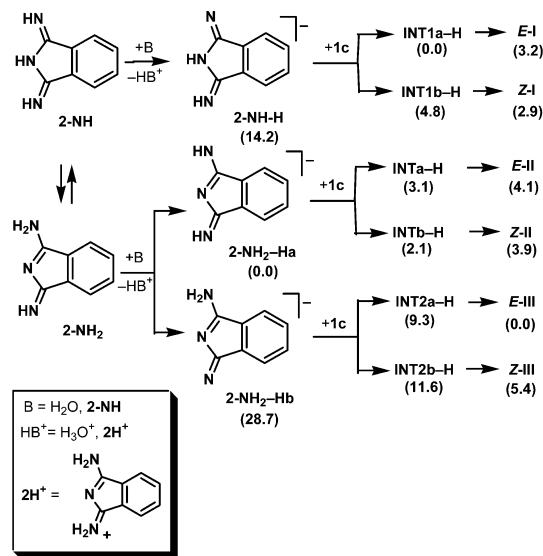
reaction		$\Delta H_s^\ddagger$	$\Delta G_s^\ddagger$	ΔH_s	ΔG_s
2-NH $\rightarrow$ 2-NH ₂				0.7	0.5
1c + 2-NH ₂ $\rightarrow$ E-II	via TS1	23.5	41.1	-14.9	-4.8
1c + 2-NH $\rightarrow$ INT1a	via TS4a	10.1	20.0	1.6	11.8
1c + 2-NH $\rightarrow$ INT1b	via TS4b	13.1	22.9	6.9	17.3
1c + 2-NH ₂ $\rightarrow$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

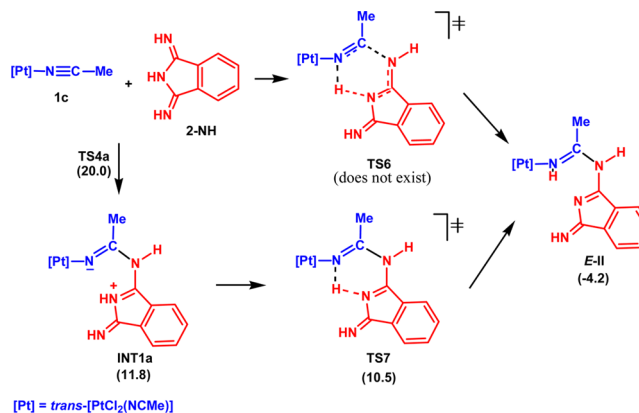


The analysis of the energy profiles of all pathways discussed above indicates that three of the most favorable routes, that is, 1–3, have the same rate limiting step (formation of INT1a) and, hence, the same overall activation barrier of 20.0 kcal/mol. The lowest-energy route leading to the formation 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)



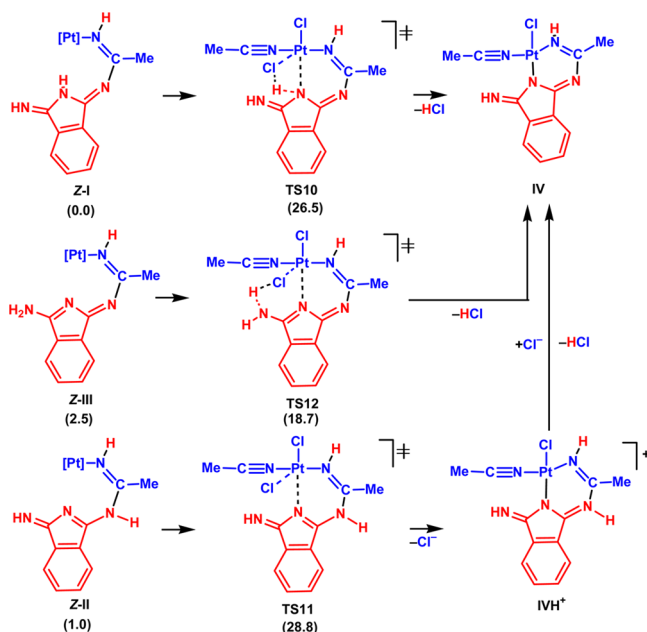
routes 1–3 and thus it may effectively operate concurrently. The second step of the route 4 is rate limiting: the energy of the deprotonated complex INTb-H relative to 1c + 2-NH is 21.5 kcal/mol vs the energy of TS5b of 19.8 kcal/mol. The activation barriers of the routes 1–4 (20.0 and 21.5 kcal/mol) are close to the experimentally determined Gibbs free energy of activation for the NA of hydroxylamine $\text{HON}(p\text{-CH}_2\text{C}_6\text{H}_4\text{Cl})_2$ to the Pt(II) complex $[\text{PtCl}_3(\text{NCeT})]^-$ (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

water-assisted H-transfers involving TS8a,b and TS9a,b (Scheme 5). The activation barriers of the $E\text{-II} \rightarrow E\text{-I}$, $Z\text{-II} \rightarrow Z\text{-I}$, $E\text{-I} \rightarrow E\text{-III}$, and $Z\text{-I} \rightarrow Z\text{-III}$ 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



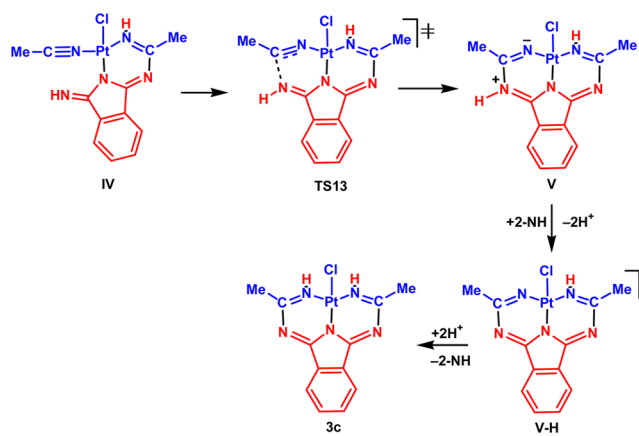
^aGibbs free energies relative to Z-I are indicated in parentheses in kcal/mol.

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 → 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*-CH₂C₆H₄Cl)₂ with [PtCl₃(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-diiminoisindoline (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-diiminoisindoline 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-NH₂) 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 60F₂₅₄ plates have been used. C, H, and N elemental analyses were carried out by the Microanalytical Service of the Instituto Superior Técnico. ¹H and ¹³C{¹H} spectra (in CDCl₃) were measured on Bruker Avance II 300 and 400 MHz (UltraShield Magnet) spectrometers at ambient temperature. ¹H and ¹³C{¹H} chemical shifts (δ) are expressed in ppm relative to Si(Me)₄ and ¹⁹⁵Pt

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

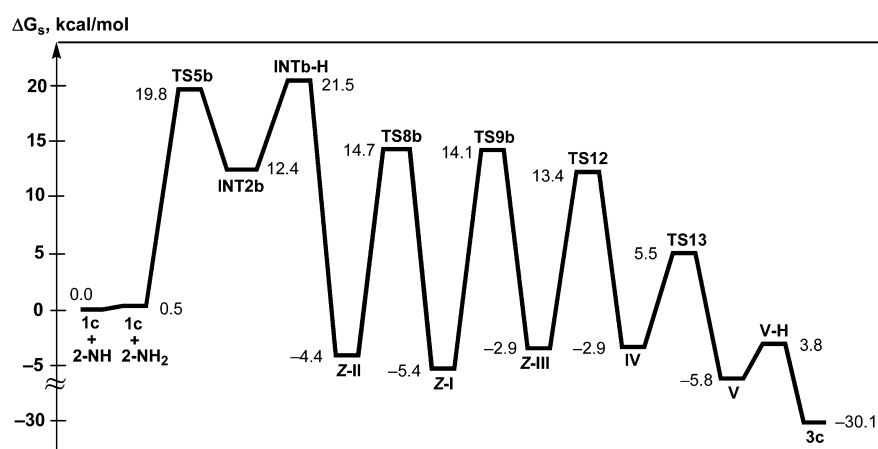
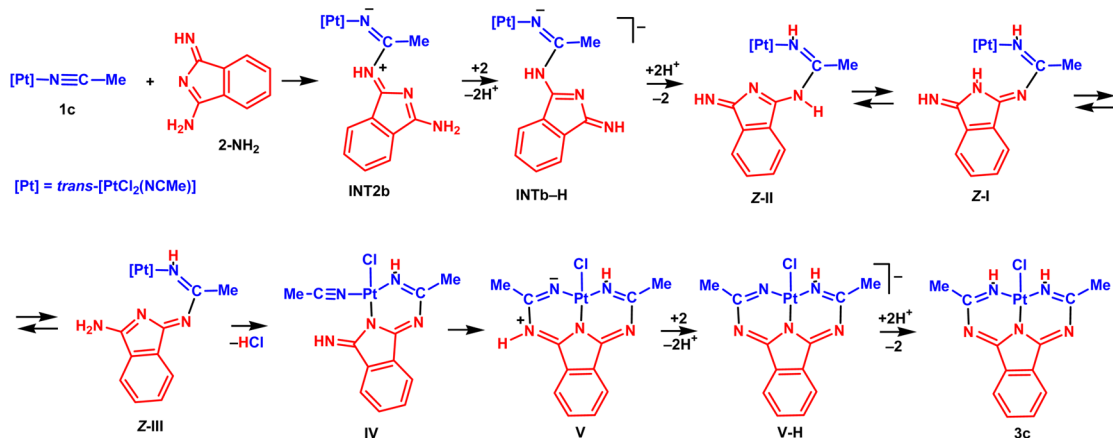


Figure 4. Energy profile of the most plausible mechanism of the reaction between 2 and 1c leading to 3c.

chemical shifts are relative to Na₂[PtCl₆] (by using aqueous K₂[PtCl₄], $\delta = -1630$ 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 μ L/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-[PtCl₂(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 CH₂Cl₂ (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 (CH₂Cl₂ 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 SiO₂: $R_f = 0.81$ (eluent CH₂Cl₂). IR (cm⁻¹): 3255 (NH), 1648 (C=N). ¹H NMR (CDCl₃), δ : 1.47 (t, $J_{\text{HH}} = 7.5$ Hz, 6H, CH₃CH₂), 2.82 (q, $J_{\text{HH}} = 7.5$ Hz, 4H, CH₃CH₂), 7.75 (dd, $J_{\text{HH}} = 3.0$ and 5.4 Hz, 2H, CH_{aromatic}), 8.26 (dd, $J_{\text{HH}} = 3.0$ and 5.4 Hz, 2H, CH_{aromatic}), 9.77 (s, br, 2H, NH). ¹³C{¹H} NMR (CDCl₃), δ : 11.0 (CH₃), 35.1 (CH₂), 123.2, 132.1, 137.9 (C_{aromatic}), 153.2 and 163.8 (C=N). ¹⁹⁵Pt NMR (CDCl₃), δ : -2233. ESI⁺-MS, m/z : 486.2 [M + 1]⁺. Anal. Calcd for C₁₄H₁₆N₅ClPt (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 SiO₂: $R_f = 0.83$ (eluent CH₂Cl₂). IR (cm⁻¹): 3454 (NH), 1641 (C=N). ¹H NMR (CDCl₃), δ : 7.56–7.60 (m, 4H, CH_{aromatic}), 7.68 (t, $J_{\text{HH}} = 7.6$ Hz, 2H, CH_{aromatic}), 7.80 (q, $J_{\text{HH}} = 2.8$ Hz, 2H, CH_{aromatic}), 8.27–8.30 (m, 4H, CH_{aromatic}), 8.38 (q, $J_{\text{HH}} = 2.8$ Hz, 2H, CH_{aromatic}), 10.38 (s, br, 2H, NH). ¹³C{¹H} NMR (CDCl₃), δ : 123.4, 127.5, 129.2, 131.6, 132.2, 136.7, 138.1 (C_{aromatic}), 153.8 and 156.3 (C=N). ¹⁹⁵Pt NMR (CDCl₃), δ : -2163. ESI⁺-MS, m/z : 581.3 [M + 1]⁺. Anal. Calcd for C₂₂H₁₆N₅ClPt (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-[PtCl₂(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 CH₂Cl₂ (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.

Complex 5a. Yield: 65%. TLC on SiO₂; *R_f* = 0.67 (eluent acetone). IR (cm⁻¹): 3442 (NH), 2229 (N≡C), 1637 (C=N). ¹H NMR (CDCl₃), δ: 1.12–1.39 (m, 6H, CH₃CH₂), 2.83–2.88 (m, 4H, CH₃CH₂), 2.97 (s, 6H, CH₃N), 3.06 (s, 6H, CH₃N), 6.61 (s, br, 1H, NH). ¹³C{¹H} NMR (CDCl₃), δ: 9.5, 9.6, 12.1, and 13.3 (CH₃CH₂), 29.1, 29.3, 29.9, and 30.8 (CH₂CH₃), 39.9, 40.1, 40.2, and 40.3 (C(NMe₂)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 C₁₁H₂₃N₃Cl₃Pt (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 SiO₂; *R_f* = 0.69 (eluent acetone). IR (cm⁻¹): 3449 (NH), 2227 (N≡C), 1635 (C=N). ¹H NMR (CDCl₃), δ: 3.14 (s, 12H, CH₃N), 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}). ¹³C{¹H} NMR (CDCl₃), δ: 40.4 (Me groups), 110.4 (C_{ipso}, N≡CPh), 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 C₁₉H₂₃N₃Cl₂Pt (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*-[PtCl₂(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 CH₂Cl₂ (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 (CH₂Cl₂ or CH₂Cl₂/Et₂O 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*-[PtCl₂(NCPH)₂] (1b) with Acetone Oxime (8). A solution of 1b (200 mg, 0.423 mmol) in CH₂Cl₂ (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 (CH₂Cl₂ 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*-[PtCl₂(NCPH)₂] (1b) with the Acyclic Nitron ⁺O⁺N(Me)=C(H)(2,4,6-Me₃C₆H₄) (10). A solution of 1b (200 mg, 0.423 mmol) in CH₂Cl₂ (4 mL) was added at room temperature to acyclic nitron 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 (CH₂Cl₂ as the eluent), followed by evaporation of the solvent in vacuo to give the final product 11.

Complex 11. Yield: 67%. TLC on SiO₂; *R_f* = 0.56 (eluent CH₂Cl₂). IR (cm⁻¹): 2287 (N≡C), 1634 (C=N). ¹H NMR (CDCl₃), δ: 2.32, 2.49, and 2.82 (three s, 3H each, CH₃Ph), 3.09 (s, 3H, CH₃N), 6.41 (s, 1H, N-CH-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}). ¹³C{¹H} NMR (CDCl₃), δ: 20.1, 20.9, and 21.1 (CH₃Ph), 47.4 (CH₃N), 91.9 (N-CH-N), 109.8 (C_{ipso}, N≡CPh), 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 C₂₅H₂₅N₃Cl₂OPt (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*-[PtCl₂(NH=C(R)N=C(NMe₂)₂)(NCR)] [R = Et (5a), Ph (5b)], [PtCl₂(NH=C(R)N=C(NHPh)=NPh)(NCR)] [R = Et (7a), Ph (7b)] and *trans*-[PtCl₂(NH=C(Ph)ON=CMe₂)(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 CH₂Cl₂ (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 (CH₂Cl₂ 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-*K*α (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 SAINT³² on all the observed reflections. Absorption corrections were applied using SADABS.³² Structures were solved by direct methods by using the SHELXS-97 package³³ 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-03³⁷ 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 CH₂Cl₂ as solvent. The UAKS model was applied for the molecular cavity. The entropic term in CH₂Cl₂ solution (*S_s*) was calculated according to the procedure described by Wertz⁴³ and Cooper and Ziegler⁴⁴ using eqs 1–4

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

$$\Delta S_2 = R \ln V_m^o / V_{m,liq}^s \quad (2)$$

$$\alpha = \frac{S_{liq}^{o,s} - (S_{gas}^{o,s} + R \ln V_{m,liq}^s / V_{m,gas}^s)}{S_{gas}^{o,s} + R \ln V_{m,liq}^s / V_{m,gas}^s} \quad (3)$$

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

where *S_g* = gas-phase entropy of solute, *ΔS_{sol}* = solvation entropy, *S_{liq}^{o,s}*, *S_{gas}^{o,s}* and *V_{m,liq}^s* = 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 CH₂Cl₂), *V_{m,gas}* = molar volume of the ideal gas at 25 °C (24450 mL/mol), *V_m^o* = 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

the expressions 5 and 6

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

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

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.

■ ACKNOWLEDGMENTS

This work has been partially supported by the Fundação para a Ciência e a Tecnologia (FCT), Portugal, and its PEst-OE/QUI/UI0100/2011 project. J.L. and M.L.K express gratitude to the FCT and the Instituto Superior Técnico (IST) for their research contracts (Ciência 2007 program). The authors gratefully acknowledge the Portuguese NMR Network (IST-UTL Center) for access to the NMR facility.

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