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Platinum-Mediated Dinitrogen Liberation from 2-Picolyl Azide through a Putative Pt═N Double Bond Containing Intermediate

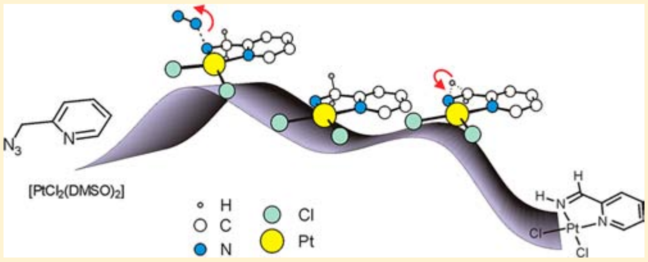
Balazs Pinter,[†] Damijana Urankar,[‡] Andrej Pevec,[‡] Frank De Proft,*[,†] and Janez Košmrlj*[,‡]

[†]Eenheid Algemene Chemie (ALGC), Member of the QCMM VUB-UGent Alliance Research Group, Vrije Universiteit Brussel, Pleinlaan 2, B-1050 Brussels, Belgium

[‡]Faculty of Chemistry and Chemical Technology, University of Ljubljana, Aškerčeva 5, Ljubljana, Slovenia

Supporting Information

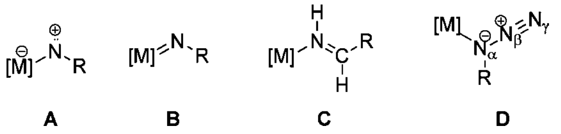
ABSTRACT: 2-Picolyl azide reacts with *cis*-[$PtCl_2(DMSO)_2$] to form the diimino complex [$Pt^{II}Cl_2$\{NH═C(H)Py\}] with subsequent dinitrogen liberation. The formation of the latter complex is scrutinized in a combined experimental and theoretical analysis. We establish in silico that the transformation involves a highly reactive intermediate containing a Pt═N double bond formed after the extrusion of N_2 from the azide functionality. The prerequisites for N_2 liberation and for the stabilization of the nitrene-related intermediate are analyzed in detail.



INTRODUCTION

One of most remarkable aspects in the chemistry of organoazides is the loss of dinitrogen, which can occur thermally, photochemically, or by acid or transition-metal catalysis.[1] In the presence of a transition metal the liberation of dinitrogen from a metal−organoazide adduct yields either a metal-stabilized nitrene intermediate (**A**; Chart 1)[2,3] or a metal−imido complex (**B**).[4] The transformation of alkyl azides into metal−imine complexes (**C**)[5] has also been documented for a few cases, more specifically for ruthenium,[6,7] iridium,[8] rhenium,[9] and osmium.[10] These metal−imine derivatives are presumably formed via metal−azide adducts of the η^1-diazoamino type (**D**), although well-defined complexes of this type are very uncommon.[11] In spite of this, **D**-type coordination has been reported for palladium,[12] iridium,[8] silver,[13] and copper.[14,15]

Chart 1[16]

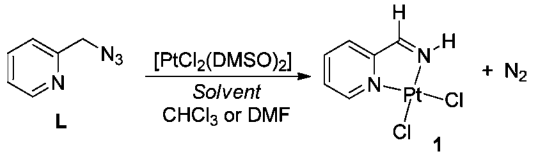


Our research interest in coordination chemistry has been focused on "click triazole" containing ligands.[17] In a quest for azide-tagged Pt^{II} complexes that would allow postfunctionalization through azide−alkyne cycloaddition chemistry directly into metalated "click" cycloadducts,[18] 2-picolyl azide has appeared as a simple and promising precursor. As a ligand it was anticipated to afford mono- or bidentate coordination to Pt^{II} through the pyridine and azido nitrogen atoms. Coordination of picolyl azide ligand to Pt^{II} indeed took place with the *cis*-[$PtCl_2(DMSO)_2$] precursor; however, the resulting complex could not be isolated. Instead, platinum promoted N_2 liberation from the azide functionality of the picolyl azide ligand followed by β-C−H activation. Since this behavior is novel for noble metals, we fully scrutinized the mechanism of the process and analyzed the electronic and structural requirements of N_2 liberation from organic azides.

RESULTS AND DISCUSSION

The reaction of a chloroform solution of 2-picolyl azide with *cis*-[$PtCl_2(DMSO)_2$] at ambient temperature affords diiminoplatinum(II) complex [$PtCl_2$\{NH═C(H)Py\}] (**1**)[19,20] as analytically pure, orange crystals in 89% isolated yield (Scheme 1). Unlike some transformations of alkyl azides into the corresponding iridium−imine[8] and rhenium−imine[9] complexes that require photochemical stimulation, the reaction from Scheme 1 also occurs in the absence of light.

Scheme 1. Reaction of 2-Picolyl Azide (L) with *cis*-[$PtCl_2(DMSO)_2$]



Conclusive support for the formation of square-planar [$PtCl_2$\{NH═C(H)Py\}] (**1**) came from X-ray structure determination (Figure 1). The orange, air-stable compound

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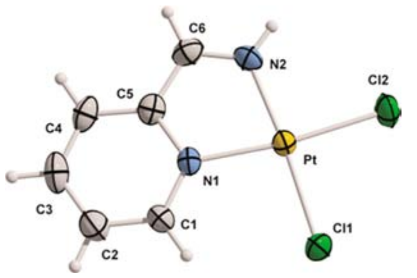


Figure 1. Molecular structure of **1** (ellipsoids set to 50%). Selected interatomic distances (Å) and angles (deg): Pt–Cl(1), 2.3053(10); Pt–Cl(2), 2.2842(12); Pt–N(1), 2.019(3)l; Pt–N(2), 1.976(4); C(6)–N(2), 1.278(6); Cl(1)–Pt–N(1), 95.89(11); Cl(1)–Pt–Cl(2), 91.30(4); Cl(2)–Pt–N(2), 93.41(10); N(1)–Pt–N(2), 79.43(14); C(5)–C(6)–N(2), 116.0(4); C(6)–N2–Pt, 117.2(3).

crystallizes in the monoclinic $P2_1/c$ space group via vapor diffusion of methanol to a DMSO solution of **1**. In the crystal lattice of **1** the short intermolecular N–H···Cl distances indicate the formation of hydrogen-bonded chains (Figure S17, Supporting Information).

The evidence for complex **1** in solution was obtained from HRMS and multinuclear (^{1}H, ^{13}C, ^{15}N, ^{195}Pt) 1D and 2D NMR data (Supporting Information). The proton spectrum of **1** displays well-resolved ^{195}Pt satellites for NH, CH, and H6^{Py} protons (Figure 2). In the ^{1}H–^{195}Pt HMBC spectrum these satellites correlate with the ^{195}Pt resonance at $\delta = -2327$ ppm, a chemical shift that is typical for the N_2Cl_2 coordination environment at Pt^{II}.[21]

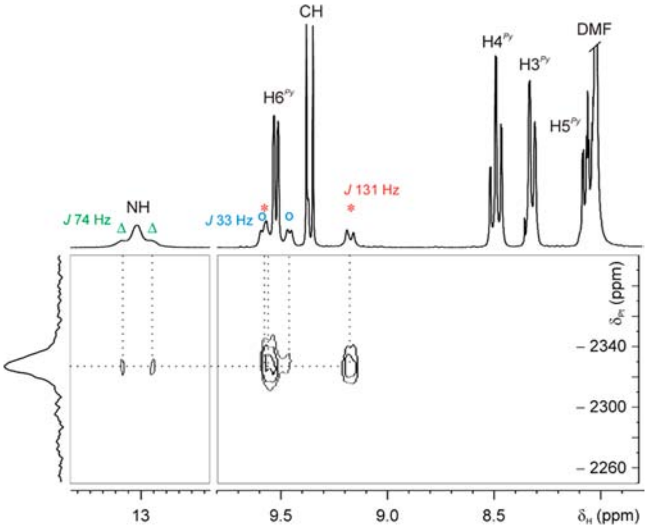


Figure 2. Selected parts of the 2D ^{1}H–^{195}Pt HMBC NMR spectrum of **1** in DMF-d_7 recorded on a 300 MHz instrument with indicated ^{195}Pt satellites for NH (Δ), CH (*), and H6^{Py} (o) protons.

Density functional calculations were performed to shed light into the mechanism of the formation of **1**. The most likely pathway is illustrated in Figure 3, whereas the considered paths are summarized in Scheme S2 (Supporting Information). The former pathway was also determined and is given for the analogous copper complex (**1^{Cu}**), which serves as a reference in our study. Since Cu^{II} does not liberate N_2 from 2-picolyl azide,[15] in contrast to Pt^{II}, the comparison of the two systems will indeed provide insights into the prerequisites for the metal-mediated extrusion of N_2 from organic azides.

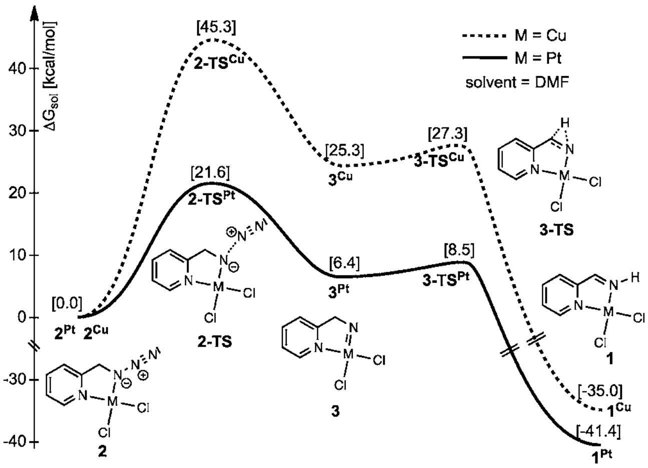


Figure 3. Computed reaction profile in DMF for Pt- and Cu-mediated N_2 liberation from organic azides.

It can be anticipated that the platinum precursor *cis*-[PtCl$_2$(DMSO)$_2$] and 2-picolyl azide first form the chelate[22] complex **2^{Pt}** with a square-planar structure in which the ligand binds through the pyridine nitrogen atom and N_α, analogous to that of the reported Cu^{II} complex **2^{Cu}**.[15] Subsequent N_2 loss via the breaking of the N_α–N_β bond (**2-TS**) yields the highly reactive intermediate **3** with a relative free energy of 6.4 kcal mol^{-1} in the solution phase (DMF). Finally, a concerted migration of a methylene hydrogen atom to N_α gives the imine complex **1** through **3-TS**. This last step is associated with a minor barrier of 1.9 kcal mol^{-1}. The Pt–imine product **1** lies 47.8 kcal mol^{-1} lower in energy than intermediate **3**, rendering the last step irreversible within plausible reaction conditions and in good agreement with our experimental observations. Also, the very low barrier connecting **3** and **1** hinders the NMR spectroscopic detection of **3**. Trapping experiments with cyclohexene were equally unsuccessful (see the Supporting Information for details).[23]

The structure of **2-TS**, depicted in Figure 4, indicates a significantly bent azido functionality (∠N1–Pt–N_α–N_β = 73.41°; see Figure 4 for numbering), in which the N_α–N_β bond is elongated to a distance of 1.66 Å. Such a distortion is a prerequisite for the N–N bond breaking and subsequent N_2 extrusion: most importantly, to break the N_α–N_β bond, a significant amount of electron density has to be donated to the antibonding σ^*-orbital between N_α and N_β. To be able to utilize the electrons of the metal for this purpose, the N_α–N_β bond has to bend out of the coordination plane (the N1–N_α–Pt–Cl–Cl plane). With such a bending, the π-type d orbitals of the metal, d_{xz} and d_{yz}, have the right orientation to interact with the σ-type orbitals of the azido fragment, and back-donation can occur from the metal to the σ^* orbital of the N_α–N_β bond. The molecular orbital (MO) that represents this π-back-donation is provided in Figure 5. This rationalization is analogous to that of the characteristic zigzag transition state[24,25] in splitting of N_2 with transient d^3 complexes[25,26] to allow the formation of two equimolar terminal nitrides.

As evinced by these calculations, Pt^{II} can donate a sufficient amount of electrons to break the N_α–N_β bond in **2^{Pt}**, in spite of the fact that late transition metals, including platinum(II), are generally considered to be poor π-back-donors due to their high effective nuclear charge.[27] Accordingly, these metals typically form so-called class II type carbonyl complexes, in

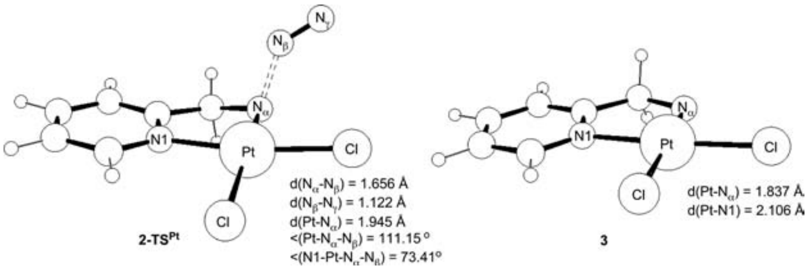


Figure 4. Structures of **2-TS**^{Pt} and **3**^{Pt} with the most important metrics.

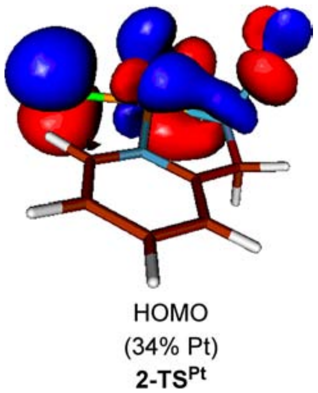


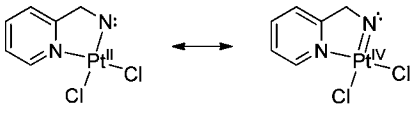
Figure 5. Molecular orbital (HOMO) representing the back-donation from Pt^{II} to the antibonding σ^* of N_α−N_β in **2-TS**^{Pt}.

which the CO vibration frequency is red-shifted.[28] This hypothesis foreshadows that metals of groups 8 and 9 should promote N_2 liberation more efficiently from an azide functionality due to their better π-back-donation ability, whereas early and late transition metals should exhibit lower activity. Thus, it is not surprising that such reactions were reported for Ru,[6,7] Os,[7,10] and Co[2] complexes under mild conditions. In addition, ligands trans to the azide functionality may also influence the magnitude of π-back-donation from the metal to N_3. In silico results suggest that when the weak π-base Cl^- is substituted by the weak π-acid DMSO in **2**^{Pt} (**2**$_{DMSO}$), the activation barrier of the N_2 extrusion step increases by as much as 8.8 kcal mol^{-1} (Figure S18, Supporting Information). Experimentally, we could confirm the N_2 extrusion if the Cl^- is replaced by a CH_3^-; exposure of 2-picolyl azide to $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ in DMF-d_7 resulted in $[PtMe_2\{NH{=}C(H)Py\}]$, as indicated by NMR spectroscopy (for details, see the Supporting Information).

Figure 3 also clearly indicates that dinitrogen elimination is, however overall exothermic, kinetically forbidden for the copper analogue (**3**^{Cu}). The breaking of the N_α−N_β bond requires an activation energy of about 45 kcal mol^{-1}, which is unattainable under thermal conditions. It is in line with π-back-donation rationalization introduced above for **2-TS**^{Pt}: since copper(II) has nine d electrons, the $d_{x^2-y^2}$ metal orbital, which is of strong antibonding character with the ligands, is singly occupied, resulting in a relatively long Cu−N_α distance of d_{Cu-N} = 2.19 Å in **2**^{Cu} compared to **2**^{Pt} (d_{Pt-N} = 2.09 Å). An elongated metal−ligand distance results in a significantly reduced overlap integral between the corresponding π-type d orbital and the p_z orbital of N_α; i.e., the π-back-donation is diminished in **2**^{Cu}. Thus, the existence of **2**^{Cu} and its inactivity toward N_2 elimination can be linked to the weak π-back-donating ability of copper(II) ion in a square-planar arrangement.

Intermediate **3** is calculated to exhibit a uniquely short Pt−N_α distance of 1.837 Å (Figure 4). Although it is reasonable to interpret this short distance as a strong indicator of a Pt^{IV}−imido moiety, i.e., a Pt═N double bond, which we denote as **3b**, the alternative assignment of a Pt^{II}−nitrene structure (**3a**) is equally plausible, as highlighted in Scheme 2. Since fundamentally different reactivities may emerge from these two resonance structures, it is important to characterize the dominant electronic structure of **3**^{Pt}. Note that platinum can be *formally* associated with an oxidation number of +4 in **3b**; however, its electronic structure differs from that of typical platinum(IV) complexes, which are predominantly octahedral and lack electrons on the d_{z^2} orbital. Rather, in **3b** the electron density of one of the π-type d orbitals (d_{xz} and d_{yz}) shifts significantly toward the p_z orbital of the coordination nitrogen (N_α). A straightforward way of approximating the weight of these resonance extremes is to determine the metal character in the molecular orbital corresponding to the $d_{xz}(Pt)$−$p_z(N_\alpha)$ interaction.[29] Mainly HOMO-11 represents the $d_{xz}(Pt)$−$p_z(N_\alpha)$ bonding interaction (Figure 6) consisting of a 52% contribution by the metal d orbitals, thus predicting a hybrid electronic structure for **3** with almost equivalent **3a** and **3b** character. Note, however, that this orbital is not solely based on N_α and Pt, and thus, the contributions of other atoms might interfere with this simple analysis predicting a N_α contribution of only 10%. A better estimation can be deduced from the corresponding antibonding orbital, which is the LUMO, with a

Scheme 2. Resonance Extremes To Describe the Electronic Structure of 3^{Pt}



3a **3b**

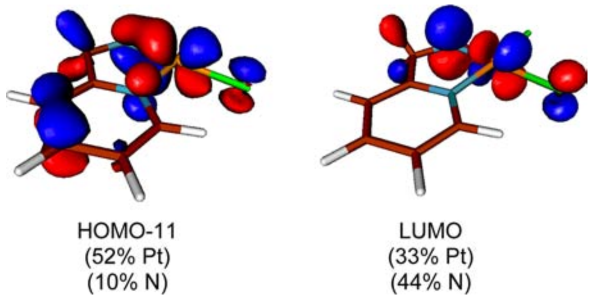


Figure 6. Molecular orbitals of **3**^{Pt} representing the main π-type Pt−N_α bonding (left) and antibonding (right) interactions.

reduced, but still significant metal character of 33% (Figure 6) and a nitrogen contribution of 44%.

The latter analysis also suggests that the π-bond between Pt and N_α is strongly covalent, and not a typical dative-type ligand−metal interaction. The computed Mayer bond order of 1.69 for the Pt−N_α interaction supports this assignment and predicts a very strong metal−ligand bond.[30] As such, actually, **3b** is the very reasonable Lewis structure to describe **3**. In this case, however, the Pt═N_α double bond contains a covalent π-bond in which one electron belongs to the metal and one to the ligand. In other words, the traditional assignment of bonding electrons of inorganic chemists, which would result in a separation of Pt^{IV} and N^{2-} in **3b**, and similarly in an oxo functionality, M═O, in which one also typically splits the bonds heterolytically to M^{2+} and O^{2-}, is not valid for structure **3** when described with **3b**. Thus, one can *formally* imagine the structure of intermediate **3** as the association of a Pt^{III} and a nitrene radical ligand, strongly coupled antiferromagnetically.

In the case of open shell systems, such as $\mathbf{3^{Cu}}$, the spin density distribution allows the clear-cut assignment of the unpaired electron(s). For $\mathbf{3^{Cu}}$, the spin density distribution reveals a localized unpaired electron on the N_α atom (Figure S19, Supporting Information). In addition, the short Cu−N distances indicate that the $d_{x^2-y^2}$ orbital is unoccupied. Thus, the electronic structure of $\mathbf{3^{Cu}}$ can be unambiguously assigned as containing Cu^{III} and nitrene radical fragments, analogous to $\mathbf{3^{Pt}}$.

It is worth putting our results into context with the recent findings of Cundari and Warren,[31,32] who presented catalytic C−H amination through copper(I)−nitrene complexes, generated from azides. On one hand, although Cu^I has properties and reactivity profoundly different from those of Cu^{II}, it is still not a good π-back-donor, and in line with our concept presented above, it should not split the N_α−N_β bond of the azide to free N_2. We tested this hypothesis in silico with 2-picolyl azide coupled to a Cu^I and found that the barrier is indeed too high to form the corresponding nitrene species (Figure S20, Supporting Information). This preliminary result, together with the structure of the characterized nitrene precursor $[\{(Me_3NN)Cu\}_2(\mu\text{-NAr})]$ containing two Cu^I centers, indicates that the formation of the transient Cu^I−nitrene species in Warren's systems occurs probably via a bimetallic mechanism. On the other hand, the Cu−nitrene intermediate was computationally characterized to have an open shell electronic structure and assigned to consist of a Cu^{II} and a nitrene radical fragment weakly coupled in an antiferromagnetic fashion.[32] This behavior is concomitant with the weak back-donation ability of either Cu^I or Cu^{II}; otherwise, the overlap between the metal d orbital and p orbital of the nitrogen would be large enough to result in a closed shell singlet state.

In relation to this work, driven by the attempt to generate reactive nitrene-related species in an environmentally harmless way for C−H amination, organic azides were reacted recently with cobalt(II) porphyrin.[1,2] This complex also mediates N_2 loss from azides efficiently, and the intermediate generated readily functionalizes various C−H bonds. The reaction is catalytic due to the ease with which the amine product leaves the complex. Scrutinized by DFT, the reaction was shown to follow a similar mechanism discussed above for $LPtCl_2$, whereas the electronic structure of the intermediate was assigned using its spin density distribution. The predicted Co^{III}−nitrene radical assignment for the intermediates was experimentally justified with characteristic g values (EPR) indicating ligand-based radicals in these species. This assignment is analogous with the one we concluded for the platinum-based intermediate, $\mathbf{3^{Pt}}$.

■ SUMMARY AND CONCLUSIONS

To our knowledge, this is the first report on platinum-mediated dinitrogen liberation from an organoazide. Combined experimental and theoretical analyses demonstrated that after 2-picolyl azide (**L**) coordinated to platinum(II) the transformation of $\mathbf{2^{Pt}}$ to $\mathbf{1^{Pt}}$ follows a two-step mechanism, where the N_2 elimination in the first step is followed by a H-abstraction by the generated nitrene radical from the adjacent CH_2 group. The analysis of the transition state corresponding to the N_2 extrusion step revealed that π-back-donation from the metal into the σ^* orbital of the N_α−N_β bond is the most critical component of the activation. This finding indicates that if π-back-donation is limited either by structural constraints, e.g., an elongated metal−ligand distance, or electronic reasons, e.g., early and late transition metals, then N_2 liberation from organic azides becomes kinetically unfavorable, which was demonstrated for a reference reaction involving $\mathbf{2^{Cu}}$. Since the generated nitrene species, however, have desirable reactivity, the demand for the latter transformation is high. Thus, understanding the factors governing N_2 liberation is critical for the rational design of active species with specific properties.

Scrutinizing the electronic structure of the "nitrene-like" intermediates for both Pt and Cu, we found that they are very similar and can be best described as a metal(III) interacting with a nitrene radical ligand in both complexes. It is also in line with the assigned cobalt(III)−nitrene radical intermediate detected recently in a similar reaction of cobalt(II) porphyrin.[2] On the basis of these results, one can confidently assume intermediates with similar electronic structure in analogous transformations with other metals, where the mechanism is not completely determined or the intermediate is too short-lived to be detected. Also, in general, metals, which form stable complexes in oxidation state +3, may also form detectable intermediates with controllable and tunable reactivity toward, for example, C−H activation.[33]

■ EXPERIMENTAL SECTION

Materials. The reagents and solvents were used as purchased from commercial sources. 2-Picolyl azide,[34] *cis*-$[PtCl_2(DMSO)_2]$,[35] and $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$[36] were prepared by known procedures.

Instrumentation. *NMR Spectroscopy.* NMR spectra were measured on Bruker Avance 300 and Bruker Avance III 500 spectrometers, using $Si(CH_3)_4$ as the internal standard. The ^{195}Pt NMR spectra were referenced with respect to $Na_2[PtCl_6]$ (325 mg/0.65 mL of D_2O, T = 302 K)[37] external standard at δ = 0 ppm. The nitrogen chemical shifts were extracted from ^1H−^{15}N HMBC spectra. The reported ^{15}N chemical shifts were measured with respect to external 90% CH_3NO_2 in $CDCl_3$ and converted to the $\delta(^{15}N)$(liquid NH_3) = 0 ppm scale using the relation $\delta(^{15}N)(CH_3NO_2) = \delta(^{15}N)(\text{liquid } NH_3) + 380.50$ ppm. Chemical shifts are given on the δ scale (ppm). Coupling constants (J) are given in hertz.

Mass Spectrometry. HRMS spectra were recorded with an Agilent 6224 Accurate Mass TOF LC/MS system.

Elemental analysis. Elemental analysis was performed with a Perkin-Elmer 2400 series II CHNS/O analyzer.

Synthesis of $[PtCl_2\{NH{=}C(H)Py\}]$ (1). A suspension of 2-picolyl azide (67 mg, 0.50 mmol) and *cis*-$[PtCl_2(DMSO)_2]$ (212 mg, 0.50 mmol) in chloroform (5 mL) was stirred at ambient temperature for 6 days. The resulting orange precipitate was collected by filtration and washed with dichloromethane (2 mL), methanol (2 mL), and dichloromethane (2 mL) to afford pure **1** (166 mg, 0.45 mmol, 89%). Mp: >300 °C. ^{1}H NMR (500 MHz, DMF-d_7): 8.07 (1H, ddd, J = 7.5, 5.7, 1.6 Hz, H-5), 8.33 (1H, dd, J = 7.8, 1.6 Hz, H-3), 8.50 (1H, ddd, J = 7.8, 7.8, 1.5 Hz, H-4), 9.37 (1H, d, J = 9.3 Hz, CH, $^3J_{\text{PtH}}$ = 111 Hz), 9.52 (1H, dd, J = 5.8, 1.4 Hz, H-6, $^3J_{\text{PtH}}$ = 31 Hz), 13.07 (1H, br s, NH, $^2J_{\text{PtH}}$ = 64 Hz). ^{13}C NMR (125 MHz, DMF-d_7): 129.4 (C-3), 130.3 (C-5), 141.3 (C-4), 150.1 (C-6), 159.0 (C-2), 173.7 (CH). ^{15}N NMR (50 MHz, DMF-d_7): 209.8 (N^{Py}), 222.6 (NH). ^{195}Pt NMR (64 MHz, DMF-d_7): −2327. HRMS (ESI+): m/z calcd for $C_6H_7Cl_2N_2Pt^+$ $[M + H]^+$ 372.9631, found 372.9600. Anal. Calcd for $C_6H_6Cl_2N_2Pt$: C, 19.30; H, 1.65; N, 7.15. Found: C, 19.37; H, 1.63; N, 7.53.

X-ray Structure Analysis. Crystal data and refinement parameters of compound **1** are listed in Table S1 (Supporting Information). Diffraction data were collected on a Nonius Kappa CCD diffractometer with an area detector at room temperature. Graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) was employed. The data were processed by using DENZO.[38] The structure was solved by direct methods using SIR-92[39] and refined by a full-matrix least-squares procedure based on F^2 using SHELXL-97.[40] All the non-hydrogen atoms were refined anisotropically. The hydrogen atoms bonded to nitrogen atom N2 and carbon atom C6 were located in a difference map and refined with the distance restraints (DFIX) with $d_{\text{N−H}}$ = 0.86 Å and $d_{\text{C−H}}$ = 0.98 Å and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$ or $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$, respectively. All other hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model.

Computational Methods. Geometry and transition-state optimizations and intrinsic reaction coordinate calculations were performed using the M05[41] density functional using the cc-pVDZ-pp[42] basis set with the relativistic core potential for Pt and the cc-pVDZ basis for light atoms and Cu.[43] Energies of the optimized structures were reevaluated with the same density functional using the triple-ζ basis set cc-pVTZ(-pp).[44] Analytical vibrational frequencies within the harmonic approximation were computed with the cc-pVDZ(-pp) basis to confirm minima or saddle points on the potential energy surface (PES). To simulate solvent effects, the polarizable continuum model (PCM)[45] was used, in which DMF (ε = 37.219) was chosen as the solvent. PCM solvation free energies were evaluated on the gas-phase geometries at the same level of theory as used for the geometry optimizations (M05/cc-pVDZ(-PP) applying the united atom topological model (UAHF)[46] to build the cavity around the solute molecule. M05/cc-pVTZ(-pp) wave functions were used to analyze the electronic structures with methods including molecular orbitals, Mayer bond orders,[47] charges, and spin densities. All calculations were carried out with Gaussian 09.[48]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures giving spectral characterization data, computational and crystallographic details, CIF file, and Cartesian coordinates of optimized structures. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: janez.kosmrlj@fkkt.uni-lj.si (J.K.), fdeprof@vub.ac.be (F.D.P.).

Notes

The authors declare no competing financial interest.

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■ DEDICATION

Dedicated to Professor Slovenko Polanc on the occasion of his 65th birthday.

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