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# Amidines Derived from Pt(IV)-Mediated Nitrile–Amino Alcohol Coupling and Their Zn(II)-Catalyzed Conversion into Oxazolines

**Anastassiya V. Makarycheva-Mikhailova,[†,‡] Vadim Yu. Kukushkin,*[,†] Alexey A. Nazarov,[‡] Dmitrii A. Garnovskii,[§] Armando J. L. Pombeiro,*[,§] Matti Haukka,[||] Bernhard K. Keppler,[‡] and Markus Galanski*[,‡]**

*Department of Chemistry, St. Petersburg State University, 198504 Stary Petergof, Russian Federation, Institute for Inorganic Chemistry, University of Vienna, Währinger Strasse 42, A-1090 Vienna, Austria, Centro de Química Estrutural, Complexo I, Instituto Superior Técnico, Av. Rovisco Pais, 1049-001 Lisbon, Portugal, and Department of Chemistry, University of Joensuu, P.O. Box 111, FIN-80101, Joensuu, Finland*

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The reaction between the platinum(IV) complex *trans*-$[PtCl_4(EtCN)_2]$ and the amino alcohols $NH_2CH_2CH_2OH$, $NH_2CH_2CH(Me)OH$-(*R*)-(–), $NH_2CH(Ph)CH_2OH$-(*R*)-(–), $NH_2CH(Et)CH_2OH$-(*R*)-(–), $NH_2CH(Et)CH_2OH$-(*S*)-(+), and $NH_2CH(Pr^n)CH_2OH$ proceeds rapidly at room temperature in $CH_2Cl_2$ to furnish the amidine complexes $[PtCl_4\{HN{=}C(Et)NH\frown OH\}_2]$ (**1**–**6**) in good yield (70–80%). The related reaction between the platinum(II) complex *trans*-$[PtCl_2(EtCN)_2]$ and monoethanolamine in a molar ratio of 1:2 in $CH_2Cl_2$ results in the addition of 4 equiv of $NH_2CH_2CH_2OH$ per mole of complex to give $[Pt\{HN{=}C(Et)NHCH_2CH_2OH\}_2(NH_2CH_2CH_2OH)_2]^{2+}$ (**7**). Formulation of **1**–**6** is based upon satisfactory C, H, N elemental analyses, electrospray mass spectrometry, IR spectroscopy, and $^1H$, $^{13}C\{^1H\}$, $^{15}N$, and $^{195}Pt$ NMR spectroscopies, while the structures of *trans*-$[PtCl_4\{(Z)\text{-}NH{=}C(Et)NHCH_2CH_2OH\}_2]$ (**1**), *trans*-$[PtCl_4\{(Z)\text{-}NH{=}C(Et)NHCH_2CH(Me)OH\text{-}(R)\text{-}(-)\}_2]$ (**2**), and *trans*-$[PtCl_4\{(Z)\text{-}NH{=}C(Et)NHCH(Et)CH_2OH\text{-}(R)\text{-}(-)\}_2]$ (**4**) were determined by X-ray single-crystal diffraction. The *Z*-amidine configuration of the ligands is preserved in $CDCl_3$ solutions as confirmed by gradient-enhanced $^{15}N,^1H$-HMQC spectroscopy and NOE experiments. The amidines, formed upon Pt(IV)-mediated nitrile–amino alcohol coupling, were liberated from their platinum(IV) complexes **1**, **3**, and **4** by reaction with $Ph_2PCH_2CH_2PPh_2$ (dppe) giving free $NH{=}C(Et)NHCHRCH_2OH$ (R = H **8**, Et **9**, Ph **10**), with the substituents R of different types, and dppe oxides; the P-containing species were identified by $^{31}P\{^1H\}$ NMR spectroscopy. NOESY spectroscopy indicates that the liberated amidines retained the same configuration relative to the C=N double bond, i.e., *syn*-(H,Et)-$NH{=}C(Et)NHCHRCH_2OH$. The liberated hydroxo-functionalized amidines **8**–**10** were converted into oxazolines $\overline{N{=}C(Et)OCH_2}CH(R)$ (**11**–**13**) in the presence of a catalytic amount of $ZnCl_2$. A similar catalytic effect has also been reached using anhydrous $MSO_4$ (M = Cu, Co, Cd), $CdCl_2$, and $AlCl_3$.

## Introduction

Oxazolines (or 4,5-dihydrooxazoles) constitute one of the most intensely studied classes of heterocycles, a fact confirmed by the 150 or so references which result when *Chemical Abstracts* is searched (from 1964 up until the end of 2002) for the combination "oxazoline and review". These naturally occurring (e.g., microbial metal chelators such as vibriobactin,[1] parabactin,[2] fluvibactin,[3] and agrobactin[4]) or

* To whom correspondence should be addressed. E-mail: kukushkin@VK2100.spb.edu (V.Yu.K.), pombeiro@ist.utl.pt (A.J.L.P.), and galanski@ap.univie.ac.at (M.G.).
† St. Petersburg State University.
‡ University of Vienna.
§ Instituto Superior Técnico.
|| University of Joensuu.

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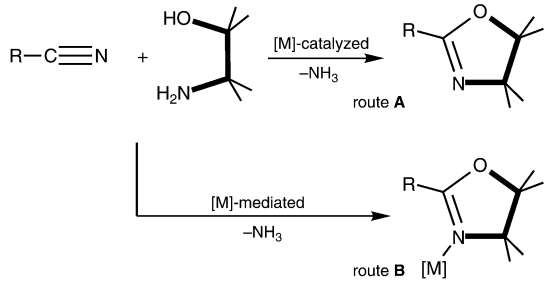
synthetic[5−10] compounds have a broad application in both organic[5−10] and coordination chemistries[11] as useful synthons (for preparation of more complex fragments) and in polymer chemistry (in step-growth[12] and ring-opening polymerizations,[13] as amphiphilic block copolymers for micellar catalysis,[14] and as reactive modifiers in the compatibilization of polymer blends[15]), and they also have intrinsic practical applications as insecticides and acaricides.[16] However, the basic idea that drives the overwhelming majority of the recent achievements in the chemistry of these heterocycles is that chiral oxazolines, bis(oxazolines), and oxazoline-based metal complexes can be employed as highly efficient *inducers of asymmetry* in many kinds of organic reactions. The synthesis, properties, and valuable applications of chiral oxazolines and their metal complexes in the asymmetric synthesis and catalysis were repeatedly surveyed along the past two decades, e.g., see recent books[17] and reviews.[18−24]

**Scheme 1**




Synthesis of oxazolines[7−10] and oxazoline type monomers for further polymerization[10] has been reviewed. The most developed synthetic approaches to furnish these heterocycles include dehydration and cyclization of some carboxamides (e.g., hydroxyamides), reaction between halocarboxamides and strong bases, additions of oxiranes to nitriles and amino alcohols to carboxylic acids or imino esters, and, eventually, two routes involving metal centers: (i) addition of halo alcohols/base or oxirane/$Cl^-$ systems to Pt(II)-bound nitriles[25] and (ii) reactions between nitriles and amino alcohols which are *catalyzed* by zinc(II),[26−29] cadmium(II),[28] nickel(II),[30] and aluminum(III)[29] ions (Scheme 1, route A) or *mediated* by cobalt(II) and copper(II)[31] centers (Scheme 1, route B). The metal-catalyzed reaction between nitriles and amino alcohols (Scheme 1, route A) is one of the most advantageous synthetic methods leading to the oxazolines owing to its superior simplicity and the commercial availability of (or the easy synthetic access to) the starting materials; some of these processes have been patented.[27,29]

The synthesis of the oxazolines from nitriles and amino alcohols has been performed at highly labile metal centers, and it is not surprising that intermediates in the conversion were neither isolated nor even detected in situ. Being interested in the reactions of metal-activated nitriles (a topic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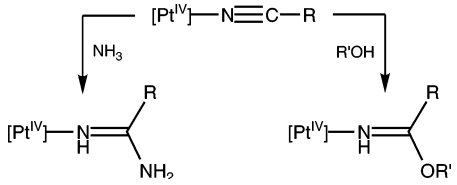
recently reviewed by two of us[34] and also by others[35−37]), we observed that the platinum(IV) nitrile complexes [$PtCl_4$-$(RCN)_2$] are very reactive toward various protic nucleophiles (HNuc)[38−43] achieving imino complexes [$PtCl_4${HN=C(R)-Nuc}$_2$] which exhibit substantial inertness toward substitution and hydrolysis, and the latter fact gave the hope that some intermediates in the reaction between nitriles and amino alcohols could be trapped at the Pt(IV) center and stored in the form of the imino complexes.

We decided to extend our research in the chemistry of nitrile-based systems to amino alcohols, and the scenario of the current work was the following: (i) to perform the addition of amino alcohols to Pt(IV)-bound nitrile species and to establish, by both X-ray solid and NMR solution structural studies, the mode of addition of the amino alcohols to complexed nitriles; (ii) to liberate the ligands formed in the course of the metal-mediated reaction; and (iii) to perform their conversion into oxazolines. In this work, we succeeded in isolating (amidine)Pt(IV) complexes, establishing their fine structure both in the solid state and in solution, liberating the hydroxo-functionalized amidines, and performing their Zn(II)-catalyzed conversion to oxazolines, and all these results are presented in the article.

## Results and Discussion

Although amino alcohols, as ambidentate nucleophiles, can be added to nitriles by either N or O atoms, it is reasonable to assume that the addition would occur via the more nucleophilic N center. Indeed, although the mechanism of the reaction is yet unknown, a few nonsystematic approaches allowed the assumption that the reaction between RCN and $NH_2$⁀OH proceeds via the intermediate formation of the amidine HN=C(R)NH⁀OH rather than the imino ester HN=C(R)O⁀$NH_2$. Thus, the Cu(II)-[32] or Ni(II)-mediated[33] reactions between *o*-(N≡C)$C_5H_4$N and amino alcohols led to amidine complexes, but liberation of the hydroxo-functionalized amidines followed by their conversion into oxazolines—thus unambiguously proving that the amidines are intermediates in the reaction—was not attempted.[32,33] In organic chemistry, it is anticipated that the second step of the Pinner synthesis[44] should give the amidines (which are then converted to oxazolines), but formulation of the amidines is only weakly supported by $^1$H NMR study. Hence, until now there were no reports where (i) the intermediates in the oxazoline synthesis were generated and identified and (ii) the Zn(II)-catalyzed conversion of the amidines HN=C(R)NH⁀OH into oxazolines was conducted. We endeavored to fill these gaps in the current work.

**Scheme 2**




**Pt(IV)-Mediated Nitrile−Amino Alcohol Coupling.** As a source of coordinated nitrile for this study we addressed the rather soluble (in organic solvents) platinum(IV) complex *trans*-[$PtCl_4(EtCN)_2$] because it has been demonstrated by our previous work that nitrile ligands in compounds of such type are highly activated toward the addition of nucleophiles such as oximes,[39] dione monoximes,[40] *vic*-dioximes,[41] hydroxamic acids,[42] and imines and sulfimides[43] and they are also quite reactive in 1,3-dipolar cycloaddition of nitrones[45,46] and nitrile oxides.[47] In the context of the current work, one should mention that the nitrile platinum(IV) complexes easily react with both ammonia[48] and alcohols[38] to form amidine and imino ester complexes, respectively (Scheme 2) but their reaction with amino alcohols bearing both functionalities has not yet been studied.

In addition, it was reported that (benzonitrile)Pt(II) complexes are involved in both substitution of the nitrile and addition of monoethanolamine to the nitrile,[49] but available data are insufficient to determine whether the amino alcohol adds via either the N or O nucleophilic center.

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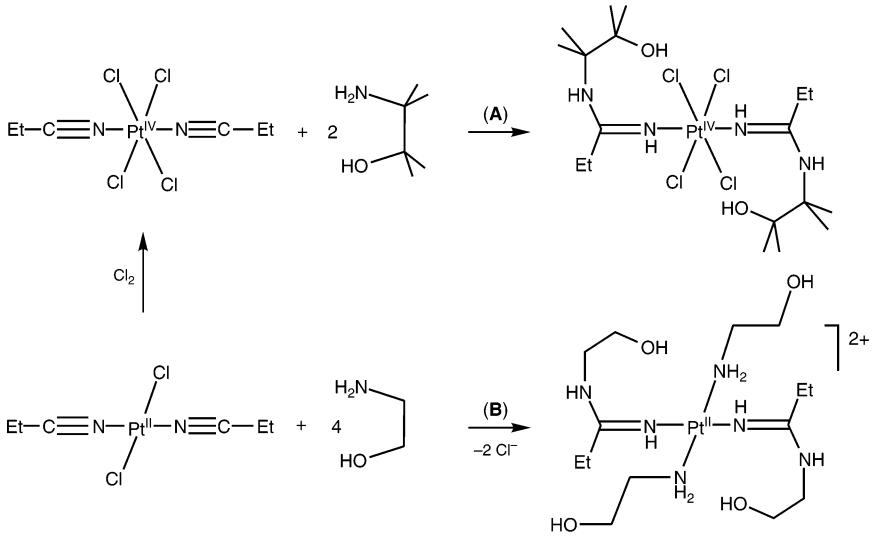
**Scheme 3**



The reaction between *trans*-$[PtCl_4(EtCN)_2]$ and the amino alcohols with different degrees of substitution in the methylene groups, i.e., $NH_2CH_2CH_2OH$, $NH_2CH_2CH(Me)OH$-(*R*)-(−), $NH_2CH(Ph)CH_2OH$-(*R*)-(−), $NH_2CH(Et)CH_2OH$-(*R*)-(−), $NH_2CH(Et)CH_2OH$-(*S*)-(+), and $NH_2CH(Pr^n)CH_2OH$, proceeds rapidly at room temperature in $CH_2Cl_2$ to furnish the platinum complexes $[PtCl_4\{HN{=}C(Et)NH\text{-}OH\}_2]$ (**1**−**6**) in good yield (70−80%). Electrospray mass spectrometry was performed using ca. $2 \times 10^{-6}$ mol/L solutions of the complexes in acetone, and the spectra obtained, in all cases, display the fragment $[M - H]^-$ (where M denotes the molecular ion of a product of the addition of 2 equiv of the $NH_2\text{-}OH$ per 1 equiv of the starting platinum complex) having isotopic patterns which agree well with the calculated ones. The 2:1 stoichiometry of the addition was additionally confirmed by satisfactory C, H, and N analyses. The IR spectra show no band due to $\nu$(C≡N) but very strong bands of the imino $\nu$(C═N) [1623−1637 $cm^{-1}$] along with less specific weak-to-medium $\nu$(O−H) and $\nu$(N−H) stretching vibrations. The combined data of NMR study (in solution) and X-ray determinations (in the solid state) presented later led to the conclusion on the formation of the amidine structure of **1**−**6**, i.e., $[PtCl_4\{HN{=}C(Et)NH\text{-}OH\}_2]$, and, consequently, on the N-addition of the N,O-bifunctional nucleophile (Scheme 3, route A). The process is metal-mediated because $^1$H NMR experimentation shows that EtCN does not react with the amino alcohols under the reaction or even more harsh (70 °C, 12 h) conditions. Complexes are presumably formed by nucleophilic attack of the nitrogen on the highly electrophilically activated carbon atom of the organonitrile.

We have also studied, for comparativity reasons, the reaction between the platinum(II) complex *trans*-$[PtCl_2(EtCN)_2]$ and monoethanolamine in a molar ratio 1:2 in $CH_2Cl_2$ (Scheme 3, route B) and observed, in accord with the previous study on the related benzonitrile complex,[49] the addition of 4 equiv of $NH_2CH_2CH_2OH$ per 1 mol of the complex. The IR and NMR spectra clearly show that 2 equiv of monoethanolamine adds to the coordinated nitriles. Moreover, NMR data favor the addition of monoethanolamine via the N atom thus forming the metal-bound amidine.

In general, the addition of *asymmetrical* bifunctional nucleophiles to metal-activated nitriles is only poorly explored,[32,33,49] albeit the reactions with *symmetric* bifunctional nucleophiles, e.g., ethylenediamine,[50,51] has been much more broadly investigated.

**X-ray Structure Determinations of Amidine Pt(IV) Complexes.** The structures of compounds *trans*-$[PtCl_4\{(Z)\text{-}NH{=}C(Et)NHCH_2CH_2OH\}_2]$ (**1**), *trans*-$[PtCl_4\{(Z)\text{-}NH{=}C(Et)NHCH_2CH(Me)OH\text{-}(R)\text{-}(-)\}_2]$ (**2**), and *trans*-$[PtCl_4\{(Z)\text{-}NH{=}C(Et)NHCH(Et)CH_2OH\text{-}(R)\text{-}(-)\}_2]$ (**4**) were determined by X-ray single-crystal diffraction. The coordination geometry of the three complexes is slightly distorted octahedral (Figures 1−3).

The values of the Pt−Cl bond distances are in the range from 2.322 to 2.329 Å, and these distances agree well with those in the previously characterized platinum(IV) chloride compounds.[40−43,52] Although the X-ray crystallography, in some instances, has certain restrictions in a reliable localization of N and O atoms, e.g., in **1**, the availability of the substituents in the methylene chain of **2** and **3** allowed the conclusion that amino alcohols were added by their N ends. The two amidine ligands in **1**−**3** are mutually trans, which is the thermodynamically stable form for complexes having metal centers in a high oxidation state.[53] In the amidine ligands, the values of the C(1)−N(1) bond lengths (1.304−1.318 Å) are similar within the 3$\sigma$ range, while the bonds

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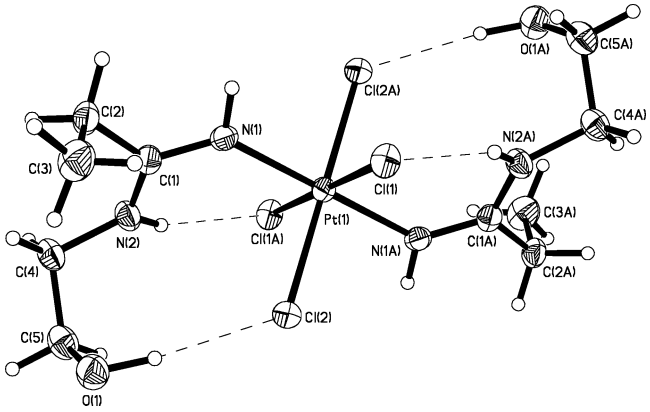


**Figure 1.** Molecular structure of *trans*-[$PtCl_4${(*Z*)-NH═C(Et)NHCH$_2$CH$_2$-OH}$_2$] **1**. The thermal ellipsoids are drawn at the 50% probability level. The shortest intramolecular hydrogen interactions: N(2)−H 0.94 Å, N(2)···Cl(1A) 3.151(5) Å, H···Cl(1A) 2.29 Å, N(2)−H···Cl(1A) 153.1°; O(1)−H 1.04 Å, O(1)···Cl(2) 3.346(4) Å, H···Cl(2) 2.31 Å, O(1)−H···Cl(2) 174.2°.

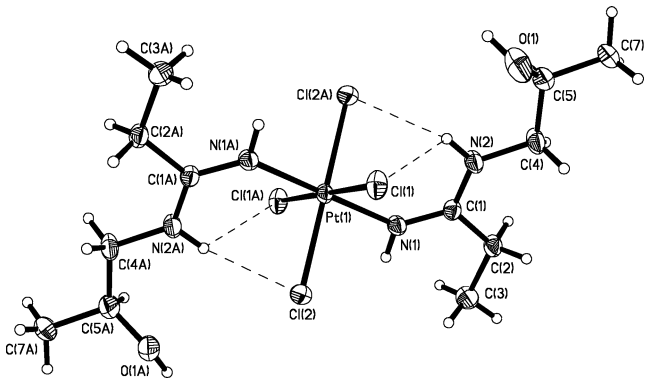


**Figure 2.** Molecular structure of *trans*-[$PtCl_4${(*Z*)-NH═C(Et)NHCH$_2$CH-(Me)OH-(*R*)-(−)}$_2$] **2**. The thermal ellipsoids are drawn at the 50% probability level. The shortest intramolecular hydrogen interactions: N(2)−H 0.94(5) Å, N(2)···Cl(1) 3.325(3) Å, H···Cl(1) 2.72(5) Å, N(2)−H···Cl(1) 123(4)°; N(2)−H 0.94(5) Å, N(2)···Cl(2A) 3.210(3) Å, H···Cl(2A) 2.47(5) Å, N(2)−H···Cl(2) 145.7°.

C(1)−N(2) are slightly longer (1.324−1.328 Å), thus indicating that the N(2)H group is of the amido type, although some degree of the electron delocalization within the amidine moiety should be taken into account as in the previously observed (amidine)Pt(II) system.[54a] Similar values of the C−N bonds have been earlier found in the (amidine)Pt(IV) complex [1.305(7)/1.315(7) Å[43a]]. The complexed amidines in **1**−**3** are in the *Z*-configuration, and in all three structures the amido hydrogens are involved in intramolecular H-bonding with the chloride ligands as depicted in Figures 1−3. In **1**, an additional hydrogen bonding is observed between the OH tails and Cl atoms.

Recently, the reaction between *trans*-[$PtCl_2(NCMe)_2$] and $MeNH_2$ to give the bis-amidine complex *trans*-[$PtCl_2${(*Z*)-N(H)═C(NHMe)Me}$_2$] has been studied, and it was

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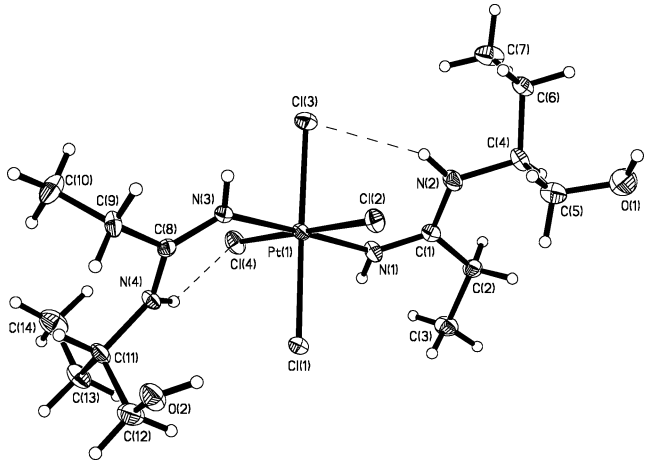
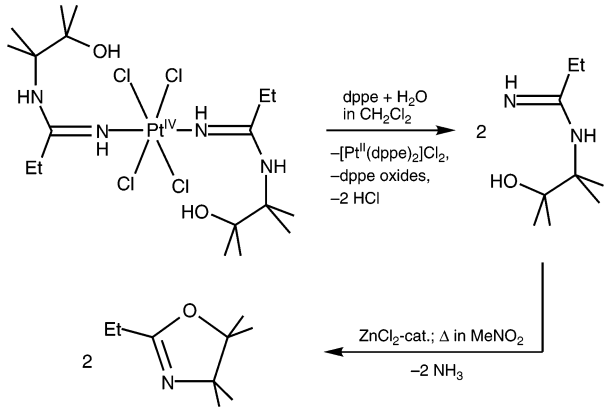



**Figure 3.** Molecular structure of *trans*-[$PtCl_4${(*Z*)-NH═C(Et)NHCH(Et)-CH$_2$OH-(*R*)-(−)}$_2$] **4**. The thermal ellipsoids are drawn at the 50% probability level. The shortest intramolecular hydrogen interactions: N(2)−H 0.88 Å, N(2)···Cl(3) 3.334(3) Å, H···Cl(3) 2.55 Å, N(2)−H····Cl(1) 149.3°; N(4)−H 0.88 Å, N(4)···Cl(4) 3.236(3) Å, H···Cl(4) 2.47 Å, N(2)−H···Cl(2) 146°.

concluded—after careful inspection of the X-ray data—that the *Z*-configuration of N(H)═C(NHMe)Me species is determined by the formation of strong intramolecular hydrogen bonds between each chlorine atom and the amino proton of the NHMe moiety to give a six-membered ring.[54] In our cases, the hydrogen bonding is not particularly strong, the shortest donor−acceptor distances (N···Cl or O···Cl) being between 3.151(5) and 3.346(4) Å. Therefore, it is hardly solely responsible for the configuration of the coordinated amidines.

**NMR Solution Structural Study of the Amidine Pt(IV) Complexes.** The addition of the amino alcohols to the nitrile complex *trans*-[$PtCl_4(EtCN)_2$] can be conveniently monitored by NMR spectroscopy because the changes in the $^1$H, $^{13}$C, and $^{15}$N NMR spectra—upon addition of the corresponding amino alcohols through the amino group along the C≡N bond—are very indicative for the investigated reaction. After the addition, the proton signals of the products show high field shifts of the ethyl group in comparison with the starting complex *trans*-[$PtCl_4(EtCN)_2$]. In the latter compound, the resonances at 1.55 ($CH_3CH_2$) and 3.20 ($CH_3CH_2$) ppm were found, whereas in the products the corresponding groups resonate at 1.3 and 2.6 ppm, respectively. In the $^{13}$C NMR spectra, the carbon of the imino group of the amidine complexes was detected at ca. 171 ppm, in comparison to the resonance at 119 ppm for the nitrile carbon of the starting platinum complex. The chemical shifts of both nitrogen atoms of the HN═C(NHR) moiety were obtained using gradient-enhanced $^{15}$N,$^1$H-HMQC spectroscopy. The coordinated NH groups show shift correlation signals between 84.4 and 97.3 ppm ($^{15}$N) and 5.40 and 5.61 ppm ($^1$H). Typical coupling constants of 333−360 Hz ($^1J_{N,Pt}$) and 25−27 Hz ($^2J_{H,Pt}$) were observed. Addition of the potentially ambidentate amino alcohols through the N atom is reflected by a significant shift of the $^{15}$N resonance, which is detected at 62 ppm in the amidines in comparison to ca. −10 ppm of the free amines. In the $^1$H NMR spectra, the *H*N═C resonance was found in the range 7.39−8.11 ppm, and these

**Scheme 4**




rather high values indicate the involvement of the imino proton in the hydrogen bonding. $^{195}$Pt resonances were observed between −101 and −75 ppm, which is in accord with the ligand sphere around the platinum(IV) center of the amidine complexes.

Previously, NOE experiments have been effectively used by us for observation of the *E*−*Z* forms in Pt(IV)-bound imino esters,[38] and it was proved that this method allows the determination of the configuration even when only one form is available. The NOE experiment for studying the *E*−*Z* isomerism has now been applied to the amidine complexes, and NOE shift correlation signals between the imino proton [Pt]−*H*N═C($CH_2CH_3$) and the methylene protons [Pt]−HN═C(C$H_2$$CH_3$) were found in the NOESY spectra. The latter gives explicit evidence that the platinum amidine compounds in *solution* retain the *Z*-configuration observed in the *solid state* by the X-ray diffraction (see above).

**Liberation of the Hydroxo-Functionalized Amidines.** The amidine Pt(IV) complexes exhibit substantial inertness (characteristic for Pt(IV) complexes[55]) toward substitution with such strong chelating ligands as 2,2′-bipyridyl, ethylenediamine, EDTA, and 1,5,9-triazacyclododecane. However, the amidine has been displaced from **1** by reaction with pyridine in $CH_2Cl_2$ (2 days, reflux) giving NH═C(Et)-$NHCH_2CH_2OH$ and the well-known $[PtCl_4(py)_2]$;[56] the very poor solubility of the latter is the apparent driving force for the reaction. However, the substitution for pyridine of the other amidines (from **2**−**6**) failed and only the starting platinum complexes were detected in the mass spectra.

The most general and facile method for the liberation of the hydroxo-functionalized amidines we found so far is based on the reaction of the amidine complexes with 1,2-bis-(diphenylphosphine)ethane (dppe), which acts as both replacing and reduction agent (Scheme 4), giving the amidine along with the platinum(II) complex $[Pt(dppe)_2]Cl_2$ and the dppe oxides; the P-containing species were identified by $^{31}P\{^1H\}$ NMR. This reaction was illustrated by use of complexes **1**, **3**, and **4**. The treatment of these complexes with dppe followed by subsequent workup allowed the isolation of the amidines NH═C(Et)$NHCHRCH_2OH$ (R = H **8**, Et **9**, Ph **10**) with the substituents R of different type.

Liberation of the amidines was monitored by NMR and IR spectroscopies and also by electrospray mass spectrometry ($[M + H]^+$ ions were detected for **8**−**10**). It was shown, using NOESY spectroscopy, that the liberated hydroxo-functionalized amidines retained the same configuration relative to the C═N double bond, i.e., *syn*-(H,Et)−NH═C(Et)$NHCHRCH_2OH$. Indeed, NOE shift correlation signals between the imino proton *H*N═C($CH_2CH_3$) and the methylene protons HN═C(C$H_2$$CH_3$) were found for all the amidines.

**Zn(II)-Catalyzed Conversion of the Amidines into Oxazolines.** The liberated amidines **8**−**10** were converted into oxazolines **11**−**13**, respectively, upon reflux in nitromethane for 3 days. The formation of the heterocycles is much faster in the presence of a catalytic amount of $ZnCl_2$ (0.024 mol per 1 mol of the amidine; Scheme 4) when the conversion is complete after 4 h. A similar catalytic effect has also been reached using anhydrous $MSO_4$ (M = Cu, Co, Cd), $CdCl_2$, and $AlCl_3$.

Although the synthesis of oxazolines from amino alcohols and nitriles is known, the metal-catalyzed synthesis of oxazolines from the amidines HN═C(R)$NH^{\frown}OH$ has never been reported in the past. We anticipate that, in general, the role of metal ions in the metal-catalyzed synthesis of oxazolines is at least dual. First, metal centers activate nitriles toward the nucleophilic addition of amino alcohols, and, second, they provide conditions for the facile cyclization of the amidines HN═C(R)$NH^{\frown}OH$ formed in the first step of the reaction.

**Final Remarks.** Besides the contribution to the chemistry of oxazolines, this work adds more on the synthetic routes to amidines and their complexes, and the importance of the latter is manifested in the following: (i) In accord with the recent data, some amidine complexes of platinum exhibit substantial antitumor activity,[57] and the bioinorganic chemistry of amidine compounds will certainly be further investigated. (ii) Despite the intrinsic pharmacological significance, high synthetic utility, and number of industrial applications of amidines,[58−60] information on synthetic pathways to their alcohol HN═C(R)$NH^{\frown}OH$ derivatives is scarce and limited to only the reactions between amidines and 2-haloethanol or ethylene oxide,[61] monoethanolamine with 3-cyano-4,5-dialkyl-2-butenolides or 3-cyano-4,5-dialkylbutyrolac-

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tones,[62] L-arginine and monoethanolamine (giving 2-guanidinoethanol),[63] and imidates with amino alcohols.[44] In addition, it has recently been reported that the platinum(II) complex $[(Me_2PO\cdots H\cdots OPMe_2)PtH(PMe_2OH)]$ efficiently catalyzes the direct conversion of propionitrile and monoethanolamine into $NH{=}C(Et)NHCH_2CH_2OH$; the latter was characterized only by GCMS.[64] The current work is the first one where a general pathway to this type of hydroxo-functionalized amidines is developed and the compounds $HN{=}C(R)NH\bar{}OH$ have been fully characterized both in solution and in the solid state. The synthetic significance of such compounds toward the formation of oxazolines was also clearly recognized in this work. The only handicap to achieve a great variety of such amidines is the extreme kinetic inertness of the platinum(IV) complexes making difficult the substitution of the $HN{=}C(R)NH\bar{}OH$ formed in the metal-mediated reaction. However, the metal enhancement of the activation of the ligated nitriles is expected to promote other amino alcohol reactions, and we anticipate the discovery of much more labile metal systems to furnish those organic compounds; work in this direction is underway in our group.

## Experimental Section

**Materials and Instrumentation.** Solvents were obtained from commercial sources and used as received. *trans*-$[PtCl_n(EtCN)_2]$ ($n$ = 2, 4) were prepared accordingly to the published methods.[65] Amino alcohols were purchased from Fluka and Aldrich. C, H, and N elemental analyses were carried out by the laboratory for elemental analyses of the Institute of Physical Chemistry, University of Vienna, with a Perkin-Elmer 2400 CHN elemental analyzer. Melting points were determined on a Büchi B-540 melting point apparatus and are uncorrected. For TLC, Merck 60 $F_{254}$ $SiO_2$-plates have been used. Mass spectra were obtained on a Bruker esquire$_{3000}$ (ESI) instrument. Infrared spectra (4000−400 $cm^{-1}$) were recorded on a Perkin-Elmer FTIR instrument in KBr pellets.

**NMR Measurements.** $^1H$, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$, $^{195}Pt$, and $^{15}N$ NMR spectra were measured on a Bruker DPX 400 spectrometer (Ultrashield Magnet) at 400.13 MHz ($^1H$), 100.63 MHz ($^{13}C$), 162.0 MHz ($^{31}P$), 85.99 MHz ($^{195}Pt$), and 40.55 MHz ($^{15}N$), correspondingly, at ambient temperature. $^{195}Pt$ chemical shifts are given relative to $Na_2[PtCl_6]$ (by using $K_2[PtCl_4]$, $\delta = -1630$ ppm, as a standard), and the half-height line width is given in parentheses. Peak attribution is based on gradient-enhanced $^1H,^1H$-DQF-COSY, $^{13}C,^1H$-HMQC, $^{13}C,^1H$-HMBC, $^{15}N,^1H$-HMQC, and NOESY spectroscopy using standard pulse programs.

**X-ray Structure Determinations of 1, 2, and 4.** The X-ray diffraction data were collected on a Nonius Kappa CCD diffractometer using Mo Kα radiation ($\lambda$) 0.71073 Å. The Denzo-Scalepack[66] program package was used for cell refinements and data reduction. Structures were solved by direct methods using the SIR97 or SHELXS-97 programs.[67,68] An empirical absorption correction based on equivalent reflections[69] was applied to all data. The structures were refined with the SHELXL-97[70] program and the WinGX graphical user interface.[71] In **2**, the OH group was disordered in two positions with approximately equal occupation parameters. OH and NH hydrogens were located from the difference Fourier map. In the case of **4**, NH hydrogens were refined isotropically. All other hydrogens either were not refined or were constrained to ride on their parent atom. Crystallographic data are summarized in Table 1, and selected bond lengths and angles, in Table 2 and the figure captions.

**Table 1.** Crystal Data for Complexes **1**, **2**, and **4**

| | **1** | **2** | **4** |
|---|---|---|---|
| emp formula | $C_{10}H_{24}Cl_4N_4O_2Pt$ | $C_{12}H_{28}Cl_4N_4O_2Pt$ | $C_{14}H_{30}Cl_4N_4O_2Pt$ |
| fw | 569.22 | 597.27 | 623.31 |
| temp, K | 120(2) | 150(2) | 100(2) |
| $\lambda$, Å | 0.71073 | 0.71073 | 0.71073 |
| cryst syst | monoclinic | triclinic | orthorhombic |
| space group | $P2_1/n$ | $P\bar{1}$ | $P2_12_12_1$ |
| $a$, Å | 7.8130(4) | 7.9911(2) | 8.89200(10) |
| $b$, Å | 13.1622(8) | 8.5378(2) | 11.0774(2) |
| $c$, Å | 8.7544(5) | 9.0101(3) | 22.7956(3) |
| α, deg | | 104.2530(10) | 90 |
| $\beta$, deg | 97.909(3) | 98.8570(10) | 90 |
| $\gamma$, deg | | 116.112(2) | 90 |
| $V$, Å$^3$ | 891.71(9) | 510.11(2) | 2245.37(6) |
| $Z$ | 2 | 1 | 4 |
| $\rho_{calcd}$, g/cm$^3$ | 2.120 | 1.944 | 1.850 |
| $\mu$(Mo Kα), mm$^{-1}$ | 8.475 | 7.412 | 6.740 |
| R1[a] ($I \geq 2\sigma$) | 0.0267 | 0.0203 | 0.0175 |
| wR2[b] ($I \geq 2\sigma$) | 0.0543 | 0.0493 | 0.0406 |

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

**Synthetic Work and Characterization. Addition of Amino Alcohols to EtCN Ligands in *trans*-$[PtCl_4(EtCN)_2]$.** Monoethanolamine (5.5 mg, 0.095 mmol) was added to a suspension of *trans*-$[PtCl_4(EtCN)_2]$ (20.0 mg, 0.0447 mmol) in $CH_2Cl_2$ (2 mL) at room temperature. After ca. 2 min the orange crystalline precipitate was formed; it was filtered off, washed with three 3-mL portions of $CH_2Cl_2$, two 3-mL portions of $Et_2O$, and one 3-mL portion of EtOH, and dried in vacuo for 1 day at 20−25 °C. The yield is 82%, based on Pt.

The other amino alcohols (0.095 mmol) were added to a suspension of *trans*-$[PtCl_4(EtCN)_2]$ (20.0 mg, 0.0447 mmol) in $CH_2Cl_2$ (2 mL) at room temperature to give an orange solution, which, after 2 h, was evaporated to dryness at 20−25 °C under reduced pressure; the orange oily residue formed was washed with three 3-mL portions of $Et_2O$, whereupon it was dried in vacuo at room temperature to give crystalline material. The yields were 70−80%, based on Pt.

***trans*-$[PtCl_4\{(Z)\text{-}NH{=}C(Et)NHCH_2CH_2OH\}_2]$ (1).** Anal. Calcd for $C_{10}H_{24}N_4Cl_4O_2Pt$: C, 21.10; H, 4.25; N, 9.84. Found: C, 21.26; H, 4.46; N, 9.47. ESI-MS (acetone), $m/z$: 567 $[M - H]^-$. Mp = 145−146 °C. TLC: $R_f = 0.51$ (eluent $CH_2Cl_2$:acetone = 1:1). IR,


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

| | 1 | 2 | 4 |
|---|---|---|---|
| Pt(1)−Cl(1) | 2.3270(14) | 2.3216(8) | 2.3288(8) |
| Pt(1)−Cl(2) | 2.3271(14) | 2.3207(8) | 2.3251(7) |
| Pt(1)−Cl(3) | | | 2.3194(7) |
| Pt(1)−Cl(4) | | | 2.3142(8) |
| Pt(1)−N(1) | 2.039(4) | 2.033(3) | 2.034(3) |
| N(1)−C(1) | 1.315(7) | 1.318(4) | 1.304(4) |
| C(1)−N(2) | 1.324(7) | 1.327(4) | 1.328(4) |
| N(2)−C(4) | 1.474(7) | 1.462(4) | 1.462(4) |
| C(4)−C(5) | 1.517(8) | 1.475(5) | 1.564(5) |
| C(5)−O(1) | 1.407(7) | 1.337(7)/1.304(7)[a] | 1.389(4) |
| Pt(1)−N(3) | | | 2.026(2) |
| N(3)−C(8) | | | 1.308(4) |
| C(8)−N(4) | | | 1.339(4) |
| N(4)−C(11) | | | 1.466(4) |
| C(11)−C(12) | | | 1.527(5) |
| C(12)−O(2) | | | 1.423(4) |
| Cl(1)−Pt(1)−Cl(2) | | 90.13(3) | 89.33(3) |
| Cl(1)−Pt(1)−Cl(3) | | | 178.81(3) |
| Cl(2)−Pt(1)−Cl(4) | | | 179.57(3) |
| N(1)−Pt(1)−N(3) | | | 177.82(11) |
| Cl(1)−Pt(1)−N(1) | | 92.99(8) | 84.59(8) |
| Cl(2)−Pt(1)−N(1) | | 86.13(8) | 92.56(8) |
| Pt(1)−N(1)−C(1) | | 133.8(2) | 134.5(2) |
| C(4)−C(5)−O(1) | | 118.3(4)/116.1(4)[a] | 113.3(3) |
| Pt(1)−N(3)−C(8) | | | 131.6(2) |
| C(11)−C(12)−O(2) | | | 113.1(3) |

[a] Oxygen is disordered in two positions.

cm$^{-1}$: 3504 m−w $\nu$(O−H), 3298 and 3253 m−w $\nu$(N−H), 1636 vs $\nu$(C═N). $^1$H NMR spectrum in $CDCl_3$, $\delta$: 7.54 (t, 1H, −N*H*−), 5.48 (t, 1H, −NH═), 3.81 (s, br, 2H, C$H_2$OH), 3.45 (q, 2H, C$H_2$NH), 2.59 (q, 2H, C$H_2$ from Et), 1.32 (t, 3H, C$H_3$). $^{13}$C{$^1$H} NMR spectrum in $CDCl_3$, $\delta$: 170.69 (C═N), 61.90 ($CH_2$OH), 45.88 ($CH_2$NH), 27.17 ($CH_2$ from Et), 10.61 ($CH_3$ from Et). This complex exhibits poor solubility in $CDCl_3$ to measure its $^{195}$Pt NMR spectra even at high acquisition time; the solubility is higher in $(CD_3)_2SO$, but the complex is decomposed in this solvent.

***trans*-[PtCl$_4${(*Z*)-NH═C(Et)NHCH$_2$CH(Me)OH-(*R*)-(−)}$_2$] (2).** Anal. Calcd for $C_{12}H_{28}N_4Cl_4O_2Pt$: C, 24.12; H, 4.69; N, 9.38. Found: C, 24.23; H, 4.63; N, 9.24. ESI-MS (acetone), *m*/*z*: 595 [M − H]$^-$. Mp = 128 °C. TLC: $R_f$ = 0.47 (eluent $Me_2CO$:MeCOOEt = 1:2). IR, cm$^{-1}$: 3561 m−w $\nu$(O−H), 3403 and 3343 m−w $\nu$(N−H), 1623 vs $\nu$(C═N). $^1$H NMR spectrum in $CDCl_3$, $\delta$: 7.70 (t, 1H, −N*H*−), 5.48 (t, 1H, −NH═), 4.00 (m, 1H, C*H*), 3.33 and 3.21 (two m, 2H, C$H_2$NH−), 2.56 (q, 2H, C$H_2$ from Et), 1.29 and 1.27 (two t, 6H, C$H_3$ from Et and Me). $^{13}$C{$^1$H} NMR spectrum in $CDCl_3$, $\delta$: 170.61 (C═N), 67.18 (CH), 50.66 ($CH_2$NH), 27.16 ($CH_2$ from Et), 20.66 (CH(*C*$H_3$)OH), 10.56 ($CH_3$ from Et). $^{195}$Pt NMR spectrum in $CDCl_3$, $\delta$: −83.0 (450 Hz). $^{15}$N NMR spectrum in $CDCl_3$, $\delta$: 84.4, 62.0 ($^1J_{N,Pt}$ = 354 Hz, $^2J_{H,Pt}$ = 26 Hz).

***trans*-[PtCl$_4${(*Z*)-NH═C(Et)NHCH(Ph)CH$_2$OH-(*R*)-(−)}$_2$] (3).** Anal. Calcd for $C_{22}H_{32}N_4Cl_4O_2Pt$: C, 36.61; H, 4.38; N, 7.77. Found: C, 36.44; H, 4.40; N, 7.50. ESI-MS (acetone), *m*/*z*: 719 [M − H]$^-$. Mp = 161 °C. TLC: $R_f$ = 0.46 (eluent MeCOOEt). IR, cm$^{-1}$: 3492 m−w $\nu$(O−H), 3402 and 3342 m−w $\nu$(N−H), 1637 vs $\nu$(C═N). $^1$H NMR spectrum in $CDCl_3$, $\delta$: 8.11 (d, 1H, −N*H*−), 7.50−7.30 (m, 5H, Ph), 5.61 (t, 1H, −NH═), 4.68 (m, 1H, C*H*), 3.92 and 3.84 (two m, 1H, C$H_2$NH−), 2.57 (two m, 2H, C$H_2$ from Et), 1.23 (t, 3H, C$H_3$ from Et). $^{13}$C{$^1$H} NMR spectrum in $CDCl_3$, $\delta$: 170.68 (C═N), 137.90 ($C_{ipso}$), 129.57 (*p*-Ph), 128.79 and 126.91 (*o*-Ph and *m*-Ph), 67.54 ($CH_2$NH), 60.81 (CH), 26.97 ($CH_2$ from Et), 10.56 ($CH_3$). $^{195}$Pt NMR spectrum in $CDCl_3$, $\delta$: −101.0 (400 Hz). $^{15}$N NMR spectrum in $CDCl_3$, $\delta$: 94.2, 63.0 ($^1J_{N,Pt}$ = 360 Hz, $^2J_{H,Pt}$ = 26 Hz).

***trans*-[PtCl$_4${(*Z*)-NH═C(Et)NHCH(CH$_2$CH$_3$)CH$_2$OH-(*R*)-(−)}$_2$] (4).** Anal. Calcd for $C_{14}H_{32}N_4Cl_4O_2Pt$: C, 26.92; H, 4.48; N, 8.97. Found: C, 26.87; H, 4.70; N, 8.75. ESI-MS (acetone), *m*/*z*: 623 [M − H]$^-$. Mp = 140 °C. TLC: $R_f$ = 0.63 (eluent MeCOOEt). IR, cm$^{-1}$: 3499 m−w $\nu$(O−H), 3407 and 3334 m−w $\nu$(N−H), 1632 vs $\nu$(C═N). $^1$H NMR spectrum in $CDCl_3$, $\delta$: 7.39 (d, 1H, −N*H*−), 5.42 (t, 1H, −NH═), 3.72 and 3.60 (two m, 2 *H*, C$H_2$OH), 3.49 (m, 1H, C*H*), 2.60 (two q, 2H, C$H_2$ from Et), 1.63 and 1.53 (two m, 2H, CH(C$H_2$)$CH_3$), 1.31 (t, 3H, C$H_3$ from Et), 1.03 (t, 3H, C$H_3$). $^{13}$C{$^1$H} NMR spectrum in $CDCl_3$, $\delta$: 170.85 (C═N), 65.68 ($CH_2$OH), 58.23 (CH), 27.17 ($CH_2$ from Et), 24.77 (CH(*C*$H_2$)$CH_3$), 10.93 ($CH_3$ from Et), 10.86 ($CH_3$). $^{195}$Pt NMR spectrum in $CDCl_3$, $\delta$: −75.5 (450 Hz). $^{15}$N NMR spectrum in $CDCl_3$, $\delta$: 96.7, 61.4 ($^1J_{N,Pt}$ = 333 Hz, $^2J_{H,Pt}$ = 27 Hz).

***trans*-[PtCl$_4${(*Z*)-NH═C(Et)NHCH(CH$_2$CH$_3$)CH$_2$OH-(*S*)-(+)}$_2$] (5).** Anal. Calcd for $C_{14}H_{32}N_4Cl_4O_2Pt$: C, 26.92; H, 4.48; N, 8.97. Found: C, 26.67; H, 4.78; N, 8.68. ESI-MS (acetone), *m*/*z*: 623 [M − H]$^-$. Mp = 142 °C. TLC: $R_f$ = 0.35 (eluent $Me_2CO$: $CHCl_3$ = 1:5). IR, cm$^{-1}$: 3501 m−w $\nu$(O−H), 3403 and 3356 m−w $\nu$(N−H), 1629 vs $\nu$(C═N). $^1$H NMR spectrum in $CDCl_3$, $\delta$: 7.40 (d, 1H, −N*H*−), 5.42 (t, 1H, −N*H*═), 3.72 and 3.60 (two m, 2 *H*, C$H_2$OH), 3.49 (m, 1H, C*H*), 2.60 (q, 2H, C$H_2$ from Et), 1.63 and 1.53 (two m, 2H, CH(C$H_2$)$CH_3$), 1.31 (t, 3H, C$H_3$ from Et), 1.03 (t, 3H, C$H_3$). $^{13}$C{$^1$H} NMR spectrum in $CDCl_3$, $\delta$: 170.84 (C═N), 65.66 ($CH_2$OH), 58.22 (CH), 27.17 ($CH_2$ from Et), 24.78 (CH(*C*$H_2$)$CH_2$), 10.93 ($CH_3$ from Et), 10.86 ($CH_3$). $^{195}$Pt NMR spectrum in $CDCl_3$, $\delta$: −76.0 (450 Hz). $^{15}$N NMR spectrum in $CDCl_3$, $\delta$: 96.7, 61.6 ($^1J_{N,Pt}$ = 355 Hz, $^2J_{H,Pt}$ = 26 Hz).

***trans*-[PtCl$_4${(*Z*)-NH═C(Et)NHCH(CH$_2$CH$_2$CH$_3$)CH$_2$OH}$_2$] (6).** Anal. Calcd for $C_{16}H_{36}N_4Cl_4O_2Pt$: C, 29.40; H, 5.51; N, 8.57. Found: C, 29.11; H, 5.24; N, 8.27. ESI-MS (acetone), *m*/*z*: 651 [M − H]$^-$. Mp = 131 °C (dec). TLC: $R_f$ = 0.63 (eluent $Me_2CO$: $CHCl_3$ = 1:5). IR, cm$^{-1}$: 3507 m−w $\nu$(O−H), 3345 and 3294 m−w $\nu$(N−H), 1628 vs $\nu$(C═N). $^1$H NMR spectrum in $CDCl_3$, $\delta$: 7.40 (d, 1H, −N*H*−), 5.40 (t, 1H, −N*H*═), 3.70 (m, 1H, C*H*), 3.58 (m, 2H, −C$H_2$OH), 2.59 (q, 2H, C$H_2$ from Et), 1.51 (m, 4H, 2C$H_2$), 1.30 (t, 3H, C$H_3$ from Et), 0.95 (t, 3H, C$H_3$). $^{13}$C{$^1$H} NMR spectrum in $CDCl_3$, $\delta$: 170.75 (C═N), 65.98 (−$CH_2$OH), 56.64 (CH), 33.75 (CH(*C*$H_2$)$CH_2$), 27.07 ($CH_2$ from Et), 19.52 ($CH_2$(*C*$H_2$)$CH_3$), 14.39 ($CH_3$), 10.87 ($CH_3$ from Et). $^{195}$Pt NMR spectrum in $CDCl_3$, $\delta$: −76.7 (450 Hz). $^{15}$N NMR spectrum in $CDCl_3$, $\delta$: 97.3, 61.2 ($^1J_{N,Pt}$ = 356 Hz, $^2J_{H,Pt}$ = 25 Hz).

**Reaction between NH$_2$CH$_2$CH$_2$OH and the Platinum(II) Complex *trans*-[PtCl$_2$(EtCN)$_2$].** Monoethanolamine (L) (6.5 mg, 0.106 mmol) was added to a solution of *trans*-[$PtCl_2$(EtCN)$_2$] (20.0 mg, 0.053 mmol) in $CH_2Cl_2$ (2 mL) at room temperature, and the reaction mixture was kept for 1 h (during this time the oily residue was released), whereupon the yellow solution was decanted and the oily residue was subject to ESI-MS, TLC, IR, and NMR and monitoring.

**[Pt{NH═C(Et)NHCH$_2$CH$_2$OH}$_2$L$_2$]Cl$_2$ (7).** ESI-MS (acetone), *m*/*z*: 585 [M − Cl]$^+$, 524 [M − L − Cl]$^+$, 463 [M − 2L − Cl]$^+$. TLC: $R_f$ = 0.56 (eluent $CH_2Cl_2$:acetone = 1:2). IR, cm$^{-1}$: 3299 m−w $\nu$(N−H), 1628 vs $\nu$(C═N). $^1$H NMR spectrum in $CDCl_3$, $\delta$: 7.36 (s, br, 1H, −N*H*−), 5.32 (s, br, 1H, −NH═), 3.78 (m, 2H, C$H_2$OH), 3.37 (m, 2H, C$H_2$NH), 2.41 (q, 2H, C$H_2$ from Et), 1.20 (t, 3H, C$H_3$). $^{13}$C{$^1$H} NMR spectrum in $CDCl_3$, $\delta$: 170.69 (C═N), 61.90 ($CH_2$OH), 45.88 ($CH_2$NH), 27.17 ($CH_2$ from Et), 10.61 ($CH_3$ from Et). The $^1$H and $^{13}$C signals for ethanolamine coordinated to platinum could not be unequivocally assigned.

**Liberation of the Amidines from the Platinum(IV) Complexes. Method I.** In a preparative experiment, dppe (0.125 mmol)

is added to a solution of the amidine complex (0.050 mmol) in nondried $CH_2Cl_2$ (2 mL) at 20−25 °C, the color turns from yellow to colorless for 10 min, and a colorless precipitate of $[Pt(dppe)_2]Cl_2$ is released. The solvent is decanted and evaporated until half of the initial volume and $Et_2O$ (1 mL) is added, whereupon the mixture is left to stand at ca. −5 °C for 2−3 min. The precipitate of $[Pt(dppe)_2]Cl_2$ formed in almost quantitative yield ($^{31}P\{^1H\}$ NMR in $CDCl_3$, $\delta$, 45.7, $J_{Pt-P}$ 2360.5 Hz; lit.[72]); it is separated by filtration, the filtrate is evaporated until dryness, and the residue is washed with $Et_2O$ (1 mL) [$^{31}P\{^1H\}$ NMR of the ether washings in $CDCl_3$, $\delta$: $Ph_2P(=O)(CH_2)_2PPh_2$ (31.2, d, $J_{P-P}$ 48.5 Hz for $Ph_2P(=O)(CH_2)_2PPh_2$ and −13.5, d, $J_{P-P}$ 48.5 Hz for $Ph_2P(=O)(CH_2)_2PPh_2$; lit.[73−75]), $Ph_2P(=O)(CH_2)_2P(=O)Ph_2$ (31.2 s; lit.[76]), and $Ph_2P(CH_2)_2PPh_2$ (−14.1 s)] and dried in a vacuum. Yield: ca. 70%. **Method II.** In a preparative experiment, pyridine (0.40 mmol) is added to a solution of the amidine complex **1** (0.05 mmol) in $CH_2Cl_2$ (1 mL) and, upon reflux, the color turns from deep orange to orange for 2 days and a yellow precipitate of $[PtCl_4(py)_2]$[56] is quantitatively released. The precipitate is separated by filtration, the filtrate is evaporated until dryness, and the residue of amidine is dried in a vacuum; the yield is almost quantitative. The attempts to liberate other amidines apart from NH=C(Et)NHCH$_2$CH$_2$OH with pyridine failed, and only the starting platinum complexes were detected in mass spectra.

**NH=C(Et)NHCH$_2$CH$_2$OH (8).** ESI-MS (MeOH), *m*/*z*: 117 [M + H]$^+$. IR, cm$^{-1}$: 3425 m−w $\nu$(O−H) and $\nu$(N−H), 1635 s $\nu$(C=N). $^1$H NMR spectrum in $CDCl_3$, $\delta$: 8.47 (t, 1H, −N*H*−), 6.64 (t, 1H, −NH=), 3.71 (s, br, 1H, C*H*$_2$OH), 2.84 (q, 1H, C*H*$_2$NH), 1.88 (s, br, 2H, C*H*$_2$ from Et), 0.35 (t, 3H, C*H*$_3$). $^{13}C\{^1H\}$ NMR spectrum in $CDCl_3$, $\delta$: 171.1 (C=N), 61.0 ($CH_2OH$), 45.7 (CH), 26.2 ($CH_2$ from Et), 10.9 (*C*H$_3$).

**NH=C(Et)NHCH(CH$_2$CH$_3$)CH$_2$OH (9).** ESI-MS (MeOH), *m*/*z*: 145 [M + H]$^+$. IR, cm$^{-1}$: 3390 m−w $\nu$(O−H) and $\nu$(N−H), 1633 s $\nu$(C=N). $^1$H NMR spectrum in $CDCl_3$, $\delta$: 8.46 (t, 1H, −N*H*−), 6.68 (t, 1H, −NH=), 3.73 (m, 2H) and 2.94 (m, 1H) (C*H* and C*H*$_2$OH), 1.93 (q, 2H, C*H*$_2$ from Et), 1.36 (m, 2H, CH$_3$C*H*$_2$), 0.72 (t, 3H, C*H*$_3$), 0.37 (t, 3H, C*H*$_3$ from Et). $^{13}C\{^1H\}$ NMR spectrum in $CDCl_3$, $\delta$: 171.16 (C=N), 64.15 ($CH_2OH$), 61.01 ($CH_2$), 58.83 (CH), 26.49 ($CH_2$ from Et), 12.02 (CH$_3$*C*H$_2$), 10.98 ($CH_3$), 10.88 ($CH_3$ from Et).

**NH=C(Et)NHCH(Ph)CH$_2$OH (10).** ESI-MS (MeOH), *m*/*z*: 193 [M + H]$^+$. IR in KBr, selected bands, cm$^{-1}$: 3416 m−w $\nu$(O−H) and $\nu$(N−H), 1633 s $\nu$(C=N). $^1$H NMR spectrum in $CDCl_3$, $\delta$, 9.95 (s, br, 1H, −N*H*−), 7.90−7.45 (m, 5H, Ph, NH=), 4.96 (m, 1H, C*H*), 4.07−3.94 (m, 2H, C*H*$_2$NH−), 2.77−2.71 (m, 2H, C*H*$_2$ from Et), 1.21 (t, 3H, C*H*$_3$ from Et). $^{13}C\{^1H\}$ NMR spectrum in $CDCl_3$, $\delta$: 171.77 (C=N), 136.80 ($C_{ipso}$), 129.32 (*p*-Ph), 129.13 and 126.39 (*o*-Ph and *m*-Ph), 68.57 ($CH_2NH$), 64.07 (CH), 27.01 ($CH_2$ from Et), 10.56 ($CH_3$).

**Conversion of the Amidines into the Appropriate Oxazolines.** In a preparative experiment, zinc chloride (1 mg, 0.006 mmol) was added to a solution of the amidine (0.25 mmol) in $MeNO_2$ (2 mL) and the solution was refluxed for 4 h, whereupon the complete conversion (NMR yield of oxazolines is almost quantitative) of the amidine into the oxazoline was observed. A similar catalytic effect has been reached using anhydrous $MSO_4$ (M = Cu, Co, Cd), $CdCl_2$, and $AlCl_3$. In the blank experiment, i.e., without the added metal salt, no traces of the oxazoline were detected after 4 h, but the slow conversion is complete after 3 days of refluxing.

**N=C(Et)OCH$_2$CH$_2$ (11).** ESI-MS (MeOH), *m*/*z*: 100 [M + H]$^+$. TLC: $R_f$ = 0.42 [eluent is MeC(=O)OEt] which correspond to the $R_f$ value of N=C(Et)OCH$_2$CH$_2$ purchased from Aldrich. $^1$H NMR spectrum in $CDCl_3$ ($MeNO_2$) $\delta$: 3.82 (s, br, 2H, C*H*$_2$O), 2.69 (q, 2H, C*H*$_2$ from Et), 2.66 (m, 2H, C*H*$_2$N), 1.28 (t, 3H, C*H*$_3$). $^{13}C\{^1H\}$ NMR spectrum in $CDCl_3$ ($MeNO_2$) $\delta$: 173.28 (C=N), 44.85 ($CH_2O$) 35.02 ($CH_2N$), 20.69 ($CH_2$ from Et), 11.01 ($CH_3$).

**N=C(Et)OCH$_2$CH$_2$ (12).** ESI-MS (MeOH), *m*/*z*: 128 [M + H]$^+$. $^1$H NMR spectrum in $CDCl_3$ ($MeNO_2$) $\delta$: 3.98−3.51 (m, 2H, C*H*$_2$O), 2.64 (q, 2H, C*H*$_2$C=), 1.59 (m, 2H, CH$_3$C*H*$_2$CHN), 1.20 (t, 3H, C*H*$_3$CH$_2$C=), 0.87 (t, 3H, C*H*$_3$CH$_2$CH); the signal for C*H*N could not unequivocally be assigned. $^{13}C\{^1H\}$ NMR spectrum in $CDCl_3$ ($MeNO_2$) $\delta$: 172.30 (C=N), 49.9 ($CH_2O$), 28.05 (CH*C*H$_2$-CH$_3$), 21.26 (*C*H$_2$C=), 10.70 ($CH_3$), 9.29 (CHCH$_2$*C*H$_3$); the signal for *C*HN could not be unequivocally assigned.

**N=C(Et)OCH$_2$CH$_2$ (13).** ESI-MS (MeOH), *m*/*z*: 176 [M + H]$^+$. $^1$H NMR spectrum in $CDCl_3$ ($MeNO_2$) $\delta$: 3.83−3.64 (m, 2H, C*H*$_2$O), 2.69 (q, 2H, C*H*$_2$C=), 1.22 (t, 3H, C*H*$_3$CH$_2$C=); the C*H*N resonance overlaps with $CH_2$ signals from dppe and dppe oxides.

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**Supporting Information Available:** Tables S1−S21 listing crystallographic data, atomic coordinates, bond lengths and bond angles, anisotropic displacement parameters, hydrogen coordinates, isotropic displacement parameters, and hydrogen bonds for all structures. X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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