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Direct Addition of Alcohols to Organonitriles Activated by Ligation to a Platinum(IV) Center

Nadezhda A. Bokach,[†,‡] Vadim Yu. Kukushkin,*[,†] Maxim L. Kuznetsov,[‡] Dmitrii A. Garnovskii,[‡] Giovanni Natile,[§] and Armando J. L. Pombeiro*[,‡]

Department of Chemistry, St. Petersburg State University, 198904 Stary Petergof, Russian Federation, Centro de Química Estrutural, Complexo I, Instituto Superior Técnico, Av. Rovisco Pais, 1049-001 Lisbon, Portugal, and Dipartimento Farmaco-Chimico, University of Bari, via E. Orabona 4, I-70125 Bari, Italy

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Treatment of *trans*-$[PtCl_4(RCN)_2]$ (R = Me, Et) with R′OH (R′ = Me, Et, *n*-Pr, *i*-Pr, *n*-Bu) at 45 °C in all cases allowed the isolation of the *trans*-$[PtCl_4\{(E)\text{-}NH{=}C(R)OR'\}_2]$ imino ester complexes, while the reaction between *cis*-$[PtCl_4(RCN)_2]$ and the least sterically hindered alcohols (methanol and ethanol) results in the formation of *cis*-$[PtCl_4\{(E)\text{-}NH{=}C(R)OR'\}_2]$ (R/R′ = Me/Me) or *trans*-$[PtCl_4\{(E)\text{-}NH{=}C(Et)OR'\}_2]$ (R′ = Me, Et), the latter being formed via thermal isomerization (ROH, reflux, 3 h) of the initially formed corresponding cis isomers. The reaction between alcohols R′OH and *cis*-$[PtCl_4(RCN)_2]$ (R = Me, R′ = Et, *n*-Pr, *i*-Pr, *n*-Bu; R = Et; R′ = *n*-Pr, *i*-Pr, *n*-Bu), exhibiting greater R/R′ steric congestion, allowed the isolation of *cis*-$[PtCl_4\{(E)\text{-}NH{=}C(R)OR'\}\{(Z)\text{-}NH{=}C(R)\text{-}OR'\}]$ as the major products. The alcoholysis reactions of poorly soluble $[PtCl_4(RCN)_2]$ (R = CH_2Ph, Ph) performed under heterogeneous conditions, directly in the appropriate alcohol and for a prolonged time and, for R = Ph, with heating led to *trans*-$[PtCl_4\{(E)\text{-}NH{=}C(R)OR'\}_2]$ (R = CH_2Ph, R′ = Me, Et, *n*-Pr, *i*-Pr; R = Ph, R′ = Me) isolated in moderate yields. In all of the cases, in contrast to platinum(II) systems, addition of R′OH to the organonitrile platinum(IV) complexes occurs under mild conditions and does not require a base as a catalyst. The formed isomerically pure (imino ester)Pt(IV) complexes can be reduced selectively, by $Ph_3P{=}CHCO_2Me$, to the corresponding isomers of (imino ester)Pt(II) species, exhibiting antitumor activity, without change in configuration of the imino ester ligands. Furthemore, the imino esters NH=C(R)OR′ can be liberated from both platinum(IV) and platinum(II) complexes $[PtCl_n\{NH{=}C(R)OR'\}_2]$ (*n* = 2, 4) by reaction with 1,2-bis(diphenylphosphino)ethane and pyridine, respectively. All of the prepared compounds were characterized by elemental analyses (C, H, N), FAB mass spectrometry, IR, and ^1H, $^{13}C\{^1H\}$, and ^{195}Pt (metal complexes) NMR spectroscopies; the *E* and *Z* configurations of the imino ester ligands in solution were determined by observation of the nuclear Overhauser effect. X-ray structure determinations were performed for *trans*-$[PtCl_4\{(E)\text{-}NH{=}C(Me)OEt\}_2]$ (**2**), *trans*-$[PtCl_4\{(E)\text{-}NH{=}C(Et)\text{-}OEt\}_2]$ (**10**), *trans*-$[PtCl_4\{(E)\text{-}NH{=}C(Et)OPr\text{-}i\}_2]$ (**11**), *trans*-$[PtCl_4\{(E)\text{-}NH{=}C(Et)OPr\text{-}n\}_2]$ (**12**), and *cis*-$[PtCl_4\{(E)\text{-}NH{=}C(Et)OMe\}_2]$ (**14**). Ab initio calculations have shown that the *EE* isomers are the most stable ones for both platinum(II) and platinum(IV) complexes, whereas the most stable configurations for the *ZZ* isomers are less stable than the respective *EZ* isomers, indicating an increase of the stability on moving from the *ZZ* to the *EE* configurations which is more pronounced for the Pt(IV) complexes than for the Pt(II) species.

Introduction

It is commonly recognized in organic chemistry that organonitriles are intrinsic synthons for making C−O, C−S, and C−N bonds due to the addition of nucleophiles to the nitrile carbon, e.g., in the course of the Pinner[1,2] and thio-Pinner[3] reactions. Often such processes require *activation* of RCN toward the addition, either by an electron-acceptor

* Authors to whom correspondence should be addressed. E-mail: kukushkin@VK2100.spb.edu (V.Yu.K.); pombeiro@ist.utl.pt (A.J.L.P.).
† St. Petersburg State University.
‡ Instituto Superior Técnico.
§ University of Bari. E-mail: natile@farmchim.uniba.it.

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group R or by use of acids, for instance HX (X = Cl, Br),[1] which, by protonating the N atom, increase the electrophilicity of the adjacent carbon atom thus facilitating the reaction with nucleophiles. Instead of H^+, metal ions can be used in the addition reactions to enhance the reactivity of organonitriles, thus accomplishing the dream of organic chemists for smooth additions of nucleophiles to RCN molecules (especially those *inactivated* by electron-releasing R radicals). Many of these metal-mediated processes have been summarized in review articles on the subject.[4−6]

Our own investigation on the reactivity of coordinated organonitriles toward nucleophiles has so far been focused on couplings between platinum(IV) complexes of the type $[PtCl_4(RCN)_2]$ and oximes ($R^1R^2C{=}NOH$[7]), *vic*-dioximes [HON=(spacer)=NOH[8]], or dialkylhydroxylamines (R^1R^2-NOH[9]) which led to the formation of $[PtCl_4\{NH{=}C(R)ON{=}CR^1R^2\}_2]$, $[PtCl_4\{NH{=}C(R)ON{=}(spacer){=}NOH\})_2]$, and $[PtCl_4\{NH{=}C(R)ONR^1R^2\}_2]$, respectively. The latter reactions have also been extended to Re(IV)[10] and Rh(III)[11] organonitrile complexes. We also found that Ag^+ or Cu^{2+} ions catalyze the coupling of dialkylcyanamides with oximes at a platinum(II) center[12] and that nitrones of the type $O^-N^+(R^3){=}C(R^1)(R^2)$ can give [2 + 3] cycloaddition to the acetonitrile ligands in the complex $[PtCl_4(MeCN)_2]$ furnishing Δ^4-1,2,4-oxadiazoline complexes of the type $[PtCl_4\{N{=}C(Me)O{-}N(R^3){-}C(R^1)(R^2)\}_2]$ from which the heterocycles can be quantitatively liberated.[13] Finally, platinum-mediated coupling of ligated organonitriles and benzophenone imine can lead to coordinated 1,3-diaza-1,3-dienes.[14]

We have now focused our attention on the addition of alcohols to (organonitrile)Pt(IV) species leading to formation of imino ester complexes. Our aim was to clarify the effects of the oxidation state of the platinum center upon the coupling reaction by comparing our results with those already reported for appropriate platinum(II) systems.[15,16] Interest in the chemistry of platinum complexes with imino esters stems also from the discovery, by one of us, that some of these complexes break the rule of higher antitumor activity expected for cis than for trans isomers.[17] Moreover, we have recently found an efficient method[18] for the reduction of platinum(IV) complexes to the corresponding platinum(II) species, in nonaqueous media, and our idea was to extend the reduction to imino ester complexes and to verify if there could be any advantage in the preparation of biologically relevant (imino ester)Pt(II) compounds starting from the platinum(IV) rather than from the platinum(II) nitrile complexes.

We have found that, in contrast to platinum(II) systems, addition of R′OH to organonitrile platinum(IV) complexes occurs under mild conditions and does not require a base as a catalyst. The formed isomerically pure (imino ester)Pt(IV) complexes can be reduced selectively, by $Ph_3P{=}CHCO_2Me$, to the corresponding isomers of (imino ester)Pt(II) species without change in configuration of the imino ester ligands. Furthemore, the imino esters can be liberated from both platinum(IV) and platinum(II) complexes. All of these results, along with theoretical studies on relative stabilities

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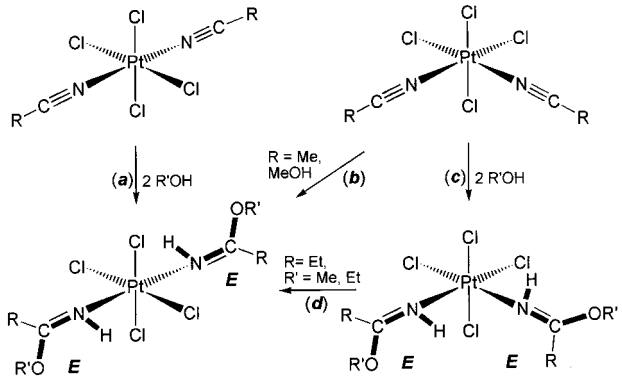
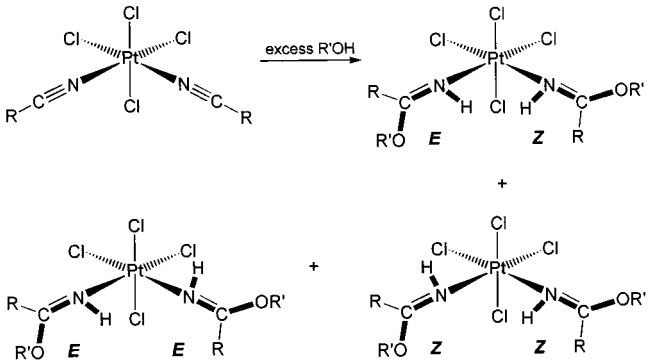
Scheme 1



Scheme 2



of the *E* and *Z* isomers of imino esters in platinum(II) and platinum(IV) complexes, are reported herein.

Results and Discussion

Nitrile-Alcohol Coupling Leading to (Imino ester)Pt-(IV) Complexes. We choose as starting materials for this study the nitrile compounds $[PtCl_4(RCN)_2]$ (R = Me, Et, CH_2Ph, Ph). The former two complexes were prepared either by chlorination of a mixture of the *cis*- and *trans*-$[PtCl_2(RCN)_2]$ isomers (ca. 5:1 for R = Me,[19] ca. 6:1 for R = Et[20]) giving a mixture of *cis/trans*-$[PtCl_4(RCN)_2]$ with almost the same isomeric ratio or by chlorination of the pure *trans*-$[PtCl_2(RCN)_2]$ isomers (R = Me,[19] Et[20]) to give the isomerically pure *trans*-$[PtCl_4(RCN)_2]$ complexes. The latter two materials were obtained as the pure *trans*-$[PtCl_4(PhCH_2CN)_2]$ isomer and as a mixture of the *cis/trans*-$[PtCl_4(PhCN)_2]$ isomers by chlorination of pure *trans*-$[PtCl_2(PhCH_2CN)_2]$[21] and of a mixture of *cis*- and *trans*-$[PtCl_2(PhCN)_2]$,[22] respectively.

(A) Reaction of R′OH with Pure *trans*-[PtCl$_4$(RCN)$_2$] and *cis*/*trans*-[PtCl$_4$(RCN)$_2$] (R = Me, Et). Treatment of *trans*-$[PtCl_4(RCN)_2]$ (R = Me, Et) with R′OH (R′ = Me, Et, *n*-Pr, *i*-Pr, *n*-Bu) at 45 °C in all cases allowed the isolation of *trans*-$[PtCl_4\{(E)\text{-}NH{=}C(R)OR'\}_2]$ complexes (route a in Scheme 1) which are stable both in solution ($CDCl_3$, 45 °C, 1 day) and in the solid state at room temperature. The reaction between *cis*-$[PtCl_4(RCN)_2]$ (which contains also some trans form, see above) and the least sterically hindered alcohols (methanol and ethanol) results in the formation of *trans*-$[PtCl_4\{(E)\text{-}NH{=}C(R)OR'\}_2]$ (R/R′ = Me/Me) (route b) or *trans*-$[PtCl_4\{(E)\text{-}NH{=}C(Et)OR'\}_2]$ (R′ = Me, Et) via thermal isomerization (ROH, reflux, 3 h) of the initially formed *cis*-$[PtCl_4\{(E)\text{-}NH{=}C(Et)OR'\}_2]$ (routes c−d).

The reaction between alcohols R′OH and *cis*-$[PtCl_4(RCN)_2]$ [R = Me, R′ = Et, *n*-Pr, *i*-Pr, *n*-Bu; R = Et; R′ = *n*-Pr, *i*-Pr, *n*-Bu], exhibiting greater R/R′ steric congestion, allowed the isolation of *cis*-$[PtCl_4\{(E)\text{-}NH{=}C(R)OR'\}\{(Z)\text{-}NH{=}C(R)OR'\}]$ (Scheme 2) as major products, whereas *cis*-$[PtCl_4\{(E)\text{-}NH{=}C(R)OR'\}_2]$ and *cis*-$[PtCl_4\{(Z)\text{-}NH{=}C(R)OR'\}_2]$ were only detected, by ^{1}H NMR spectroscopy, as minor byproducts.

The possibility of isomerization of the coordinated imino ester ligand was demonstrated by warming up of a $CDCl_3$ solution of pure *cis*-$[PtCl_4\{(E)\text{-}NH{=}C(R)OR'\}\{(Z)\text{-}NH{=}C(R)OR'\}]$ at 45 °C for 3−4 h. Formation of the other two isomers, i.e., *cis*-$[PtCl_4\{(E)\text{-}NH{=}C(R)OR'\}_2]$ (ca. 15−20%) and *cis*-$[PtCl_4\{(Z)\text{-}NH{=}C(R)OR'\}_2]$ (ca. 5−10%), was detected by NMR. However, on further heating this mixture is subject to overall degradation giving a large number of unidentified products.

All of the prepared compounds gave satisfactory elemental analyses and show good agreement between observed and calculated FAB mass spectra. Comparison of the IR spectra of the products with those of the starting materials indicates the disappearance of the C≡N stretching vibrations and the appearance of strong ν(C=N) vibrations in the range 1650−1629 cm^{-1}, a new medium-intensity band at ca. 1250 cm^{-1} [which might be assigned[23] to ν(C−O)], and N−H stretching vibrations which emerge in the range 3250−3360 cm^{-1}. In the $^{13}C\{^1H\}$ NMR spectra, the chemical shifts of the imino N=*C* carbon exhibit a relatively low variation (175.4−177.3 ppm) due to rather similar environments introduced by the OR′ substituents. The ^{195}Pt NMR resonances of the trans and cis isomers differ, by 140 ppm, with the cis isomer being at lower field. The same trend has been observed in the ^{195}Pt NMR spectra of the cis and trans isomers of other $[PtCl_4L_2]$ complexes.[8,24]

In *trans*-$[PtCl_4\{(E)\text{-}NH{=}C(Me)OR'\}_2]$, the *E* configuration of the imino ester ligands in solution was supported by the observation of the nuclear Overhauser effect (NOE) between the NH and the OCH_2 protons (OCH_3 protons for R′OH = MeOH). In *cis*-$[PtCl_4\{(E)\text{-}NH{=}C(Me)OR'\}\{(Z)\text{-}NH{=}C(Me)OR'\}]$, the imino ester ligands display two distinct sets of ^{1}H NMR signals of 1:1 intensity. For one ligand a NOE is observed between the protons of the NH and those of the CH_3 groups, while for the second ligand the NOE was between the NH and the OCH_2 protons (Figure

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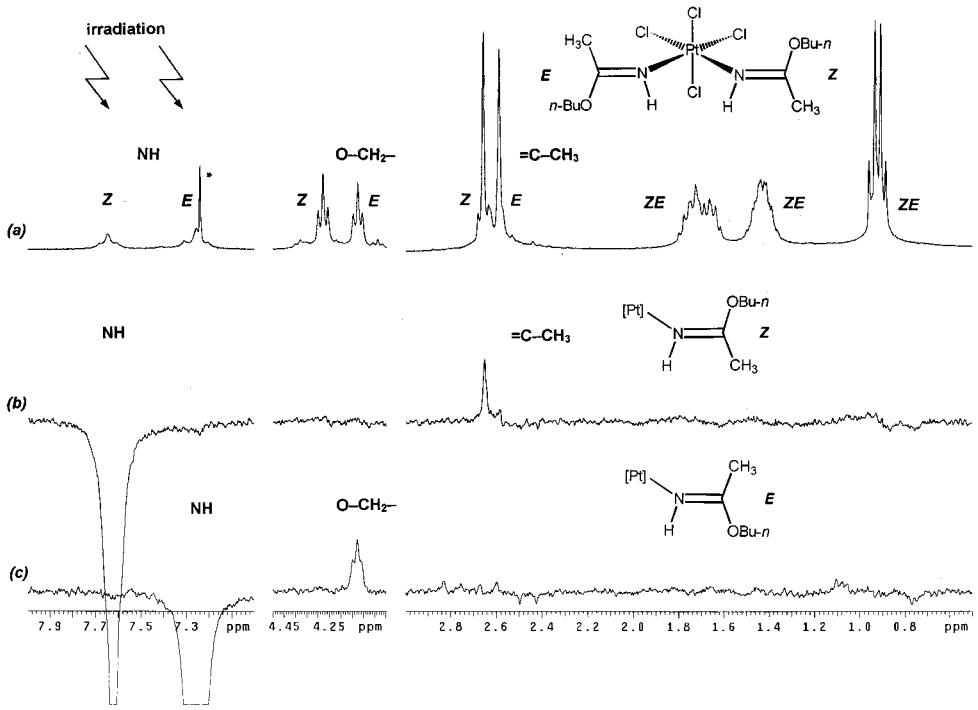

Figure 1. (a) ^{1}H NMR spectrum (in $CDCl_3$) of *cis*-[$PtCl_4${(*E*)-NH=C(Me)OBu-*n*}{(*Z*)-NH=C(Me)OBu-*n* }]; (*) $CHCl_3$. (b) NOE difference spectrum upon irradiation at the higher frequency NH (*Z* configuration). (c) NOE difference spectrum upon irradiation at the lower frequency NH (*E* configuration).

1, for complex with R′ = *n*-Bu), thus indicating that the imino ester ligands have the *Z* and *E* configurations, correspondingly. It is worthwhile to mention that only one approach providing the distinction between the *E* and *Z* configurations of ligated imino ester ligands *in solution* was known to date, i.e., it was reported[15] that the NH proton of the imino group in the *E* configuration was shifted to a higher field in comparison with that of the *Z* configuration. This estimate requires availability of both conformers, whereas the NOE experiment allows the determination of the configuration even when only one form is available. It is important to note that in the case of *cis*-[$PtCl_4${(*E*)-NH=C(Me)OR′}{(*Z*)-NH=C(Me)OR′}] both methods led to the same conclusions, although the difference in chemical shifts between *E* and *Z* configurations is lower for the platinum(IV) complexes (0.3−0.4 ppm; 0.1 ppm for R = Et) than for the platinum(II) compounds (0.6−0.7 ppm[15]).

(B) Reaction of R′OH with *trans*-[$PtCl_4(PhCH_2CN)_2$] and *cis*/*trans*-[$PtCl_4(PhCN)_2$]. The complexes [$PtCl_4(RCN)_2$] (R = CH_2Ph, Ph) exhibit poor solubility in the most common organic solvents. Hence, the alcoholysis reactions were performed under heterogeneous conditions, directly in the appropriate alcohol and for a prolonged time and, for R = Ph, with heating. As a consequence of such harsh conditions, (i) the imino ester complexes *trans*-[$PtCl_4${(*E*)-NH=C(R)OR′}$_2$] (R = CH_2Ph, R′ = Me, Et, *n*-Pr, *i*-Pr; R = Ph, R′ = Me) were isolated as solids in moderate yields, while a broad mixture of byproducts derived from uncontrolled hydrolysis and overall degradation of the starting materials and/or final products remains in solution; (ii) only the *trans-EE* form was detected. It is worthwhile to mention that, in the case of benzyl and phenyl cyanide complexes, the alcoholysis reaction failed with R′OH higher than propanol.

All experiments described in A and B along with literature data on platinum(II) complexes[15,16] indicate that the addition reaction strongly depends upon the oxidation state of the metal. In the case of higher oxidation state [platinum(IV) ion], the RCN−R′OH coupling does not require the use of a base which, instead, is required for the lower oxidation state [platinum(II) ion]. The alkoxylation of coordinated nitriles is dramatically affected by the electronic and steric properties of the alcohol. Indeed, the reaction proceeds smoothly with sterically unhindered R′OH, e.g., R′ = Me, Et, *n*-Pr, while it is less efficient with more sterically demanding alcohols, e.g., R′ = *i*-Pr or *n*-Bu, or does not proceed at all, e.g., *t*-Bu. Moreover, no RCN−R′OH coupling was observed with phenol or even phenolate in this study or in other works.[16a] Sterical hindrance of the R and R′ groups as well as the configuration of the starting complex (trans vs the more sterically encumbered cis form) affects greatly the stereochemistry of the addition reaction. Indeed, when steric factors are less important, the general trend is formation of the *trans-EE* form.

X-ray Structure Determinations of the (Imino ester)-Pt(IV) Complexes. X-ray structure determinations of [$PtCl_4${NH=C(Me)OEt}$_2$] (**2**), [$PtCl_4${NH=C(Et)OEt}$_2$] (**10**), [$PtCl_4${NH=C(Et)OPr-*i*}$_2$] (**11**), and [$PtCl_4${NH=C(Et)OPr-*n*}$_2$] (**12**) disclosed their overall trans configuration, while the imino ester ligands in [$PtCl_4${NH=C(Et)OMe}$_2$] (**14**) are mutually cis. The coordination polyhedra of the five complexes are slightly distorted octahedra (Figures 2−6).

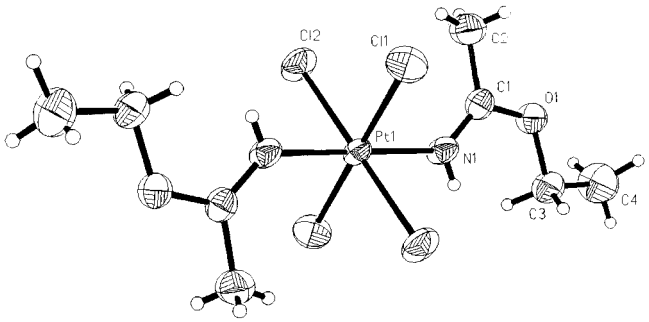

Figure 2. ORTEP drawing of **2** with atomic numbering scheme.

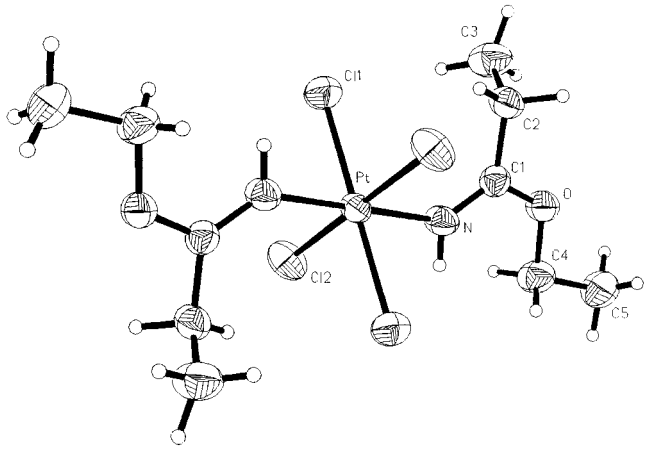

Figure 3. ORTEP drawing of **10** with atomic numbering scheme.

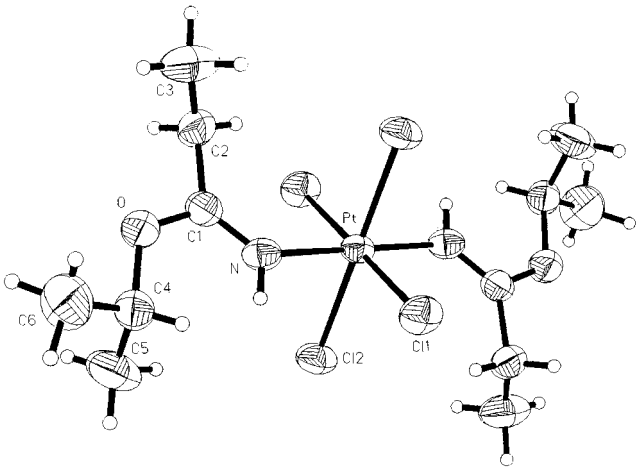

Figure 4. ORTEP drawing of **11** with atomic numbering scheme.

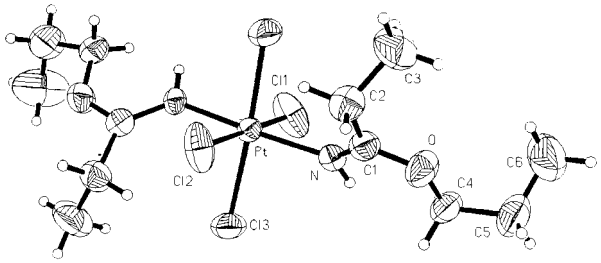

Figure 5. ORTEP drawing of **12** with atomic numbering scheme.

In general, the values of the Pt−Cl bond distances (2.31−2.32 Å) agree well with previously characterized platinum(IV) chloride compounds.[7,8,25] However, two noticeable differences should be pointed out: (i) in *cis*-[$PtCl_4${NH═C(Et)OMe}$_2$] (**14**), the Pt−Cl bonds trans to N atoms [2.299(2) and 2.301(2) Å] are shorter than the other two in mutually trans positions, 2.322(2) and 2.312(2) Å, and this allows the assumption of a higher ground state trans influence of Cl as compared to the imine (however, the difference is rather subtle and more similar structures are needed to support this assumption); (ii) in *trans*-[$PtCl_4${NH═C(Et)OPr-*n*}$_2$] (**12**), the Pt−Cl(2) bond [2.397(15) Å] is longer than the normal one, while the Pt−Cl(1) [2.228(15) Å] on the same coordinate is shorter than the average value for Pt^{IV}−Cl bonds. The deviation from the normal bond distances is probably due to an intermolecular hydrogen bond between the Cl(2) atom and the imine H atom from a neighboring molecule [N−H 0.88 Å, H···Cl(2) 2.86 Å, N···Cl(2) 3.732 Å; N−H···Cl(2) angle is 167°]. A similar trend in values of the Pt−Cl bond lengths, agreeable within 3σ with our results, was observed for [$PtCl_2(NH_3)_4$][C_4O_4], where one chloride involved in an intermolecular Cl···H−N−Pt hydrogen bond had a longer Pt−Cl bond distance [2.34(1) Å] while the chloride in the trans position had a rather short Pt−Cl distance [2.25(1) Å].[26]

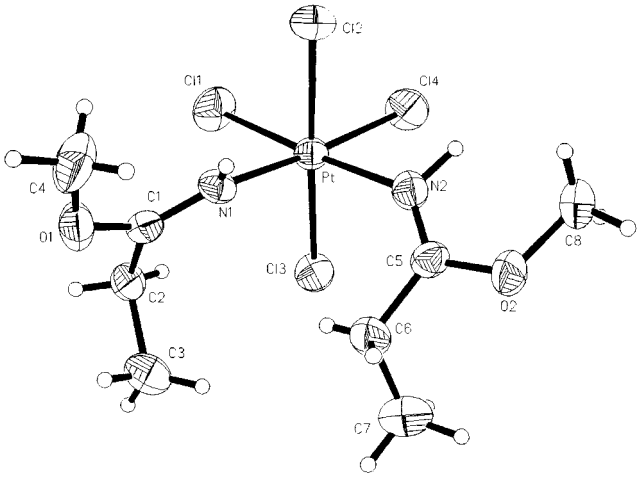

Figure 6. ORTEP drawing of **14** with atomic numbering scheme.

In all complexes, the imino ester ligands are in the *E* configuration. The N═C bond lengths all equal within 3σ and correspond to the mean values of the N═C double bonds in (imino ester)Pt(II) complexes[15,16] and also the N═C bonds in the previously characterized Pt(IV)-bound iminoacylated oximes.[7,8] All other bond distances and angles are normal and agree perfectly with the values already reported for imino ester complexes of platinum(II).[15,16]

Theoretical Studies. To the best of our knowledge to date there are two basic but *not coherent* reports on the stereochemistry of alcohol addition to coordinated nitriles. Thus, it was reported[27] that the methanol or ethanol additions to coordinated acetonitrile in the iridium(III) cationic complex [Cp*Ir(η^3-$CH_2CHCHPh$)(NCMe)](SO_3CF_3) (Cp* = η^5-C_5-

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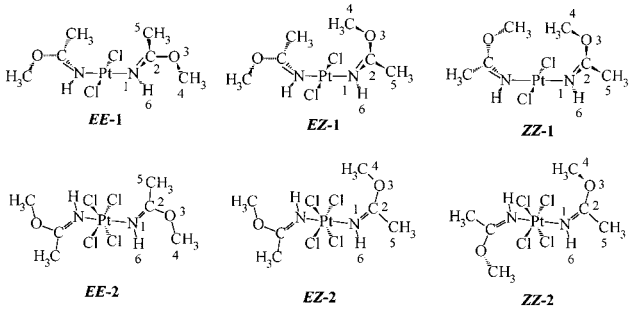

Figure 7. The *EE*, *EZ*, and *ZZ* conformations of the complexes *trans*-[$PtCl_2${NH═C(Me)OMe}$_2$] (**I**) and *trans*-[$PtCl_4${NH═C(Me)OMe}$_2$] (**II**) with numbering of selected atoms.

Me_5) proceed readily at room temperature to give mixtures of the *E* and *Z* isomers of [Cp*Ir(η^3-$CH_2CHCHPh$){NH═C(Me)OR′}]$^+$ (R′ = Me, Et). In the presence of the appropriate R′OH, the complete *E*-to-*Z* isomerization occurs and this direction is *opposite* to that found[15] for the platinum(II) complexes. Although in the current study we did not observe *E*−*Z* transformations, the synthetic experiments are more supportive of the idea that the *E* configuration in the platinum(IV) imino ester complexes is more stable than the *Z* configuration. In order to get a quantitative estimate of the relative stabilities of the *E* and *Z* isomers in both platinum(II) and platinum(IV) systems, a theoretical ab initio study was performed, and the results are described in this section.

Full geometry optimization of the *EE*, *EZ*, and *ZZ* isomers for the platinum(II) and platinum(IV) complexes *trans*-[$PtCl_2$-{NH═C(Me)OMe}$_2$] (***EE*-I**, ***EZ*-I**, and ***ZZ*-I**) and *trans*-[$PtCl_4${NH═C(Me)OMe}$_2$] (***EE*-II**, ***EZ*-II**, and ***ZZ*-II**) (Figure 7) at the HF level and the single-point calculations on the basis of the equilibrium Hartree−Fock geometries at the MP2//HF level of theory have been performed. The experimental X-ray structure was chosen as the starting geometry for ***EE*-I**,[15b] and the starting geometry for ***EE*-II** was selected on the basis of the X-ray structure of *trans*-[$PtCl_4${NH═C(Me)OEt}$_2$] (this work), whereas the initial geometries for the *EZ* and *ZZ* isomers were obtained by rotation of one or two {C(Me)OMe} fragments around the N═C bond.

The coordination polyhedra of the Pt atom are either square-planar or octahedral for **I** and **II**, respectively. The overall conformations of ***EE*-I** and ***EE*-II** obtained by the present calculations correspond to those observed in the X-ray experiments. One major difference between the calculated and the experimental parameters for ***EE*-I** is the dihedral angle between imino ester ligands which is greater in the theoretical model (79.2°) than in the X-ray structure (33.3°), while this angle decreases to 63.2° and 40.7° in the ***EZ*-I** and ***ZZ*-I** isomers, correspondingly. The analysis of the experimental X-ray data for ***EE*-I** indicates that the internuclear distances Cl···H−CH_2 between the chlorine atom and one of hydrogens of the methyl group is about 3 Å. For the theoretical equilibrium structure of ***EE*-I**, this distance remains also of ca. 2.96 Å. Thus, taking into account the overestimate of the Pt−Cl bond lengths at the HF level in comparison with experimental values, the imino esters are forced to be more inclined over the coordination plane in order to keep the Cl···H distance short. It is worthwhile to note that the total energy of the system depends on this dihedral angle rather weakly. For ***EE*-II**, both NH═C(C)-OC fragments are coplanar and their plane bisects the Pt−Cl bond angles. In the most stable conformations of both *EZ* and *ZZ* structures, the methoxy group(s) in *Z* position is (are) turned toward the Pt or Cl atoms; the other conformations formed by rotation of the OCH_3 group(s) around the C(2)O bond are less stable and are not discussed further.

The Pt−Cl and Pt−N bond lengths of ***EE*-I** and ***EE*-II** are overestimated in comparison with the experimental values, and the difference is more significant for the Pt(II) complex (Table 7). The calculated N−H distance is, by 0.08 Å, shorter than the experimental value for ***EE*-I** and, by 0.27 Å, longer than that for ***EE*-II** most likely as a consequence of the inaccurate localization of hydrogen atoms by X-ray methods[28] particularly in the case of ***EE*-II**. All other calculated bond lengths are in good agreement with the experimental data, and the maximum deviations do not exceed 0.04 Å for ***EE*-I** and 0.02 Å for ***EE*-II**. Bond lengths and angles within the imino ester are only slightly affected by change in the oxidation state of the platinum center (similar values are found for both **I** and **II**).

Both the HF and the MP2 calculations have shown that the *EE* isomers are the most stable ones for both types of complexes, i.e., four-coordinate platinum(II) (**I**) and six-coordinate platinum(IV) (**II**). The most stable configurations for the *EZ* isomers are less stable than those for the corresponding *EE* isomers by 1.58 kcal/mol (HF) and 0.45 kcal/mol (MP2) for **I** or by 7.37 kcal/mol (HF) and 6.69 kcal/mol (MP2) for **II** (Table 8). In turn, the most stable configurations for the *ZZ* isomers are less stable than the respective *EZ* isomers by 2.39 kcal/mol (HF) and 1.31 kcal/mol (MP2) for **I** or by 7.04 kcal/mol (HF) and 6.33 kcal/mol (MP2) for **II**, therefore indicating (i) the increase of the stability on moving from the *ZZ* to the *EE* configurations and (ii) the greater difference in energy for the Pt(IV) complexes than for the Pt(II) species.

Thus, the theoretical study indicates that the *E* configuration of the imino ester ligand is more stable in comparison with the *Z* form, and this agrees well with previous experimental results on the *Z*-to-*E* transformation in imino ester[15] and amidine[29] platinum(II) complexes. It is obvious, however, that the conclusion cannot be extrapolated to other metals (namely, to the above-mentioned Ir system[18]) and that more examples of *E*/*Z* addition/transformation at different metal centers should be investigated before making a general conclusion.

Reduction of (Imino ester)Pt(IV) Complexes. We recently reported on an efficient method for generation of (imine)Pt(II) compounds that involves reduction of the corresponding Pt(IV)-based imines by carbonyl-stabilized phosphorus ylides, Ph_3P═$CHCO_2R$, in nonaqueous media.[18] It was also anticipated in a previous section that the facile

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Table 1. Crystal Data and Structure Refinement for *trans*-[$PtCl_4${NH=C(Me)OEt}$_2$] (**2**), *trans*-[$PtCl_4${NH=C(Et)OEt}$_2$] (**10**), *trans*-[$PtCl_4${NH=C(Et)OPr-*i*}$_2$] (**11**), *trans*-[$PtCl_4${NH=C(Et)OPr-*n*}$_2$] (**12**), and *cis*-[$PtCl_4${NH=C(Et)OMe}$_2$] (**14**)

	2	**10**	**11**	**12**	**14**
empirical formula	$C_8H_{18}N_2Cl_4O_2Pt$	$C_{10}H_{22}N_2Cl_4O_2Pt$	$C_{12}H_{26}N_2Cl_4O_2Pt$	$C_{12}H_{26}N_2Cl_4O_2Pt$	$C_8H_{18}N_2Cl_4O_2Pt$
fw	511.12	539.18	567.23	567.23	511.12
space group	monoclinic	monoclinic	triclinic	monoclinic	orthorhombic
cryst syst	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$C2$ (No. 5)	$P2_12_12_1$ (No. 19)
a, Å	6.5900(10)	8.701(2)	6.325(10)	8.8090(10)	8.839(2)
b, Å	13.268(3)	7.739(2)	8.1800(10)	8.950(2)	11.655(2)
c, Å	9.562(2)	13.920(3)	10.7290(10)	12.855(3)	15.626(3)
α, deg	90	90	98.420(10)	90	90
β, deg	103.72(3)	108.19(3)	104.790(10)	99.16(2)	90
γ, deg	90	90	104.130(10)	90	90
V, Å^3	812.2(3)	539.18(4)	507.41(12)	1000.6(3)	1609.8(6)
Z	2	2	1	2	4
D_c, Mg/m^3	2.090	2.011	1.856	1.883	2.109
F(000)	484	516	274	548	968
μ(Mo Kα), mm^{-1}	9.288	8.477	7.444	7.550	9.373
$2\theta_{max}$, deg	51.94	51.98	49.94	51.94	49.96
refinement method					full-matrix[a] least squares on F^2
cryst size, mm	0.22 × 0.26 × 0.44	0.18 × 0.20 × 0.56	0.06 × 0.17 × 0.40	0.06 × 0.30 × 0.32	0.10 × 0.26 × 0.28
index ranges	$0 < h < 8$, $0 < k < 16$, $-11 < l < 11$	$0 < h < 10$, $0 < k < 9$, $-17 < l < 16$	$0 < h < 7$, $-9 < k < 9$, $-12 < l < 12$	$0 < h < 10$, $0 < k < 10$, $-15 < l < 15$	$0 < h < 10$, $0 < k < 13$, $0 < l < 18$
collected reflns	1215	1307	1886	1076	1265
unique reflns [$F(hkl) \geq 4\sigma(F)$]	1120	1229	1715	1009	1265
refinement params	116	133	149	97	155
extinction coeff	0.0246(13)	0.0010(4)		0.0005(5)	0.00030(14)
GOF	1.036	1.086	1.095	1.086	1.057
R	0.0239	0.0198	0.0207	0.0326	0.0184
R_w	0.0604	0.0489	0.0504	0.0816	0.0444

[a] Anisotropic for all non-H atoms.

Table 2. Bond Lengths (Å) and Angles (deg) for *trans*-[$PtCl_4${NH=C(Me)OEt}$_2$] (**2**)[a]

Pt(1)−Cl(1)	2.3133(16)	O(1)−C(3)	1.459(8)
Pt(1)−Cl(2)	2.3121(14)	N(1)−C(1)	1.282(8)
Pt(1)−N(1)	2.018(5)	C(1)−C(2)	1.482(9)
O(1)−C(1)	1.319(7)	C(3)−C(4)	1.489(12)

Cl(1)−Pt(1)−Cl(2)	90.49(6)	N(1)−Pt(1)−N(1)#	180.00
Cl(1)−Pt(1)−N(1)	93.67(14)	Cl(1)#−Pt(1)−Cl(2)#	90.49(6)
Cl(1)−Pt(1)−Cl(1)#	180.00	Cl(1)#−Pt(1)−N(1)#	93.67(14)
Cl(1)−Pt(1)−Cl(2)#	89.51(6)	Cl(2)#−Pt(1)−N(1)#	95.43(16)
Cl(1)−Pt(1)−N(1)#	86.33(14)	C(1)−O(1)−C(3)	120.1(4)
Cl(2)−Pt(1)−N(1)	95.43(16)	Pt(1)−N(1)−C(1)	135.7(4)
Cl(1)#−Pt(1)−Cl(2)	89.51(6)	O(1)−C(1)−N(1)	123.5(4)
Cl(2)−Pt(1)−Cl(2)#	180.00	O(1)−C(1)−C(2)	111.4(6)
Cl(2)−Pt(1)−N(1)#	84.57(16)	N(1)−C(1)−C(2)	25.1(6)
Cl(1)#−Pt(1)−N(1)	86.33(14)	O(1)−C(3)−C(4)	106.3(6)
Cl(2)#−Pt(1)−N(1)	84.57(16)		

[a] Symmetry transformations used to generate equivalent atoms: (#) $-x + 1, -y + 1, -z + 1$.

Table 3. Bond Lengths (Å) and Angles (deg) for *trans*-[$PtCl_4${NH=C(Et)OEt}$_2$] (**10**)[a]

Pt−Cl(1)	2.3144(13)	N−C(1)	1.287(6)
Pt−Cl(2)	2.3120(14)	C(1)−C(2)	1.485(6)
Pt−N	2.021(3)	C(2)−C(3)	1.515(7)
O−C(1)	1.313(5)	C(4)−C(5)	1.499(9)
O−C(4)	1.451(6)		

Cl(1)−Pt−Cl(2)	88.88(5)	N−Pt−N#	180.00
Cl(1)−Pt−N	94.77(12)	Cl(1)−Pt−Cl(2)#	88.88(5)
Cl(1)−Pt−Cl(1)#	180.00	Cl(1)#−Pt−N#	94.77(12)
Cl(1)−Pt−Cl(2)#	91.12(5)	Cl(2)#−Pt−N#	85.99(11)
Cl(1)−Pt−N#	85.23(12)	C(1)−O−C(4)	120.5(4)
Cl(2)−Pt−N	85.99(11)	Pt−N−C(1)	135.1(3)
Cl(1)#−Pt−Cl(2)	91.12(5)	O−C(1)−C(2)	112.1(4)
Cl(2)−Pt−Cl(2)#	180.00	O−C(1)−N	122.0(4)
Cl(2)−Pt−N#	94.01(11)	N−C(1)−C(2)	125.9(4)
Cl(1)#−Pt−N	85.23(12)	C(1)−C(2)−C(3)	111.5(4)
Cl(2)#−Pt−N	94.01(11)	O−C(4)−C(5)	107.2(5)

[a] Symmetry transformations used to generate equivalent atoms: (#) $-x + 1, -y + 1, -z + 1$.

reduction of isomerically pure (imino ester)Pt(IV) compounds with the ylides could open up an alternative route to isomerically pure (imino ester)Pt(II) complexes which, in some instances, exhibit antitumor activity.[17] The reduction was exemplified for *trans*-[$PtCl_4${(*E*)-NH=C(Me)OR′}$_2$] (R′ = Me, Et) and *cis*-[$PtCl_4${(*E*)-NH=C(Me)OEt}{(*Z*)-NH=C(Me)OEt}], and, in accord with our expectations, it proceeds rapidly and under mild conditions with 1 equiv of the ylide Ph_3P=$CHCO_2Me$ to form *selectively* the platinum(II) products without change in the complex geometry (cis/trans) and ligand configuration (*E*/*Z*) and without further reduction of the platinum center (Scheme 3). The reaction products were purified by column chromatography and obtained in ca. 50% isolated yield.

General features of the IR, ^{1}H NMR, and ^{13}C{^{1}H} NMR spectra of *trans*-[$PtCl_2${(*E*)-NH=C(Me)OR′}$_2$] (R′ = Me, Et) are similar to those observed for the appropriate platinum(IV) complexes. The trans configuration of the complexes was confirmed by measuring their far-IR spectra, which display only one band of the ν(Pt−Cl) stretching vibration characteristic for this geometry.[30] In the ^{1}H NMR spectra of the platinum(II) complexes, a NOE was observed between the NH and OCH_3 or OCH_2CH_3 protons, thus indicating that the *E* configuration persists after the reduction. The most

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Table 4. Bond Lengths (Å) and Angles (deg) for *trans*-[$PtCl_4${NH=C(Et)OPr-*i*}$_2$] (**11**)[a]

Pt−Cl(1)	2.3128(12)	N−C(1)	1.272(5)
Pt−Cl(2)	2.3191(12)	C(1)−C(2)	1.489(7)
Pt−N	2.022(3)	C(2)−C(3)	1.504(10)
O−C(1)	1.321(6)	C(4)−C(5)	1.503(9)
O−C(4)	1.467(6)	C(4)−C(6)	1.499(10)
Cl(1)−Pt−Cl(2)	90.98(4)	Cl(1)#−Pt−Cl(2)#	90.98(4)
Cl(1)−Pt−N	84.70(10)	Cl(1)−Pt−N#	84.70(10)
Cl(1)−Pt−Cl(1)#	180.00	Cl(2)#−Pt−N#	86.04(10)
Cl(1)−Pt−Cl(2)#	89.02(4)	C(1)−O−C(4)	121.6(3)
Cl(1)−Pt−N#	95.30(10)	Pt−N−C(1)	136.5(3)
Cl(2)−Pt−N	86.04(10)	N−C(1)−C(2)	125.3(4)
Cl(1)#−Pt−Cl(2)	89.02(4)	O−C(1)−N	123.0(4)
Cl(2)−Pt−Cl(2)#	180.00	O−C(1)−C(2)	111.7(4)
Cl(2)−Pt−N#	93.96(10)	C(1)−C(2)−C(3)	112.5(5)
Cl(1)#−Pt−N	95.30(10)	C(5)−C(4)−C(6)	114.4(5)
Cl(2)#−Pt−N	93.96(10)	O−C(4)−C(5)	110.0(5)
N−Pt−N#	180.00	O−C(4)−C(6)	105.0(5)

[a] Symmetry transformations used to generate equivalent atoms: (#) $-x, -y, -z$.

Table 5. Bond Lengths (Å) and Angles (deg) for *trans*-[$PtCl_4${NH=C(Et)OPr-*n*}$_2$] (**12**)[a]

Pt−Cl(1)	2.228(15)	N−C(1)	1.34(2)
Pt−Cl(2)	2.397(15)	C(1)−C(2)	1.503(19)
Pt−Cl(3)	2.300(3)	C(2)−C(3)	1.52(2)
Pt−N	2.039(9)	C(4)−C(5)	1.49(3)
O−C(1)	1.317(15)	C(5)−C(6)	1.46(4)
O−C(4)	1.42(2)		
Cl(1)−Pt−Cl(2)	180(3)	Cl(3)−Pt−N	92.8(3)
Cl(1)−Pt−Cl(3)	93.6(4)	N−Pt−N#	172.4(14)
Cl(1)−Pt−N	86.2(10)	Cl(3)#−Pt−N#	87.6(3)
Cl(1)−Pt−Cl(3)#	93.6(4)	C(1)−O−C(4)	121.9(12)
Cl(1)−Pt−N#	86.2(10)	Pt−N−C(1)	129.4(17)
Cl(2)−Pt−Cl(3)	86.4(4)	O−C(1)−C(2)	111.6(11)
Cl(2)−Pt−N	93.8(10)	N−C(1)−C(2)	128.9(13)
Cl(2)−Pt−Cl3#	86.4(4)	O−C(1)−N	119.4(14)
Cl(2)−Pt−N#	93.8(10)	C(1)−C(2)−C(3)	111.7(14)
Cl(3)−Pt−N	87.6(3)	O−C(4)−C(5)	107.5(14)
Cl(3)−Pt−Cl(3)#	172.9(6)	C(4)−C5−C(6)	112.3(18)
Cl(3)−Pt−N#	92.8(3)		

[a] Symmetry transformations used to generate equivalent atoms: (#) $-x, y, -z + 1$.

significant spectroscopic difference between *trans*-[$PtCl_2$-{(*E*)-NH=C(Me)OR′}$_2$] and the appropriate platinum(IV) complexes is provided by their ^{195}Pt NMR spectra, which show the disappearance of the Pt(IV) signals at −176 (R′ = Me) and −158 (R′ = Et) ppm, while new resonances emerge at −1914 and −1910 ppm, respectively. We also reduced *cis*-[$PtCl_4${(*E*)-NH=C(Me)OEt}{(*Z*)-NH=C(Me)OEt}] (^{195}Pt NMR, δ: 14) to give the corresponding platinum(II) complex (^{195}Pt NMR, δ: −1953). The platinum(II) complex *cis*-[$PtCl_2$-{(*E*)-NH=C(Me)OEt}{(*Z*)-NH=C(Me)OEt}] shows two Pt−Cl stretching bands in the IR spectrum, specific for the cis arrangement of the Cl ligands about the Pt(II) center.[30] The NOE experiment also proved that the imino ester ligands have different configurations. Moreower, the N*H* proton resonance of the imino group in the *E* configuration occurs at a higher field than that of the *Z* configuration as observed for the Pt(IV) complexes and in accord with a previous report.[15]

Liberation of the Imino Ester Ligands. Our studies on platinum-mediated reactions of organonitriles show that the reactivity of (organonitrile)Pt(IV) complexes, in many instances, is higher than that of the corresponding platinum(II) species and the addition reactions in the former case proceed under milder conditions. This implies that the platinum(IV) center can be employed as a template for metal-mediated reactions that are not feasible in pure organic chemistry or with the use of the platinum(II) complexes. After the platinum(IV)-mediated transformation has taken place, the newly formed ligands can be liberated to give free

Table 6. Bond Lengths (Å) and Angles (deg) for *cis*-[$PtCl_4${NH=C(Et)OMe}$_2$] (**14**)

Pt−Cl(1)	2.299(2)	O(2)−C(5)	1.308(9)
Pt−Cl(2)	2.322(2)	O(2)−C(8)	1.453(11)
Pt−Cl(3)	2.312(2)	N(1)−C(1)	1.291(10)
Pt−Cl(4)	2.301(2)	N(2)−C(5)	1.286(10)
Pt−N(1)	2.038(6)	C(1)−C(2)	1.492(12)
Pt−N(2)	2.039(6)	C(2)−C(3)	1.539(13)
O(1)−C(1)	1.326(10)	C(5)−C(6)	1.486(11)
O(1)−C(4)	1.441(11)	C(6)−C(7)	1.505(14)
Cl(1)−Pt−Cl(2)	91.03(9)	N(1)−Pt−N(2)	94.1(3)
Cl(1)−Pt−Cl(3)	90.82(8)	C(1)−O(1)−C(4)	119.8(7)
Cl(1)−Pt−Cl(4)	91.35(9)	C(5)−O(2)−C(8)	118.9(6)
Cl(1)−Pt−N(1)	88.7(2)	Pt−N(1)−C(1)	134.6(5)
Cl(1)−Pt−N(2)	176.38(19)	Pt−N(2)−C(5)	135.4(5)
Cl(2)−Pt−Cl(3)	177.77(8)	O(1)−C(1)−N(1)	123.1(7)
Cl(2)−Pt−Cl(4)	90.39(8)	O(1)−C(1)−C(2)	111.7(7)
Cl(2)−Pt−N(1)	84.57(18)	N(1)−C(1)−C(2)	125.1(7)
Cl(2)−Pt−N(2)	86.99(18)	C(1)−C(2)−C(3)	112.2(7)
Cl(3)−Pt−Cl(4)	88.31(8)	O(2)−C(5)−C(6)	111.3(6)
Cl(3)−Pt−N(1)	96.72(18)	N(2)−C(5)−C(6)	125.5(7)
Cl(3)−Pt−N(2)	91.10(17)	O(2)−C(5)−N(2)	123.2(7)
Cl(4)−Pt−N(1)	174.97(18)	C(5)−C(6)−C(7)	112.9(7)
Cl(4)−Pt−N(2)	85.64(18)		

Table 7. Calculated (Selected) Bond Lengths (Å) for the Complexes *trans*-[$PtCl_2${NH=C(Me)OMe}$_2$] (**I**) and *trans*-[$PtCl_4${NH=C(Me)-OMe}$_2$] (**II**) and, for Comparison, Experimental Values for Selected Complexes

	***EE*-I** theor	***EZ*-I**	***ZZ*-I**	***EE*-I** exptl[a]
Pt−Cl	2.387	2.381, 2.391	2.384	2.299, 2.300
Pt−N	2.066	2.066, 2.070	2.071	1.989, 2.009
C=N	1.273	1.274	1.274	1.295, 1.306
C−C	1.488	1.488, 1.497	1.497	1.503, 1.518
C(2)O	1.345	1.345, 1.325	1.326	1.306, 1.314
C(4)O	1.444	1.444, 1.454	1.451	1.412, 1.456
NH	1.000	1.000, 0.998	0.999	1.080, 1.081

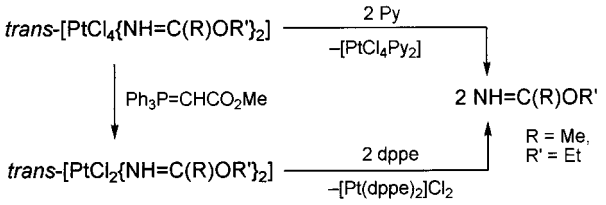
	***EE*-II**	***EZ*-II**	***ZZ*-II**	$[PtCl_4${NH=C(Me)OEt}$_2]$[b]
Pt−Cl	2.360	2.357−2.363	2.360−2.361	2.312−2.313
Pt−N	2.045	2.043, 2.064	2.059	2.018, 2.019
C=N	1.279	1.279, 1.285	1.285	1.283
C−C	1.487	1.487, 1.503	1.503	1.482
C(2)O	1.339	1.339, 1.311	1.312	1.319
C(4)O	1.449	1.449, 1.463	1.465	1.459
NH	0.999	0.999	0.999	0.730

[a] Reference 15b. [b] This work (*EE* isomer).

Table 8. Total Energies, E_{tot} (Hartree), and Relative Energies, E_{rel} (kcal/mol), of the Most Stable Conformations of the *EE*, *EZ*, and *ZZ* Isomers of Complexes **I** and **II**

	HF//HF		MP2//HF	
	E_{tot}	E_{rel}	E_{tot}	E_{rel}
***EE*-I**	−1531.262980	0.0	−1532.654603	0.0
***EZ*-I**	−1531.260466	+1.58	−1532.653886	+0.45
***ZZ*-I**	−1531.256655	+3.97	−1532.651802	+1.76
***EE*-II**	−2450.185206	0.0	−2451.913625	0.0
***EZ*-II**	−2450.173464	+7.37	−2451.902968	+6.69
***ZZ*-II**	−2450.162240	+14.41	−2451.892884	+13.02

Scheme 3



organic material. Since imino esters are useful synthons for many organic transformations[1,2] and their formation easily occurs at the Pt(IV) center, we attempted to find an efficient route for the release of the NH=C(R)OR′ species from the coordination sphere. *trans*-[$PtCl_n${(*E*)-NH=C(Me)OEt}$_2$] (*n* = 2, 4) were taken as reference compounds, and two pathways for the liberation (Scheme 3) were explored, i.e., (i) displacement, by pyridine, of the imino ester in the platinum(IV) complex, and (ii) substitution with 1,2-bis(diphenylphosphino)ethane, dppe, in the platinum(II) compound. In both cases the substitution results in precipitation of highly insoluble metal complexes which can be removed, by filtration, from the solution containing the free imino ester NH=C(Me)OEt.

Final Remarks. Imino esters are useful synthetic intermediates in organic chemistry,[1,2] but, in the vast majority of cases, their utilization involves the free HN=C(R)OR′ rather than its much more accessible hydrochloride, HN=C(R)OR′·HCl. Careful neutralization of HCl in *nonaqueous* media is sometimes difficult especially when the synthesis is performed on a micro scale. Moreover, some products of the neutralization reaction, e.g., H_2O, can interfere with the subsequent transformations. Similarly to protonation, coordination to a metal center makes imino esters quite stable, and they can be stored in this form for a prolonged time. When required, their liberation can be performed in an easier way than starting from the hydrochlorides. If the replacement is carried out in nonaqueous dried solvents and the formed complex precipitates from solution and is removed by filtration (as in the present work), the liberated imino esters, stable under anhydrous conditions retained in the filtrate, can be used in situ for further transformations.

Imino esters are much better ligands for *soft* metal centers than nitriles. Hence, the high stability of the imino ester complexes of the platinum group metals, which is a useful property for stoichiometric reactions, prevents, however, their usage in catalytic processes, and only one catalytic reaction of this kind has been reported so far.[27] We assume that further progress in the search of catalytic processes for the metal-mediated conversion of nitriles to imino esters could well be connected with the application of *hard* metal centers, where the stability of the imino ester species formed should be lower and therefore could lead to catalysis.

Experimental Section

Materials and Instrumentation. Solvents were obtained from commercial sources and used as received. [$PtCl_4(RCN)_2$] (R = Me, Et, CH_2Ph, Ph) were prepared according to the published method.[7] C, H, and N elemental analyses were carried out by the Microanalytical Service of the Instituto Superior Técnico. Melting points were determined on a Kofler table. For TLC, Merck UV 254 SiO_2 plates were used. Positive-ion FAB mass spectra were obtained on a Trio 2000 instrument by bombarding 3-nitrobenzyl alcohol (NBA) matrixes of the samples with 8 keV (ca. 1.28×10^{15} J) Xe atoms. Mass calibration for data system acquisition was achieved using CsI. Infrared spectra (4000−400 cm^{-1}) were recorded on a BIO-RAD FTS 3000MX instrument in KBr pellets. ^{1}H, ^{13}C{^{1}H}, and ^{195}Pt NMR spectra were measured on Varian UNITY 300 and Bruker AMX 300 spectrometers 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.

Synthetic Work and Characterization. Reactions of [$PtCl_4$(MeCN)$_2$] with Alcohols. A suspension of *trans*-[$PtCl_4(MeCN)_2$] (0.08 g, 0.2 mmol) is heated at 45 °C in methanol, ethanol, or *n*-PrOH (5 mL) for 36 h (R = Me) or 3 day (R = Et, *n*-Pr), whereupon the new precipitate formed is filtered off, washed with three 5-mL portions of diethyl ether, and dried in air at room temperature. In the case of *i*-PrOH and *n*-BuOH the reaction is performed in a mixture of dichloromethane (5 mL) and the alcohol (0.10−0.15 mL).

A suspension of *cis*-[$PtCl_4(MeCN)_2$] (0.08 g, 0.2 mmol; the complex contains ca. 20% of the trans isomer) is heated at 45 °C in methanol or ethanol (2 mL) for 36 h (R = Me) or 3 days (R = Et), whereupon the new precipitate formed is filtered off, washed with three 5-mL portions of diethyl ether, dried in air at room temperature, and then recrystallized from CH_2Cl_2/Et_2O at room temperature. In the case of *n*-PrOH and *n*-BuOH, the reaction is performed in a mixture of dichloromethane (2 mL) and the alcohol (0.1 mL) for 3 days, whereupon solvents are evaporated under flow of dinitrogen and the yellow residues are washed with Et_2O (three 2-mL portions), dissolved at 20−25 °C in a minimum amount of CH_2Cl_2, and then purified on silica gel by column chromatography.

***trans*-[$PtCl_4${(*E*)-NH=C(Me)OMe}$_2$] (1).** Yield: 72%. Anal. Calcd for $C_6H_{14}N_2Cl_4O_2Pt$: C, 14.90; H, 2.89; N, 5.79. Found: C, 14.53; H, 2.65; N, 5.52. FAB$^+$-MS, *m*/*z*: 475 [M − Cl]$^+$, 440 [M − 2Cl]$^+$. TLC, $R_f = 0.68$ (eluent CH_2Cl_2). IR spectrum in KBr, selected bands, cm^{-1}: 3250 m−w ν(N−H), 1650 s ν(C=N), 1258 m ν(C−O). ^{1}H NMR in $CDCl_3$, δ: 2.75 (s + d, $^4J_{PtH}$ 2.8 Hz, 3*H*, =C*Me*O), 3.99 (s, 3*H*, OMe), 6.90 (s, br, 1*H*, NH). ^{13}C{^{1}H} NMR in $CDCl_3$, δ: 20.1 (=C*Me*O), 55.0 (OMe), 177.5 (C=NH). ^{195}Pt NMR in $CDCl_3$, δ: −176 (450 Hz).

***trans*-[$PtCl_4${(*E*)-NH=C(Me)OEt}$_2$] (2).** Yield: 65%. Anal. Calcd for $C_8H_{18}N_2Cl_4O_2Pt$: C, 18.78; H, 3.52; N, 5.47. Found: C, 18.85; H, 3.31; N, 5.31. FAB$^+$-MS, *m*/*z*: 482 [M]$^+$, 412 [M − 2Cl]$^+$. TLC, $R_f = 0.64$ (eluent CH_2Cl_2). IR spectrum in KBr, selected bands, cm^{-1}: 3358 m−w ν(N−H), 1629 s ν(C=N), 1251 m ν(C−O). ^{1}H NMR in $CDCl_3$, δ: 1.49 (t, 7.0 Hz, 3*H*, CH_3 from Et), 2.73 (s + d, $^4J_{PtH}$ 3.5 Hz, 3*H*, =C*Me*O), 4.24 (quart., 7.0 Hz, 2*H*, CH_2 from Et), 6.78 (s, br, 1*H*, NH). ^{13}C{^{1}H} NMR in $CDCl_3$, δ: 13.5 (CH_3 from Et), 20.3 (=C(*Me*)O), 64.7 (CH_2 from Et), 176.5 (C=NH). ^{195}Pt NMR in $CDCl_3$, δ: −158 (650 Hz).

***trans*-[$PtCl_4${(*E*)-NH=C(Me)OPr-*i*}$_2$] (3).** Yield: 39%. Anal. Calcd for $C_{10}H_{22}N_2Cl_4O_2Pt$: C, 22.26; H, 4.08; N, 5.19. Found: C, 21.93; H, 4.14; N, 5.03. FAB$^+$-MS, *m*/*z*: 468 [M − 2Cl]$^+$. TLC, $R_f = 0.61$ (eluent CH_2Cl_2). IR spectrum in KBr, selected bands, cm^{-1}: 3370 m−w ν(N−H), 1631 s ν(C=N), 1247 m ν(C−O). ^{1}H NMR in $CDCl_3$, δ: 1.45 (d, 6.0 Hz, 6*H*, CH_3 from *i*-Pr), 2.69 (s + d, $^4J_{PtH}$ 3.0 Hz, 3*H*, =C*Me*O), 4.77 (sept, 6.1 Hz, 1*H*, CH from *i*-Pr), 6.82 (s, br, 1*H*, NH). ^{13}C{^{1}H} NMR in $CDCl_3$, δ: 20.5 (=C*Me*O), 21.6 (CH_3 from *i*-Pr), 73.2 (CH from *i*-Pr), *C*=NH were not detected. ^{195}Pt NMR in $CDCl_3$, δ: −136 (550 Hz).

***trans*-[PtCl$_4${(*E*)-NH=C(Me)OPr-*n*}$_2$] (4).** Yield: 55%. Complex was recrystallized from $CHCl_3$. Anal. Calcd for $C_{10}H_{22}N_2Cl_4O_2Pt\cdot 0.5CHCl_3$: C, 21.51; H, 3.90; N, 4.87. Found: C, 21.50; H, 3.69; N, 5.03. FAB$^+$-MS, *m*/*z* 561 [M + Na]$^+$, 505 [M − Cl]$^+$, 491 [M − 2Cl + Na]$^+$, 468 [M − 2Cl]$^+$, 431 [M − 3Cl − 2H]$^+$, 396 [M − 4Cl − H]$^+$. TLC, $R_f = 0.58$ (eluent CH_2Cl_2). IR spectrum in KBr, selected bands, cm^{-1}: 3356 m−w ν(N−H), 2972 w and 2930 w ν(C−H), 1633 s ν(C=N), 1246 m ν(C−O). ^{1}H NMR in $CDCl_3$, δ: 1.00 (t, 7.3 Hz, 3*H*, CH_3 from Pr-*n*), 1.82 (m, 2*H*, β-CH_2 from Pr-*n*), 2.68 (s, 3*H*, =C*Me*O), 4.06 (t, 6.3 Hz, 2*H*, α-CH_2 from OPr-*n*), 6.82 (s, br, 1*H*, NH). ^{13}C{^{1}H} NMR in $CDCl_3$, δ: 10.2 (CH_3 from Pr-*n*), 20.21 (=C*Me*), 21.4 (CH_2 from Pr-*n*), 70.2 (OCH_2 of OPr-*n*), 176.6 (C=NH). ^{195}Pt NMR in $CDCl_3$, δ: −153.1 (655 Hz).

***trans*-[PtCl$_4${(*E*)-NH=C(Me)OBu-*n*}$_2$] (5).** Yield: 50%. Anal. Calcd for $C_{12}H_{26}N_2Cl_4O_2Pt\cdot 0.1C_4H_9OH$: C, 25.91; H, 4.73; N, 4.87. Found: C, 26.00; H, 5.05; N, 4.75. FAB$^+$-MS, *m*/*z* 614 [M − 2H + 2Na]$^+$, 576 [M − 2H − Cl + 2Na]$^+$, 540 [M − 2H − 2Cl + 2Na]$^+$, 496 [M − 2H − 2Cl]$^+$, 424 [M − 4Cl]$^+$. TLC, $R_f = 0.68$ (eluent CH_2Cl_2). IR spectrum in KBr, selected bands, cm^{-1} : 3360 m−w ν(N−H), 2937 m−w ν(C−H), 1637 s ν(C=N), 1247 m ν-(C−O). ^{1}H NMR in $CDCl_3$, δ: 0.95 (t, 7.3 Hz, 3*H*, CH_3 from Bu-*n*), 1.43 (m, 2*H*, γ-CH_2 from OBu-*n*), 1.77 (m, 2*H*, β-CH_2 from Pr-*n*), 2.68 (s, 3*H*, =C*Me*O), 4.10 (t, 6.3 Hz, 2*H*, α-CH_2 from OBu-*n*), 6.82 (s, br, 1*H*, NH). ^{13}C{^{1}H} NMR in $CDCl_3$, δ: 13.6 (CH_3 from Bu-*n*), 18.9 (CH_2 from Bu-*n*), 20.2 (=C*Me*), 29.9 (CH_2 from Bu-*n*), 70.2 (OCH_2 from OBu-*n*), 176.5 (C=NH). ^{195}Pt NMR in $CDCl_3$, δ: −155.4 (630 Hz).

***cis*-[PtCl$_4${(*E*)-NH=C(Me)OEt}{(*Z*)-NH=C(Me)OEt}] (6).** Yield: 60%. Anal. Calcd for $C_8H_{18}N_2Cl_4O_2Pt$: C, 18.78; H, 3.52; N, 5.47. Found: C, 18.83; H, 3.52; N, 5.46. FAB$^+$-MS, *m*/*z*: 533 [M − H + Na], 511 [M], 440 [M − 2Cl]$^+$. TLC, $R_f = 0.30$ (eluent acetone:$CHCl_3$ = 1:2). IR spectrum in KBr, selected bands, cm^{-1}: 3313 m−w ν(N−H), 2982 w and 2924 w ν(C−H), 1633 s ν(C=N), 1250 m ν(C−O). ^{1}H NMR in $CDCl_3$, δ: two sets of signals in ca. 1:1 ratio, 1.42 (t, 7.0 Hz, 3*H*, CH_2CH_3, *E*), 1.44 (t, 7.0 Hz, 3*H*, CH_2CH_3, *Z*), 2.60 (s, 3*H*, =C*Me*O, *E*), 2.61 (s, 3*H*, =C*Me*O, *Z*), 4.35 (quart., 7.0 Hz, 2*H*, CH_2CH_3, *E*), 4.37 (quart., 7.0 Hz, 2*H*, CH_2CH_3, *Z*), 7.36 (s, br, 1*H*, NH, *E*), 7.64 (s, br, 1*H*, NH, *Z*). ^{13}C-{^{1}H} NMR in $CDCl_3$, δ: 13.6 and 14.2 (CH_3 from Et), 19.6 (=C*Me*O), 64.6 and 67.4 (CH_2 from Et), 175.4 and 176.4 (C=NH). ^{195}Pt NMR in $CDCl_3$, δ: 14 (860 Hz).

***cis*-[PtCl$_4${(*E*)-NH=C(Me)OPr-*n*}{(*Z*)-NH=C(Me)OPr-*n*}] (7).** Yield: 40%. Anal. Calcd for $C_{10}H_{22}N_2Cl_4O_2Pt$: C, 22.27; H, 3.50; N, 5.20. Found: C, 22.27; H, 3.84; N, 5.13. FAB$^+$-MS, *m*/*z*: 468 [M − 2Cl]$^+$, 431 [M − 3Cl − 2H]$^+$, 396 [M − 4Cl − H]$^+$. TLC, $R_f = 0.55$ (eluent Me_2CO: CH_2Cl_2 = 3:10). IR spectrum in KBr, selected bands, cm^{-1}: 3300 m−w ν(N−H), 2963 m−w and 2929 m−w ν(C−H), 1635 s ν(C=N), 1247 m ν(C−O). ^{1}H NMR in $CDCl_3$, δ: two sets of signals in ca. 1:1 ratio, 1.00 (t, 6.9 Hz, 3*H*, CH_3 from Pr-*n*, *E*), 1.02 (t, 6.9 Hz, 3*H*, CH_3 from Pr-*n*, *Z*), 1.73 (m, 2*H*, β-CH_2 from Pr-*n*, *Z*), (m, 4*H*, β-CH_2 from Pr-*n*, *E*), 2.61 (s, 3*H*, =C*Me*O, *E*), 2.65 (s, 3*H*, =C*Me*O, *Z*), 4.12 (t, 6.3 Hz, 2*H*, α-CH_2 of OPr-*n*, *E*), 4.24 (t, 6.3 Hz, 2*H*, α-CH_2 of OPr-*n*, *Z*), 7.28 (s, br, $^3J_{PtH}$ 31.5 Hz, 1*H*, NH, *E*), 7.67 (s, br, $^3J_{PtH}$ 21.5 Hz, 1*H*, NH, *Z*). ^{13}C{^{1}H} NMR in $CDCl_3$, δ: 10.2 (CH_3 from Pr-*n*, *E* and *Z*), 19.8 (=C*Me*O, *E*), 21.6 (β-CH_2 from OPr-*n*, *E*), 22.3 (β-CH_2 from OPr-*n*, *Z*), 22.4 (=C*Me*O, *Z*), 70.8 (α-CH_2 from OPr-*n*, *E*), 74.3 (α-CH_2 from OPr-*n*, *Z*), 176.3 and 177.5 (C=NH). ^{195}Pt NMR in $CDCl_3$, δ: −11.5 (400 Hz). Attribution of the signals due to the *E* and *Z* isomers was performed using NOE, COSY and HETCOR.

***cis*-[PtCl$_4${(*E*)-NH=C(Me)OBu-*n*}{(*Z*)-NH=C(Me)OBu-*n*}] (8).** Yield: 56%. Anal. Calcd for $C_{12}H_{26}N_2Cl_4O_2Pt\cdot 0.25CH_2Cl_2$: C, 25.00; H, 4.54; N, 4.76. Found: C, 24.89; H, 4.38; N, 4.99. IR spectrum in KBr, selected bands, cm^{-1}: 3296 m−w ν(N−H), 2960 m, 2932 m−w and 2872 m−w ν(C−H), 1637 s ν(C=N), 1243 m ν(C−O). FAB$^+$-MS, *m*/*z*: 496 [M − 2Cl]$^+$, 422 [M − 4Cl − 2H]$^+$. TLC, $R_f = 0.44$ (eluent Me_2CO:$CHCl_3$ = 3:10). ^{1}H NMR in $CDCl_3$, δ: two sets of signals in ca. 1:1 ratio, 0.91 (t, 7.4 Hz, 3*H*, CH_3 from Bu-*n*, *E*), 0.94 (t, 7.4 Hz, 3*H*, CH_3 from Bu-*n*, *Z*), 1.42 (m, 4*H*, γ-CH_2 from Bu-*n*), 1.69 (m, 4*H*, β-CH_2 from Bu-*n*), 2.59 (s, 3*H*, =C*Me*O, *E*), 2.66 (s, $^3J_{PtH}$ 13.7 Hz, 3*H*, =C*Me*O, *Z*), 4.12 (t, 6.0 Hz, 2*H*, α-CH_2 from OBu-*n*, *E*), 4.28 (t, 6.3 Hz, 2*H*, α-CH_2 from OBu-*n*, *Z*), 7.25 (s, br, $^3J_{PtH}$ 31.5 Hz, 1*H*, NH, *E*), 7.64 (s, br, $^4J_{PtH}$ 21.9 Hz, 1*H*, NH, *Z*). ^{13}C{^{1}H} NMR in $CDCl_3$, δ: 13.6 (two signals, CH_3 from OBu-*n*), 18.7 (γ-CH_2 from OBu-*n*, *E*), 19.0 (γ-CH_2 of OBu-*n*, *Z*), 19.9 ($^3J_{PtC}$ 8.8 Hz, =C*Me*O, *E*), 22.6 (J_{PtC} 26.1 Hz, =C*Me*O, *Z*), 30.0 (β-CH_2 from OBu-*n*, *E*), 30.8 (β-CH_2 from OBu-*n*, *Z*), 69.4 (J_{PtC} 93.4 Hz, α-CH_2 from OBu-*n*, *E*), 72.6 (α-CH_2 from OBu-*n*, *Z*), 176.2 (C=NH, *E*), 177.6 (J_{PtC} 75.5 Hz, C=NH, *Z*). ^{195}Pt NMR in $CDCl_3$, δ: 4 (375 Hz). A suitable ratio of signals from the *E* and *Z* forms in the ^{1}H NMR spectrum, one signal in the ^{195}Pt NMR spectrum, and one spot on TLC allow one to assume that a pure single compound was obtained. Attribution of the signals due to the *E* and *Z* isomers was performed using NOE, COSY, and HETCOR.

Reactions of [PtCl$_4$(EtCN)$_2$] with Alcohols. The reactions with either *trans*- or *cis*-[$PtCl_4(EtCN)_2$] (20 mg, 0.05 mmol) are performed in suspension of the appropriate alcohol (0.1−0.2 mL) at 45 °C for 1 day. In the case of *trans*-[$PtCl_4(EtCN)_2$], the crystalline *trans*-[$PtCl_4${(*E*)-NH=C(Et)OR′}$_2$] formed is filtered off and washed with one 0.5-mL portion of the alcohol and two 0.5-mL portions of diethyl ether. Yields are 70−90%. In the case of *cis*-[$PtCl_4(EtCN)_2$], products and yields are given below for each particular case. Insofar as *cis*-[$PtCl_4(EtCN)_2$] contains admixtures of *trans*-[$PtCl_4(EtCN)_2$], NMR parameters of cis addition products were obtained by subtraction of signals due to *trans*-*E* isomers from the NMR spectra.

***trans*-[PtCl$_4${(*E*)-NH=C(Et)OMe}$_2$] (9).** Anal. Calcd for $C_8H_{18}N_2Cl_4O_2Pt$: C, 18.87; H, 3.55; N, 5.48. Found: C, 18.94; H, 3.55; N, 5.36. FAB$^+$-MS, *m*/*z*: 440 [M − 2Cl], 367 [M − 4Cl − 2H]. TLC, $R_f = 0.41$ (eluent CH_2Cl_2). IR spectrum in KBr, selected bands, cm^{-1}: 3334 m ν(N−H), 2981 and 2941 m−w ν(C−H), 1628 s ν(C=N), 1229 m ν(C−O). ^{1}H NMR in $CDCl_3$, δ: 1.23 (t, 7.5 Hz, 3*H*, CH_3 from Et), 3.13 (quart., 7.5 Hz, 2*H*, CH_2 from Et), 3.96 (s, 3*H*, OMe), 6.86 (s, br, 1*H*, NH). ^{13}C{^{1}H} NMR in $CDCl_3$, δ: 10.6 (CH_3) and 26.8 (CH_2, $^3J_{PtC}$ 8.3 Hz)(Et), 54.6 (CH_3, OMe), 179.9 (C=NH). ^{195}Pt NMR in $CDCl_3$, δ: −160 (680 Hz).

***trans*-[PtCl$_4${(*E*)-NH=C(Et)OEt}$_2$] (10).** Anal. Calcd for $C_{10}H_{22}N_2Cl_4O_2Pt$: C, 22.28; H, 4.11; N, 5.2. Found: C, 22.20; H, 4.08; N, 5.05. FAB$^+$-MS, *m*/*z*: 468 [M − 2Cl]$^+$, 431 [M − 3Cl − 2H], 396 [M − 4Cl − 2H]. TLC, $R_f = 0.56$ (eluent $CHCl_3$). IR spectrum in KBr, selected bands, cm^{-1}: 3346 m ν(N−H), 2988 m and 2943 m−w ν(C−H), 1619 s ν(C=N), 1225 m−s ν(C−O). ^{1}H NMR in $CDCl_3$, δ: 1.22 (t, 7.5 Hz, 3*H*, CH_3 from Et), 1.44 (t, 6.9 Hz, 3*H*, CH_3 from OEt), 3.09 (quart., 7.3 Hz, 2*H*, CH_2 from Et), 4.19 (quart., 7.1 Hz, 2*H*, CH_2 from OEt), 6.80 (s + d, $^2J_{PtH}$ 30 Hz, NH). ^{13}C{^{1}H} NMR in $CDCl_3$, δ: 10.8 (CH_3 from Et), 13.4 (CH_3 from OEt), 26.8 (CH_2, $^3J_{PtC}$ 8.5 Hz, CH_2 from Et), 64.2 (CH_2 from OEt), 179.7 ($^2J_{PtC}$ 33 Hz, C=NH). ^{195}Pt NMR in $CDCl_3$, δ: −144 (420 Hz).

***trans*-[PtCl$_4${(*E*)-NH=C(Et)OPr-*i*}$_2$] (11).** Anal. Calcd for $C_{12}H_{26}N_2Cl_4O_2Pt$: C, 25.41; H, 4.62; N, 4.94. Found: C, 25.78; H, 4.63; N, 4.77. FAB$^+$-MS, *m*/*z*: 532 [M − Cl]$^+$, 496 [M − 2Cl]$^+$, 459 [M − 3Cl − 2H], 424 [M − 4Cl − 2H]. TLC, $R_f = 0.73$ (eluent $CHCl_3$). IR spectrum in KBr, selected bands, cm^{-1}: 3359

m ν(N−H), 2979 and 2932 m ν(C−H), 1628 s ν(C═N), 1228 m ν(C−O). ^{1}H NMR in $CDCl_3$, δ: 1.21 (t, 7.5 Hz, 3*H*, CH_3 from Et), 3.04 (quart., 7.5 Hz, 2*H*, CH_2 from Et), 1.43 (d, 6.0 Hz, 6*H*, CH_3 from OPr-*i*), 4.73 (sept, 6.0 Hz, 1*H*, CH from OPr-*i*), 6.74 (s + d, $^2J_{PtH}$ 40 Hz, NH). ^{13}C{^{1}H} NMR in $CDCl_3$, δ: 10.8 (CH_3 from Et), 21.4 (CH_3 from OPr-*i*), 27.0 (CH_2, $^3J_{PtC}$ 8.0 Hz, CH_2 from Et), 72.4 (CH from OPr-*i*), 178.0 (C═NH). ^{195}Pt NMR in $CDCl_3$, δ: −125 (450 Hz).

***trans*-[PtCl$_4${(*E*)-NH═C(Et)OPr-*n*}$_2$] (12).** Anal. Calcd for $C_{12}H_{26}N_2Cl_4O_2Pt$: C, 25.41; H, 4.62; N, 4.94. Found: C, 25.35; H, 4.57; N, 4.89. FAB$^+$-MS, *m*/*z*: 496 [M − 2Cl]$^+$, 459 [M − 3Cl − 2H], 424 [M − 4Cl − 2H]. TLC, R_f = 0.64 (eluent $CHCl_3$). IR spectrum in KBr, selected bands, cm^{-1}: 3302 m ν(N−H), 2972, 2934 and 2880 m ν(C−H), 1626 s ν(C═N), 1228 m ν(C−O). ^{1}H NMR in $CDCl_3$, δ: 1.02 (t, 7.3 Hz, 3*H*, CH_3 from OPr-*n*), 1.23 (t, 7.5 Hz, 3*H*, CH_3 from Et), 1.85 (sext, 6.7 Hz, 2*H*, β-CH_2 from OPr-*n*), 3.12 (quart., 7.5 Hz, 2*H*, CH_2 from Et), 4.07 (t, 6.3 Hz, 2*H*, α-CH_2 from OPr-*n*), 6.79 (s + d, $^2J_{PtH}$ 37 Hz, NH). ^{13}C{^{1}H} NMR in $CDCl_3$, δ: 10.2 (CH_3 from OPr-*n*), 10.7 (CH_3 from Et), 21.3 (β-CH_2 from OPr-n), 26.9 (CH_2, $^3J_{PtC}$ 8.8 Hz, CH_2 from Et), 69.5 (α-CH_2 from OPr-*n*), 179.4 (C═NH). ^{195}Pt NMR in $CDCl_3$, δ: −147 (500 Hz).

***trans*-[PtCl$_4${(*E*)-NH═C(Et)OBu-*n*}$_2$] (13).** Anal. Calcd for $C_{14}H_{30}N_2Cl_4O_2Pt$: C, 28.25; H, 5.08; N, 4.71. Found: C, 28.52; H, 5.02; N, 4.62. FAB$^+$-MS, *m*/*z*: 524 [M − 2Cl]$^+$, 487 [M − 3Cl − 2H], 452 [M − 4Cl − H]. TLC, R_f = 0.70 (eluent $CHCl_3$). IR spectrum in KBr, selected bands, cm^{-1}: 3356 m ν(N−H), 2942 and 2873 m ν(C−H), 1629 s ν(C═N), 1231 m ν(C−O). ^{1}H NMR in $CDCl_3$, δ: 0.96 (t, 7.2 Hz, 3*H*, CH_3 from OBu-*n*), 1.23 (t, 7.5 Hz, 3*H*, CH_3 from Et), 1.44 (sext, 7.5 Hz, 2*H*, γ-CH_2 from OBu-*n*), 1.80 (quint, 6.6 Hz, 2*H*, β-CH_2 from OBu-*n*), 3.11 (quart., 7.4 Hz, 2*H*, CH_2 from Et), 4.10 (t, 6.3 Hz, 2*H*, α-CH_2 from OBu-*n*), 6.79 (s + d, $^2J_{PtH}$ 38 Hz, NH). ^{13}C{^{1}H} NMR in $CDCl_3$, δ: 10.7 (CH_3 from Et) and 26.9 (CH_2, $^3J_{PtC}$ 8.7 Hz, CH_2 from Et), 13.6 (CH_3 from OBu-*n*), 18.9 (γ-CH_2 from OBu-*n*), 29.7 (β-CH_2 from OBu-*n*), 68.0 (α-CH_2 from OBu-*n*), 179.4 (C═NH). ^{195}Pt NMR in $CDCl_3$, δ: −147 (410 Hz).

***cis*-[PtCl$_4${(*E*)-NH═C(Et)OMe}$_2$] (14).** Anal. Calcd for $C_8H_{18}N_2Cl_4O_2Pt$: C, 18.87; H, 3.55; N, 5.48. Found: C, 18.87; H, 3.54; N, 5.44. FAB$^+$-MS, *m*/*z*: 440 [M − 2Cl]$^+$, 403 [M − 2Cl − HCl]$^+$, 367 [M − 2Cl − 2HCl]$^+$. mp = 115 °C. TLC, R_f = 0.66 (eluent acetone:$CHCl_3$ = 1:2). IR spectrum in KBr, selected bands, cm^{-1}: 3284 m ν(N−H), 2980 and 2941 m ν(C−H), 1620 s ν(C═N), 1231 m ν(C−O). ^{1}H NMR in $CDCl_3$, δ: 1.23 (t, 7.5 Hz, 3*H*), 2.94 (quart., 7.8 Hz, 2*H*)(Et), 3.99 (s, 3*H*, OMe), 6.89 (s + d, $^2J_{PtH}$ 30 Hz, NH). ^{13}C{^{1}H} NMR in $CDCl_3$, δ: 10.6 (CH_3) and 26.7 (CH_2, $^3J_{PtC}$ 8.4 Hz)(Et), 55.6 (CH_3, OMe), 180.4 ($^2J_{PtC}$ 34 Hz, C═NH). ^{195}Pt NMR in $CDCl_3$, δ: −53 (390 Hz). Refluxing of a suspension of *cis*-[$PtCl_4$-{(*E*)-NH═C(Et)OMe}$_2$] in MeOH for 8 h leads to pure *trans*-[$PtCl_4$-{(*E*)-NH═C(Et)OMe}$_2$].

***cis*-[PtCl$_4${(*E*)-NH═C(Et)OEt}$_2$] (15).** Anal. Calcd for $C_{10}H_{22}N_2Cl_4O_2Pt$: C, 22.28; H, 4.11; N, 5.2. Found: C, 22.20; H, 4.08; N, 5.05. FAB$^+$-MS, *m*/*z*: 468 [M − 2Cl]$^+$, 431 [M − 3Cl − 2H], 396 [M − 4Cl − 2H]. TLC, R_f = 0.64 (eluent acetone:$CHCl_3$ = 1:3). IR spectrum in KBr, selected bands, cm^{-1}: 3297 m ν(N−H), 2987 and 2939 m ν(C−H), 1619 s ν(C═N), 1228 m ν(C−O). ^{1}H NMR in $CDCl_3$, δ: 1.22 (t, 7.5 Hz, 3*H*, CH_3 from Et), 1.46 (t, 6.9 Hz, 3*H*, CH_3 from OEt), 2.91 (quart., 7.5 Hz, 2*H*, CH_2 from Et), 4.22 (quart., 6.9 Hz, 2*H*, CH_2 from OEt), 6.80 (s + d, $^2J_{PtH}$ 30 Hz, NH,1*H*). ^{13}C{^{1}H} NMR in $CDCl_3$, δ: 10.7 (CH_3 from Et), 13.5 (CH_3 from OEt), 26.7 ($^3J_{PtC}$ 8.5 Hz, CH_2 from Et), 65.1 (CH_2 from OEt), 179.7 ($^2J_{PtC}$ 33 Hz, C═NH). ^{195}Pt NMR in $CDCl_3$, δ: −33 (390 Hz).

***cis*-[PtCl$_4${(*E*)-NH═C(Et)OPr-*i*}{(*Z*)-NH═C(Et)OPr-*i*}] (16).** The complex was purified by TLC chromatography and isolated as an oily residue. Despite our inability to obtain satisfactory C, H, N analyses, all other data agree well with the proposed composition and structure. FAB$^+$-MS, *m*/*z*: 532 [M − Cl] $^+$, 496 [M − 2Cl]$^+$. TLC: R_f = 0.30 (eluent CH_2Cl_2:Et_2O = 20:1). IR spectrum in KBr, selected bands, cm^{-1}: 3258 w ν(N−H), 2976 m−w and 2936 w ν(C−H), 1630 s ν(C═N), 1224 m ν(C−O). ^{1}H NMR in $CDCl_3$, δ: 1.21 and 1.30 (two t, 7.4 Hz, CH_3 from Et), 1.39 and 1.41 (two d, CH_3 from OPr-*i*), 2.76 and 2.82 (q, 7.4 Hz, CH_2 from Et), 4.71 and 4.85 (t, 5.9 and 6.1 Hz, 2*H*, α-CH_2 of OPr-*i*), 7.09 and 7.30 (s, br, NH). ^{195}Pt NMR in $CDCl_3$, δ: −63 (530 Hz).

***cis*-[PtCl$_4${(*E*)-NH═C(Et)OPr-*n*}{(*Z*)-NH═C(Et)OPr-*n*}] (17).** The complex was purified by TLC chromatography and isolated as an oily residue. Despite our inability to obtain satisfactory C, H, N analyses, all other data agree well with the proposed composition and structure. FAB$^+$-MS, *m*/*z*: 496 [M − 2Cl]$^+$. TLC, R_f = 0.42 (eluent CH_2Cl_2:Et_2O = 5:1). IR spectrum in KBr, selected bands, cm^{-1}: 3313 w ν(N−H), 2963 w ν(C−H), 1624 s ν(C═N), 1225 m ν(C−O). ^{1}H NMR in $CDCl_3$, δ: two sets of signals in ca. 1:1 ratio, 1.02 (t, 7.4 Hz, 6*H*, CH_3 from OPr-*n*, *E* and *Z*), 1.21 (t, 7.5 Hz, CH_3 from Et, 3*H*, *E*), 1.34 (t, 7.4 Hz, CH_3 from Et, 3*H*, *Z*), 1.75 (m, 2*H*, β-CH_2 from OPr-*n*, *Z*), 1.84 (m, 2*H*, β-CH_2 from OPr-*n*, *E*), 2.81 (q, 7.4 Hz, 2*H*, CH_2 from Et, *Z*), 2.95 (q, 7.5 Hz, 2*H*, CH_2 from Et, *E*), 4.03 (t, 6.3 Hz, 2*H*, α-CH_2 of OPr-*n*, *E*), 4.24 (t, 6.8 Hz, 2*H*, α-CH_2 of OPr-*n*, *Z*), 7.20 (s, br, 1*H*, NH, *E*), 7.29 (s, br, 1*H*, NH, *Z*). ^{13}C{^{1}H} NMR in $CDCl_3$, δ: 9.8 (CH_3 from Et; *Z*) 10.2 (CH_3 from OPr-*n*; *E* and *Z*), 10.6 (CH_3 from Et; *E*), 21.4 (β-CH_2 of OPr-*n*, *E*), 22.4 (β-CH_2 of OPr-*n*, *Z*), 26.7 (CH_2 from Et, *E*), 27.2 (CH_2 from Et, *Z*), 69.6 (α-CH_2 from OPr-*n*, *E*), 73.3 (α-CH_2 from OPr-*n*, *Z*), 178.8 and 181.0 (C═NH). ^{195}Pt NMR in $CDCl_3$, δ: −29.2 (650 Hz). Attribution of the signals due to the *E* and *Z* isomers was performed using NOE, COSY, and HETCOR.

***cis*-[PtCl$_4${(*E*)-NH═C(Et)OBu-*n*}{(*Z*)-NH═C(Et)OBu-*n*}] (18).** The complex was purified by TLC chromatography and isolated as an oily residue. Despite our inability to obtain satisfactory C, H, N analyses, all other data agree well with the proposed composition and structure. FAB$^+$-MS, *m*/*z*: 559 [M − Cl]$^+$. TLC, R_f = 0.35 (eluent CH_2Cl_2:Et_2O = 20:1). IR spectrum in KBr, selected bands, cm^{-1}: 3291 w ν(N−H), 2960 m−w and 2935 w ν(C−H), 1629 s ν(C═N), 1224 m ν(C−O). ^{1}H NMR in $CDCl_3$, δ: two sets of signals in ca. 1:1 ratio, 0.92 (t, 7.4 Hz, 3*H*, CH_3 from OBu-*n*, *Z*), 0.96 (t, 7.4 Hz, 3*H*, CH_3 from OBu-*n*, *E*), 1.20 (t, 7.4 Hz, CH_3 from Et, 3*H*, *E*), 1.34 (t, 7.3 Hz, CH_3 from Et, 3*H*, *Z*), 1.43 (m, 2*H*, γ-CH_2 from OPr-*n*, *Z*), 1.45 (m, 2*H*, γ-CH_2 from OPr-*n*, *Z*), 1.68 (m, 2*H*, β-CH_2 from OPr-*n*, *Z*), 1.79 (m, 2*H*, β-CH_2 from OPr-*n*, *E*), 2.81 (q, 7.3 Hz, 2*H*, CH_2 from Et, *Z*), 2.95 (q, 7.4 Hz, J_{PtH} 2.9 Hz, 2*H*, CH_2 from Et, *E*), 4.06 (t, 6.4 Hz, 2*H*, α-CH_2 of OPr-*n*, *E*), 4.28 (t, 6.7 Hz, 2*H*, α-CH_2 of OPr-*n*, *Z*), 7.19 (s, br, 1*H*, NH, *E*), 7.30 (s, br, 1*H*, NH, *Z*). ^{13}C{^{1}H} NMR in $CDCl_3$, δ: 9.8 (CH_3 from Et; *Z*), 10.7 (CH_3 from Et; *E*) 13.6 (CH_3 from OBu-*n*; *E* and *Z*), 18.7 (γ-CH_2 from OBu-*n*; *Z*), 19.0 (γ-CH_2 from OBu-*n*; *E*), 26.8 (J_{PtC} 9.0 Hz, CH_2 from Et, *E*), 27.2 (CH_2 from Et, *Z*), 29.9 (β-CH_2 of OPr-*n*, *E*), 31.0 (β-CH_2 of OPr-*n*, *Z*), 68.2 (α-CH_2 from OPr-*n*, *E*), 71.6 (α-CH_2 from OPr-*n*, *Z*), 178.8 and 181.1 (C═NH). ^{195}Pt NMR in $CDCl_3$, δ: −42.2 (470 Hz). Attribution of the signals due to the *E* and *Z* isomers was performed using NOE, COSY, and HETCOR.

Reactions of [$PtCl_4(RCN)_2$] (R = CH_2Ph, Ph) with Alcohols. The appropriate alcohol (0.7 mL, 5−7 mmol) is added to the solid [$PtCl_4(RCN)_2$] (0.12 g, 0.21 mmol). The reaction mixture is left to stand at room temperature (heated at ca. 50 °C for R = Ph) for 2 days, and the completeness of reaction is controlled by TLC. The released new precipitate is filtered off, washed with two 1-mL portions of ROH, and dried in air at room temperature.

***trans*-[$PtCl_4${(*E*)-NH=C(CH_2Ph)OMe}$_2$] (19).** Yield: 30%. Complex was recrystallized from $CHCl_3$. Anal. Calcd for $C_{18}H_{22}N_2Cl_4O_2Pt\cdot0.5CHCl_3$: C, 31.97; H, 3.26; N, 4.03. Found: C, 31.77; H, 3.17; N, 4.38. FAB^+-MS, *m*/*z*: 587 [M − 2Cl + Na]$^+$, 564 [M − 2Cl]$^+$. TLC, R_f = 0.47 (eluent $CHCl_3$). IR spectrum in KBr, selected bands, cm^{-1}: 3339 s ν(N−H), 2922 m ν(C−H), 1628 s ν(C=N), 1256 m ν(C−O). ^{1}H NMR in $CDCl_3$, δ: 3.96 (s, 3*H*, OMe), 4.57 (s, 2*H*, =C{CH_2Ph}O), 7.12 (s, br, 1*H*, NH), 7.36 (m, 5*H*, CH_2*Ph*). ^{13}C{^{1}H} NMR in $CDCl_3$, δ: 39.2 (=C{*C*H_2Ph}O), 55.2 (OMe), 127.5 (CH), 128.6 (CH), 130.0 (CH) and 133.0 (C_{ipso})-(CH_2*Ph*), 177.2 (C=N). ^{195}Pt NMR in $CDCl_3$, δ: −184 (450 Hz).

***trans*-[$PtCl_4${(*E*)-NH=C(CH_2Ph)OEt}$_2$] (20)**. Yield: 28%. Anal. Calcd for $C_{20}H_{26}N_2Cl_4O_2Pt$: C, 36.21; H, 3.95; N, 4.22. Found: C, 35.87; H, 3.80; N, 4.30. FAB^+-MS, *m*/*z*: 592 [M − 2Cl]$^+$. TLC, R_f = 0.68 (eluent $CHCl_3$). IR spectrum in KBr, selected bands, cm^{-1}: 3289 m ν(N−H), 2982 m ν(C−H), 1624 s ν(C=N), 1254 m ν(C−O). ^{1}H NMR in $CDCl_3$, δ: 1.38 (t, 7.0 Hz, 3*H*, Me), 4.23 (quart., 7.0 Hz, 2*H*, C$H_2$$CH_3$), 4.53 (s, 2*H*, C$H_2$Ph), 7.07 (s + d, $^2J_{PtH}$ 40 Hz, 1*H*, NH), 7.34 (m, 3*H*) and 7.41 (m, 2*H*)(CH_2*Ph*). ^{13}C{^{1}H} NMR in $CDCl_3$, δ: 13.2 (CH_3 from Et), 39.2 (CH_2, $^3J_{PtC}$ 8.2 Hz, *C*H_2Ph), 64.8 (CH_2 from Et), 127.3 (CH), 128.5 (CH), 130.0 (CH) and 133.3 (C_{ipso})(CH_2*Ph*), 176.4 ($^2J_{PtC}$ 35 Hz, C=NH). ^{195}Pt NMR in $CDCl_3$, δ: −165 (600 Hz).

***trans*-[$PtCl_4${(*E*)-NH=C(CH_2Ph)OPr-*i*}$_2$] (21)**. Yield: 11%. Anal. Calcd for $C_{22}H_{30}N_2Cl_4O_2Pt$: C, 38.22; H, 4.37; N, 4.05. Found: C, 38.17; H, 4.31; N, 3.94. FAB^+-MS, *m*/*z*: 620 [M − 2Cl]$^+$, 583 [M − 3Cl − 2H], 548 [M − 4Cl − 2H]. TLC, R_f = 0.67 (eluent $CHCl_3$). IR spectrum in KBr, selected bands, cm^{-1}: 3356 m ν(N−H), 2975 and 2928 m ν(C−H), 1623 s ν(C=N), 1242 m ν(C−O). ^{1}H NMR in $CDCl_3$, δ: 1.35 (d, 6.3 Hz, 6*H*, CH_3 from Pr-*i*), 4.48 (s, 2*H*, CH_2Ph), 4.78 (sept, 6.0 Hz, 1*H*, CH from Pr-*i*), 7.03 (s + d, $^2J_{PtH}$ 44 Hz, 1*H*, NH), 7.29 (m, 3*H*) and 7.37 (m, 2*H*) (CH_2*Ph*). ^{13}C{^{1}H} NMR in $CDCl_3$, δ: 21.2 (CH_3 from Pr-*i*), 39.4 (CH_2, *C*H_2Ph), 73.2 (CH from OPr-*i*), 127.2 (CH), 128.4 (CH), 129.8 (CH) and 133.6 (C_{ipso}) (CH_2*Ph*), 175.3 (C=NH). ^{195}Pt NMR in $CDCl_3$, δ: −147 (550 Hz).

***trans*-[$PtCl_4${(*E*)-NH=C(CH_2Ph)OPr-*n*}$_2$] (22).** Yield: 22%. Anal. Calcd for $C_{22}H_{30}N_2Cl_4O_2Pt$: C, 38.22; H, 4.37; N, 4.05. Found: C, 37.93; H, 4.03; N, 4.38. FAB^+-MS, *m*/*z*: 620 [M − 2Cl]$^+$, 583 [M − 3Cl − 2H], 548 [M − 4Cl − H]. TLC, R_f = 0.70 (eluent $CHCl_3$). IR spectrum in KBr, selected bands, cm^{-1}: 3326 m ν(N−H), 2971 m−w and 2928 m−w ν(C−H), 1624 vs ν(C=N), 1251 m ν(C−O). ^{1}H NMR in $CDCl_3$, δ: 0.83 (t, 7.5 Hz, 3*H*, CH_3), 1.73 (sext, 7.5 Hz, 2*H*, β-CH_2 from Pr-*n*), 4.08 (t, 6.3 Hz, 2*H*, α-CH_2 from Pr-*n*), 4.54 (s, 2*H*, CH_2Ph), 7.02 (s + d, $^2J_{PtH}$ 44 Hz, 1*H*, NH), 7.31 (m, 3*H*) and 7.40 (m, 2*H*) (CH_2*Ph*). ^{13}C{^{1}H} NMR in $CDCl_3$, δ: 9.90 (CH_3 from Pr-*n*), 21.10 (β-CH_2 from Pr-*n*), 39.2 (CH_2, $^3J_{PtC}$ 9.2 Hz, *C*H_2Ph), 70.0 (α-CH_2 from Pr-*n*), 127.3 (CH), 128.4 (CH), 130.0 (CH) and 133.2 (C_{ipso}) (CH_2*Ph*), 176.6 ($^2J_{PtC}$ 40 Hz, C=NH). ^{195}Pt NMR in $CDCl_3$, δ: −164 (700 Hz).

***trans*-[$PtCl_4${(*E*)-NH=C(Ph)OMe}$_2$] (23).** The complex can be purified by washing with warm (35−40 °C) acetone (2 mL) for 10−15 min. Yield: 50%. Anal. Calcd for $C_{16}H_{18}N_2Cl_4O_2Pt$: C, 31.65; H, 2.99; N, 4.61. Found: C, 31.47; H, 3.05; N, 4.32. FAB^+-MS, *m*/*z*: 629 [M + Na]$^+$. TLC, R_f = 0.48 (eluent acetone: chloroform = 1:40). IR spectrum in KBr, selected bands, cm^{-1}: 3242 w ν(N−H), 2934 w ν(C−H), 1612 s ν(C=N). ^{1}H NMR in $CDCl_3$, δ: 4.05 (s, 3*H*, OMe), 7.65 (m, 6*H*, Ph and NH). ^{13}C{^{1}H} NMR in $CDCl_3$, δ: 61.5 (OMe), 128.3 (CH), 129.0 (C_{ipso}), 129.7 (CH) and 133.6 (CH) (Ph), 179.5 (C=NH). ^{195}Pt NMR in $CDCl_3$, δ: −154 (580 Hz).

Reduction of (Imine)Pt(IV) Complexes with the Ylide Ph_3P=$CHCO_2Me$. The ylide (7 mg, 0.02 mmol) is added to a solution of *trans*-[$PtCl_4$((*E*)-NH=C(Me)$OR)_2$] (R = Me, Et) or *cis*-[$PtCl_4$((*E*)-NH=C(Me)OEt)((*Z*)-NH=C(Me)OEt)] (0.02 mmol) in cold (0−5 °C) dichloromethane (2 mL). The reaction is complete after 4 h, whereupon the solvent is evaporated and the yellow residue formed is washed with two 2-mL portions of Et_2O, dissolved in a minimum amount of CH_2Cl_2 at room temperature and purified on silica gel (70−230 mesh; 60 Å, Aldrich) column. Eluation with CH_2Cl_2/Et_2O gives an individual complex from the first fraction.

***trans*-[$PtCl_2${(*E*)-NH=C(Me)OMe}$_2$] (24).** Yield: 50%. Anal. Calcd for $C_6H_{14}N_2Cl_2O_2Pt\cdot0.1Et_2O$: C, 18.32; H, 3.51; N, 6.68. Found: C, 18.0; H, 3.27; N, 6.30. FAB^+-MS, *m*/*z*: 412 [M]$^+$, 375 [M − HCl]$^+$, 339 [M − 2HCl]. TLC, R_f = 0.34 (eluent $CHCl_3$:Et_2O = 10:1). IR spectrum in KBr, selected bands, cm^{-1}: 3254 m ν(N−H), 2983 w and 2852 w ν(C−H), 1632 s ν(C=N), 1231 m ν(C−O), 349 w ν(Pt−Cl). ^{1}H NMR in $CDCl_3$, δ: 2.64 (s, 3*H*, =C*Me*O), 3.76 (s, 3*H*, OMe), 7.72 (s, br, 1*H*, NH) [lit.[15b] ^{1}H NMR in $CDCl_3$, δ: 2.64 (=C*Me*O), 3.76 (OMe), 7.72 (NH)]. ^{13}C{^{1}H} NMR in $CDCl_3$, δ: 21.41 (=C*Me*O), 55.0 (OMe), 171.2 (C=NH). ^{195}Pt NMR in $CDCl_3$, δ: −1914 (870 Hz).

***trans*-[$PtCl_2${(*E*)-NH=C(Me)OEt}$_2$] (25).** Yield: 40%. Anal. Calcd for $C_8H_{18}N_2Cl_2O_2Pt$: C, 21.83; H, 4.12; N, 6.36. Found: C, 21.77; H, 4.13; N, 6.31. FAB^+-MS, *m*/*z*: 368 [M − 2Cl − H]$^+$. TLC, R_f = 0.56 (eluent $CHCl_3$:Et_2O = 10:1). IR spectrum in KBr, selected bands, cm^{-1}: 3253 m ν(N−H), 2983 w ν(C−H), 1648 s ν(C=N), 1226 m ν(C−O), 350 m ν(Pt−Cl). ^{1}H NMR in $CDCl_3$, δ: 1.28 (t, 6.9 Hz, 3*H*, OCH_2CH_3), 2.63 (s, 3*H*, =C*Me*O), 4.03 (quart., 6.9 Hz, 3*H*, OCH_2CH_3), 7.58 (s, br, 1*H*, NH). ^{13}C{^{1}H} NMR in $CDCl_3$, δ: 13.7 (OCH_2CH_3), 21.7 (=C*Me*O), 63.9 (OCH_2CH_3), 170.6 (C=NH). ^{195}Pt NMR in $CDCl_3$, δ: −1910 (900 Hz).

***cis*-[$PtCl_2${(*E*)-NH=C(Me)OEt}{(*Z*)-NH=C(Me)OEt}] (26).** Yield: 55%. Anal. Calcd for $C_8H_{18}N_2Cl_2O_2Pt$: C, 21.83; H, 4.12; N, 6.36. Found: C, 22.08; H, 6.25; N, 4.19. FAB^+-MS, *m*/*z*: 463 [M + Na]$^+$, 440 [M]$^+$, 367 [M − 2HCl]$^+$. TLC, R_f = 0.32 (eluent $CHCl_3$:Et_2O = 3:1). IR spectrum in KBr, selected bands, cm^{-1}: 3236 m ν(N−H), 2990 w and 2824 w ν(C−H), 1646 s ν(C=N), 1231 m ν(C−O), 340 m and 321 w ν(Pt−Cl). ^{1}H NMR in $CDCl_3$, δ: 1.25 (t, 6.9 Hz, 3*H*, OCH_2CH_3, *E*), 1.42 (t, 6.9 Hz, 3*H*, OCH_2CH_3, *Z*), 2.25 (s, 3*H*, =C*Me*O, *Z*), 2.65 (s, 3*H*, =C*Me*O, *E*), 4.81 (quart., 6.9 Hz, 2*H*, OCH_2CH_3, *Z*), 4.07 (quart., 2*H*, 6.9 Hz, OCH_2CH_3, *E*), 7.70 (s, br, 1*H*, NH, *E*), 8.85 (s, br, 1*H*, NH, *Z*). ^{13}C{^{1}H} NMR in $CDCl_3$, δ: 15.1 and 13.7 (OCH_2CH_3), 21.7 and 22.3 (=C*Me*O), 66.3 and 64.9 (OCH_2CH_3), 171.4 and 173.4 (C=NH). ^{195}Pt NMR in $CDCl_3$, δ: −1953 (850 Hz).

Liberation of the Ligand from *trans*-[$PtCl_4${(*E*)-NH=C(Me)-OEt}$_2$]. Pyridine (0.03 mL, 0.4 mmol) is added to a solution of *trans*-[$PtCl_4${(*E*)-NH=C(Me)OEt}$_2$] (20 mg, 0.04 mmol) in $CDCl_3$ (0.5 mL) in an NMR tube, and the mixture is left to stand at 40 °C for 2 days, whereupon the liberated ligand, i.e., NH=C(Me)OEt, is identified by NMR methods (^{1}H NMR in $CDCl_3$, δ: 1.99 (s, 3*H*, Me), 4.07 (quart., 7.0 Hz, 2*H*, OCH_2CH_3), 1.26 (t, 7.0 Hz, OCH_2CH_3). ^{13}C{^{1}H} NMR in $CDCl_3$, δ: 61.2 (OCH_2CH_3), 23.8 (Me), 14.1 (OCH_2CH_3), 155.7 (C=N). Addition of water (0.03 mL) to the reaction mixture allowed the quantitative formation of ethyl acetate, which is derived from hydrolysis of NH=C(Me)OEt. Before the deliberate addition of water, ethyl acetate was detected in ca. 35% yield [with 65% yield of NH=C(Me)OEt], being derived from

the hydrolysis of NH═C(Me)OEt by the moisture contained in the NMR solvent.

Liberation of the Ligand from *trans*-[$PtCl_2${(*E*)-NH═C(Me)-OEt}$_2$]. Dppe (32 mg, 0.08 mmol) is added to a solution of *trans*-[$PtCl_4${(*E*)-NH═C(Me)OEt}$_2$] (20 mg, 0.04 mmol) in $CDCl_3$ (0.5 mL), and the mixture is left to stand for 10 min until a colorless precipitate of [Pt(dppe)$_2$]Cl_2 is released. The complex is filtered off, and NH═C(Me)OEt, liberated quantitatively, is identified in the filtrate by ^{1}H and ^{13}C{^{1}H} NMR methods (for spectral data see above).

X-ray Structure Determinations. Crystals suitable for X-ray diffraction analysis were obtained directly from the reaction mixtures. Diffraction data were collected on an Enraf-Nonius CAD-4 diffractometer. Cell parameters were obtained from 24 centered reflections with Θ between 11° and 13° (**2**), 12.8° and 13.9° (**10**), 11.6° and 12.5° (**11**), 11.7° and 12.5° (**12**), and 11.7° and 12.4° (**14**). Range of *hkl*: $h = 0$ to 8, $k = 0$ to 16, $l = -11$ to 11 for **2**; $h = 0$ to 10, $k = 0$ to 9, $l = -17$ to 16 for **10**; $h = 0$ to 7, $k = -9$ to 9, $l = -12$ to 12 for **11**; $h = 0$ to 10, $k = 0$ to 10, $l = -15$ to 15 for **12**; and $h = 0$ to 10, $k = 0$ to 13, $l = 0$ to 18 for **14**. Standard reflections were measured every 60 min and showed practically no change with time (±1%). Diffractometer data were processed by the program PROFIT[31] with profile analysis of reflections. The structures were solved by means of Fourier synthesis based upon the Pt atom coordinates obtained from the Patterson synthesis using the SHELXTL package.[32] After that, all reflections with $I < 2\sigma(I)$ were excluded from calculations. Refinement was done by full-matrix least squares based on F^2 using the SHELX-97 package.[33] All non-H atoms were treated anisotropically. H atoms were located in a difference Fourier map and refined isotropically. An extinction correction has been applied for **2**, **10**, **12**, and **14**. Lorentz, polarization, and absorption corrections were made.[34] Scattering factors were obtained from *International Tables for X-ray Crystallography*.[35] Crystal data are given in Table 1 and bond distances and angles in Tables 2−6.

Computational Details. The full geometry optimization of the *EE*, *EZ*, and *ZZ* isomers of the complexes *trans*-[$PtCl_2${NH═C(Me)-OMe}$_2$] and *trans*-[$PtCl_4${NH═C(Me)OMe}$_2$] has been carried out in Cartesian coordinates using the quasi-Newton−Raphson gradient method and the restricted Hartree−Fock approximation with help of the GAMESS program package.[36] The single-point calculations on the basis of the equilibrium Hartree−Fock geometries at the MP2//HF level of theory have been applied. Symmetry operations were not applied. For the platinum atom, the Stuttgart quasi-relativistic pseudopotential for 60 core electrons and the appropriate contracted basis set for the platinum atom[37] have been used. The standard basis set of Gauss functions 6-31G[38,39] was selected for all other atoms, and d-type polarization functions with exponent 0.75[39,40] were added for the Cl atoms.

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Supporting Information Available: 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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