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Kinetic and Mechanistic Study of the Pt(II) versus Pt(IV) Effect in the Platinum-Mediated Nitrile–Hydroxylamine Coupling

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The metal-mediated coupling between coordinated EtCN in the platinum(II) and platinum(IV) complexes *cis*- and *trans*-$[PtCl_2(EtCN)_2]$, *trans*-$[PtCl_4(EtCN)_2]$, a mixture of *cis*/*trans*-$[PtCl_4(EtCN)_2]$ or $[Ph_3PCH_2Ph][PtCl_n(EtCN)]$ ($n = 3, 5$), and dialkyl- and dibenzylhydroxylamines R_2NOH (R = Me, Et, CH_2Ph, $CH_2C_6H_4Cl$-*p*) proceeds smoothly in CH_2Cl_2 at 20–25 °C and the subsequent workup allowed the isolation of new imino species $[PtCl_n\{NH{=}C(Et)ONR_2\}_2]$ ($n = 2$, R = Me, *cis*-**1** and *trans*-**1**; Et, *cis*-**2** and *trans*-**2**; CH_2Ph, *cis*-**3** and *trans*-**3**; $CH_2C_6H_4Cl$-*p*, *cis*-**4** and *trans*-**4**; $n = 4$, R = Me, *trans*-**9**; Et, *trans*-**10**; CH_2Ph, *trans*-**11**; $CH_2C_6H_4Cl$-*p*, *trans*-**12**) or $[Ph_3PCH_2Ph][PtCl_n\{NH{=}C(Et)ONR_2\}]$ ($n = 3$, R = Me, **5**; Et, **6**; CH_2Ph, **7**; $CH_2C_6H_4Cl$-*p*, **8**; $n = 5$, R = Me, **13**; Et, **14**; CH_2Ph, **15**; $CH_2C_6H_4Cl$-*p*, **16**) in excellent to good (95–80%) isolated yields. The reduction of the Pt(IV) complexes **9**–**16** with the ylide $Ph_3P{=}CHCO_2Me$ allows the synthesis of Pt(II) species **1**–**8**. The compounds **1**–**16** were characterized by elemental analyses (C, H, N), FAB-MS, IR, ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR (the latter for the anionic type complexes **5**–**8** and **13**–**16**) and by X-ray crystallography for the Pt(II) (*cis*-**1**, *cis*-**2**, and *trans*-**4**) and Pt(IV) (**15**) species. Kinetic studies of addition of R_2NOH (R = $CH_2C_6H_4Cl$-*p*) to complexes $[Ph_3PCH_2Ph][Pt^{II}Cl_3(EtCN)]$ and $[Ph_3PCH_2Ph][Pt^{IV}Cl_5(EtCN)]$ by the ^1H NMR technique revealed that both reactions are first order in $(p\text{-}ClC_6H_4CH_2)_2NOH$ and Pt(II) or Pt(IV) complex, the second-order rate constant k_2 being *three orders of magnitude* larger for the Pt(IV) complex. The reactions are intermolecular in nature as proved by the independence of k_2 on the concentrations of added EtC≡N and Cl^-. These data and the calculated values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are consistent with the mechanism involving the rate-limiting nucleophilic attack of the oxygen of $(p\text{-}ClC_6H_4CH_2)_2NOH$ at the *sp*-carbon of the C≡N bond followed by a fast proton migration.

Introduction

Reactivity of ligated nitriles has been an area of continuous interest for many years owing to their great industrial potential (e.g., for preparation of acrylamide or nicotineamide) and a variety of laboratory applications (e.g., as synthons of a broad range of imines and amides) for metal-mediated RCN reactions. In addition, nitriles are isoelectronic to other important species such as N_2, CO, RNC, and alkynes, and their behavior as ligands can model, to a certain degree, transformations of other coordinated molecules. Metal-mediated and/or metal-catalyzed reactions of RCN have been surveyed in a number of articles[1−7] including those written by some of us.[1−4]

Recently, our group has been involved in studies of the reactivity of metal-activated nitriles toward HON-nucleo-

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philes.[4] It has been observed that reactions between (RCN)[M] (M = Pt(IV), Pt(II), Rh(III), Re(IV)) complexes and HON-species such as "simple" oximes,[8−14] *vic*-dioximes,[15] oximehydrazones,[16] dialkyl hydroxylamines,[17] and hydroxamic acids[18,19] lead to formation of a C−O{N} bond upon addition of the OH group at the C≡N moiety of metal-activated RCN. It is worthwhile to notice that in the initial stage of the project, the reactions between nitriles and HON-nucleophiles observed at substitutionally *inert* metal complexes (mostly of platinum group metals) had purely a basic research character, whereas later—being performed at kinetically *labile* metal centers (for instance, Co(III),[20] Ni(II),[21,22] and Zn(II)[23,24])—these systems acquired a more applied character insofar as they opened up attractive routes to syntheses of important classes of nitrile-derived organic compounds such as amidines,[20] acyl amides,[21] imidoylamidines,[21] phthalocyanines[22] and carboxamides.[23,24] The latter findings gave a new strong impact for further exploration of the nitrile reactions with HON-type nucleophiles from a combined viewpoint of their synthetic value, recognition of general features, understanding of driving forces, and estimate of activation effects by different metal centers.

As far as the latter effect is concerned, one should notice that despite the wealth of kinetic data associated with nucleophilic addition to ligated nitriles at *diverse* metal centers, the qualitative comparison of activation effect of nitriles by *one* metal center in different oxidation states has been done only for octahedral Ru(III) and Ru(II) complexes in the hydration reaction;[3] no kinetic data on systems of one metal center in different oxidation states and different polyhedra were obtained up to date.

Upon our study of the reaction between (nitrile)Pt complexes and $HONR_2$ (R = alkyl, benzyl), we discovered that hydroxylamines react with RC≡N at both octahedral Pt(IV) and square-planar Pt(II) centers of the structurally related complexes $[PtCl_n(RCN)]^-$ (n = 3, 5). This finding prompted us to undertake a comprehensive synthetic, structural, and kinetic study to verify the difference in the activation effect between the complexes in the two oxidation states. All these results are described in this article.

Results and Discussion

Starting Materials for Synthetic and Kinetic Studies. The nitrile platinum(II) and platinum(IV) complexes $[Ph_3PCH_2Ph][PtCl_n(EtCN)]$ (n = 3 **I**,[11] 5 **II**[11]) and *cis*- and *trans*-$[PtCl_n(EtCN)_2]$ (n = 2: *cis*-**III** and *trans*-**III**;[25,26] n = 4: a mixture of *cis/trans*-**IV** and *trans*-**IV**[27]) were addressed for this study (starting materials are given in this article in Roman numerals, whereas products are given in Arabic numerals). The complex *trans*-$[PtCl_2(EtCN)_2]$ (*trans*-**III**) was prepared by solid-state heating of *cis*-$[PtCl_2(EtCN)_2]$[26] (*cis*-**III**) (route **A**). The chlorination of *trans*-**III** leads to formation of the platinum(IV) complex *trans*-$[PtCl_4(EtCN)_2]$[27] (*trans*-**IV**) (route **B**). Interaction of *cis*- or *trans*-**III** with $[Ph_3PCH_2Ph]Cl$ allows the isolation of $[Ph_3PCH_2Ph][PtCl_3(EtCN)]$[11] (**I**) (routes **C1** and **C2**), and chlorination of the latter results in the formation of $[Ph_3PCH_2Ph][PtCl_5(EtCN)]$[11] (**II**) (route **D**).

Platinum-Mediated Nitrile−Hydroxylamine Coupling. Hydroxylamine is an ambidentate nucleophile and its *N*- and *O*- addition to nitriles is known in organic chemistry.[28] In the majority of cases, NH_2OH adds to RC≡N via its N atom to form amidoximes, $RC(NH_2)$═NOH, through the

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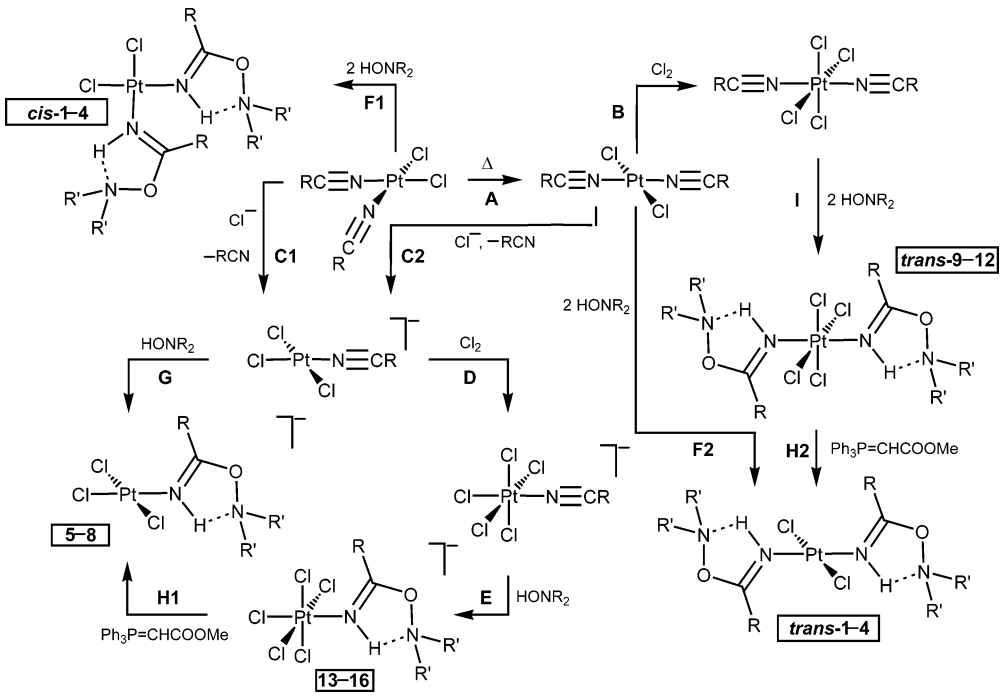
Scheme 1



RC(═NH)NHOH intermediate.[28] Very recently, it has been established that the addition of dialkylhydroxylamines to Pt(IV)-bound nitriles, in contrast to the reaction of hydroxyalmines with free nitriles, affords the imino species RC(═NH)ONR$_2$ resulting from adding of the hydroxylamines oxygen to RC≡N, route **I**.[17] Within the framework of the current project this addition is now extended to, on one hand, the anionic type Pt(IV) complex **II**, and, on the other hand, to di*benzyl*hydroxylamines. Moreover, we also found that the nitrile−hydroxylamine coupling is also mediated by the Pt(II) center although less effectively as compared to the Pt(IV) one.

Thus, the coupling between Pt-bound nitriles in **I**, **II**, *cis*- and *trans*-**III**, *trans*-**IV**, or a mixture of *cis*/*trans*-**IV** and dialkyl- and dibenzylhydroxylamines R$_2$NOH (R = Me, Et, CH$_2$Ph, CH$_2$C$_6$H$_4$Cl-*p*) proceeds smoothly in CH$_2$Cl$_2$ at 20−25 °C and the subsequent workup provides the new imino species [PtCl$_n${NH═C(Et)ONR$_2$}$_2$] (*n* = 2, R = Me, *cis*-**1** and *trans*-**1**; Et, *cis*-**2** and *trans*-**2**; CH$_2$Ph, *cis*-**3** and *trans*-**3**; CH$_2$C$_6$H$_4$Cl-*p*, *cis*-**4** and *trans*-**4**; *n* = 4, R = Me, *trans*-**9**; Et, *trans*-**10**; CH$_2$Phn *trans*-**11**; CH$_2$C$_6$H$_4$Cl-*p*, *trans*-**12**) or [Ph$_3$PCH$_2$Ph][PtCl$_n${NH═C(Et)ONR$_2$}] (*n* = 3, R = Me, **5**; Et, **6**; CH$_2$Ph, **7**; CH$_2$C$_6$H$_4$Cl-*p*, **8**; *n* = 5, R = Me, **13**; Et, **14**; CH$_2$Ph, **15**; CH$_2$C$_6$H$_4$Cl-*p*, **16**) in excellent to good (95−80%) isolated yields. In the preparative experiments, the coupling proceeds faster for the Pt(IV) species than for the Pt(II) compounds; neutral complexes react faster than the corresponding anionic ones. Thus, the formation of *trans*-[PtCl$_4${NH═C(Et)ONR$_2$}$_2$] (**9**−**12**) in reaction **I** was achieved for ca. 5 min, the formation of [Ph$_3$PCH$_2$Ph][PtCl$_5${NH═C(Et)ONR$_2$}] (**13**−**16**) in reaction **E** was complete after ca. 15 min, and the formation of *cis*- and *trans*-[PtCl$_2${NH═C(Et)ONR$_2$}$_2$] (**1**−**4**) in reactions **F1** and **F2** was achieved for ca. 0.5−2 h, whereas the generation of [Ph$_3$PCH$_2$Ph][PtCl$_3${NH═C(Et)ONR$_2$}] (**5**−**8**) in reaction **G** was accomplished for ca. 4−8 h. The absence of interaction between any of the studied hydroxylamine and free EtCN (proved by ^{1}H NMR) is in accord with a metal-mediated coupling.

Treatment of **9**−**16** with Ph$_3$P═CHCO$_2$Me leads to the reduction of the Pt(IV) center and allows the synthesis of Pt(II) species **1**−**8** by routes **H1** and **H2**, which are alternative to **G** and **F2**, respectively.

Characterization of the Imino Complexes. Elemental analyses (C, H, N), FAB-MS, IR, ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR (the latter for the anionic type complexes **5**−**8** and **13**−**16**) and X-ray data (see below) for the Pt(II) (*cis*-**1**, *cis*-**2**, and *trans*-**4**) and Pt(IV) (**15**) species are in good agreement with the proposed structures of Pt(II) and Pt(IV) complexes with the newly formed imino ligands NH═C(Et)ONR$_2$. In IR spectra, the products of the reactions (**1**−**16**) show no bands of ν(C≡N) stretching vibrations in the range 2270−2400 cm^{-1} (note that such bands appear at 2340 cm^{-1} for *trans*-[PtCl$_4$(EtCN)$_2$][27] and 2314 cm^{-1} for *trans*-[PtCl$_2$(EtCN)$_2$][25]) but display intense bands in the range of 1660−1640 cm^{-1} assigned to ν(C═N) of the imino ligand NH═C(Et)ONR$_2$; these data are in a very good agreement with those for similar complexes derived from the addition of oximes (e.g., [PtCl$_2${NH═C(Me)ON═CMe$_2$}$_2$] or [PtCl$_4${NH═C(Me)ON═CMe$_2$}$_2$][8−14]), hydroxylamines (e.g., *trans*-[PtCl$_4${NH═C(Me)ONEt$_2$}$_2$][17]), and hydroxamic acids (e.g., [PtCl$_4${NH═C(Et)ON═C(OH)(Ph)}$_2$][18,19]) to Pt-bound nitriles. Furthermore, IR spectra of the anionic complexes **5**−**8** and **13**−**16** display the vibrations of very high intensity at ca. 1110 cm^{-1} due to ν(P−C)[11] from the cation [Ph$_3$PCH$_2$Ph]$^+$; these bands are also observed in the chloride [Ph$_3$PCH$_2$Ph]Cl (1120 cm^{-1}).

^{1}H NMR spectra of **1**−**16** display a broad peak in the range δ 8.00−8.50 assigned to the imine hydrogen of the NH═C(Et)ONR$_2$ moiety involved in hydrogen bonding

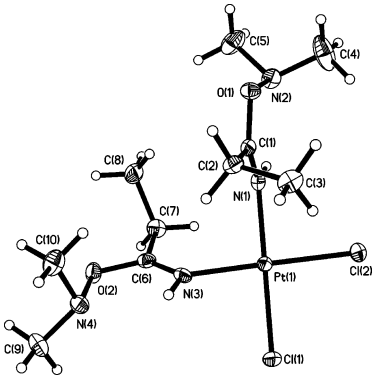


Figure 1. Crystal structure of *cis*-[$PtCl_2${NH═C(Et)ONMe$_2$}] (*cis*-**1**).

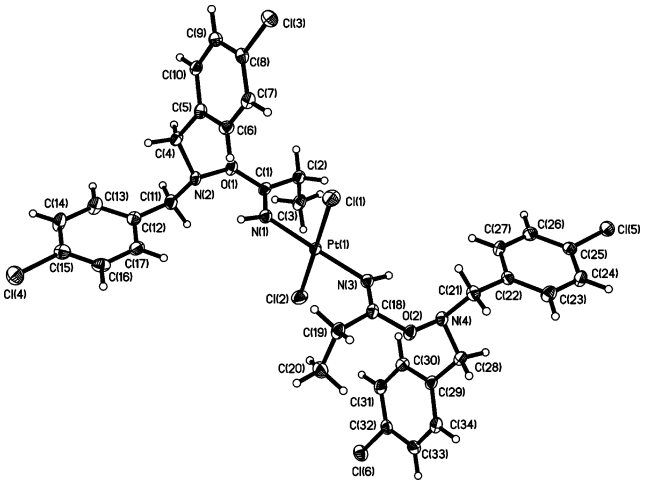


Figure 2. Crystal structure of *trans*-[$PtCl_2${NH═C(Et)ON(CH$_2$C$_6$H$_4$Cl-*p*)}$_2$] (*trans*-**4**).

(found also in the solid-state molecular structures, see later) and these data correspond well to those for the similar imino complexes, e.g., [$PtCl_n${NH═C(R)R′}$_2$] (R′ = ONR$_2$″,[17] ON═CR$_2$″,[8−14] OHNC(═O)R″[18,19]). ^{13}C{^{1}H} NMR spectra of **1**−**16** display no signal of the C≡N group from the starting material (typically it emerges in the range 115−125 ppm; e.g., 119 ppm for *trans*-[$PtCl_4$(EtCN)$_2$][27]) but show the signal from the C═N group in the range of 160−170 ppm. The position of the latter peak is similar to that observed for *trans*-[$PtCl_4${NH═C(Me)ONMe$_2$}$_2$].[17]

X-ray Structure Determinations. The X-ray structure determinations have been performed for four compounds, i.e., *cis*-[$PtCl_2${NH═C(Et)ONMe$_2$}] (*cis*-**1**), *cis*-[$PtCl_2$-{NH═C(Et)ONEt$_2$}] (*cis*-**2**), *trans*-[$PtCl_2${NH═C(Et)-ON(CH$_2$C$_6$H$_4$Cl-*p*)$_2$] (*trans*-**4**), and [Ph_3PCH_2Ph][$PtCl_5$-{NH═C(Et)ON(CH$_2$Ph)$_2$}] (**15**) (Figures 1−3 and Tables 1 and 2). The coordination polyhedra of the three Pt(II) complexes are slightly distorted square-planar and the imino ligands are mutually cis for *cis*-**1**, *cis*-**2** and trans for *trans*-**4** and are in the *E*-configuration.

The Pt−Cl and Pt−N bond lengths and also all bond angles around the Pt center are normal and they are in a good agreement with those for the related complexes, *trans*-[$PtCl_2${NH═C(Et)ON═C(Me)C(Me)(═O)}$_2$][12] and *trans*-[$PtCl_2${NH═C(Me)ON═CMe$_2$}$_2$].[9] The Pt−Cl bond distances in the complexes with the trans [*trans*-**4** 2.2982(8), 2.3069(8) Å] and cis configurations [*cis*-**1** 2.3018(12),

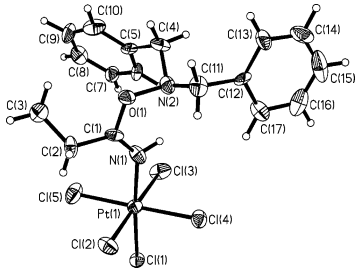


Figure 3. Crystal structure of [Ph_3PCH_2Ph][$PtCl_5${NH═C(Et)ON(CH$_2$-Ph)$_2$}] (**15**). The cation is omitted for clarity. Selected bond lengths (Å) and angles (deg): Pt(1)−N(1) 2.039(12), Pt(1)−Cl(1) 2.298(3), Pt(1)−Cl-(2) 2.320(3), Pt(1)−Cl(3) 2.318(3), Pt(1)−Cl(4) 2.318(4), Pt(1)−Cl(5) 2.315(4), N(1)−C(1) 1.301(16), C(1)−O(1) 1.350(15), N(1)−Pt(1)−Cl(1) 175.3(3), Cl(4)−Pt(1)−Cl(5) 179.09(15), Cl(2)−Pt(1)−Cl(3) 178.28(15), Pt(1)−N(1)−C(1) 136.1(10), N(1)−C(1)−O(1) 119.5(13).

2.3021(13), and *cis*-**2** 2.3041(9), 2.3046(8) Å] are the same within 3σ and this indicates that the ground-state trans influence is similar for the imine and chloride species. The two C═N bonds in each complex are equal within 3σ [1.254(7) and 1.275(7) Å for *cis*-**1**; 1.271(4) and 1.273(4) Å for *cis*-**2**; 1.272(4) and 1.277(4) Å for *trans*-**4**] and they are very close to the typical values of the C═N double bonds.[29]

Inspection of the N−H and NH···N distances and values of the H−N···H angles in the imine ligands clearly indicates that the *E*-configuration of these species is stabilized by the N−H···H hydrogen bond between the imine hydrogen and the hydroxylamine N atom with the following observed distances and angles: N(1)−H(01) 0.95(7) Å, N(1)−H(01)···N(2) 2.20(2) Å, N(1)−H(01)···N(2) 105(6)°, N(3)−H(03) 0.96(6) Å, N(3)−H(03)···N(4) 2.14(6) Å, N(3)−H(03)···N(4) 109(5)° *cis*-**1**; N(1)−H(01) 0.89 Å, N(1)−H(01)···N(2) 2.28 Å, N(1)−H(01)···N(2) 107.8°, N(3)−H(03) 0.99 Å, N(3)−H(03)···N(4) 2.06 Å, N(3)−H(03)···N(4) 117.5° *cis*-**2**; and N(1)−H(01) 0.88(4) Å, N(1)−H(01)···N(2) 2.15(3) Å, N(1)−H(01)···N(2) 115(3)°, N(3)−H(03) 0.84(4) Å, N(3)−H(03)···N(4) 2.24(3) Å, N(3)−H(03)···N(4) 112(3)° for trans-**4**. This H-bonding was also observed in the relevant complexes *trans*-[$PtCl_4${NH═C(Me)ON═CR}$_2$][8] and *trans*-[$PtCl_4${NH═C(Me)ONR$_2$}$_2$].[17]

In **15** (see Figure 3), all bond lengths and angles are normal and agree well with those in the previously studied neutral (imino)Pt(IV) complexes *trans*-[$PtCl_4${NH═C(Me)ONR$_2$}$_2$] (Figure 3).[17]

Kinetics of the Nucleophilic Addition. The structurally related platinum(II) and platinum(IV) complexes [Ph_3PCH_2Ph][$PtCl_n$(EtCN)] **I** (*n* = 3) and **II** (*n* = 5), respectively, are well soluble in $CDCl_3$ and have been selected for the kinetic investigation using the ^{1}H NMR technique. They contain only one nitrile ligand and are more appropriate for collecting and interpreting kinetic data as compared to the more common bis-nitrile complexes [$PtCl_n$(RCN)$_2$], where two consecutive processes should be taken into account. In addition, the ^{1}H NMR spectra of [$PtCl_n$(EtCN)]$^-$ are less complicated as compared with those of the bis-nitrile compounds and this allows an accurate integration of the signals from the Et groups of the starting

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Table 1. Crystallographic Data for *cis*-**1**, *cis*-**2**, *trans*-**4**, and **15**

	cis-**1**	*cis*-**2**	*trans*-**4**	**15**
empirical formula	$C_{10}H_{24}N_4Cl_2O_2Pt$	$C_{14}H_{32}N_4Cl_2O_2Pt$	$C_{34}H_{36}N_4Cl_6O_2Pt$	$C_{42}H_{42}N_2Cl_5OPPt$
fw	498.32	554.43	940.46	994.09
temp (K)	110(2)	110(2)	100(2)	150(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073
cryst syst	triclinic	monoclinic	monoclinic	orthorhombic
space group	$P\bar{1}$	$P2_1/c$	$P2_1$	*Pbca*
a (Å)	8.2530(15)	11.2917(16)	13.1961(4)	10.0914(7)
b (Å)	9.9420(12)	13.2252(15)	10.3787(2)	19.504(2)
c (Å)	10.670(2)	14.9965(14)	13.3755(4)	42.279(5)
α (deg)	103.695(10)	90	90	90
β (deg)	91.346(15)	99.251(11)	101.7230(10)	90
γ (deg)	92.089(13)	90	90	90
V (Å^3)	1793.68(8)	2210.4(5)	1793.68(8)	8321.3(15)
Z	2	4	2	8
ρ_{calc} (Mg/m^3)	1.741	1.666	1.741	1.587
μ(Mo Kα) (mm^{-1})	4.396	6.602	4.396	3.767
no. of collected reflns	8293	29451	27046	16000
no. of unique rflns	3196	5073	8162	4383
R1[a] ($I \geq 2\sigma$)	0.0300	0.0221	0.0195	0.0570
*w*R2[b] ($I \geq 2\ \sigma$)	0.0724	0.0406	0.0457	0.1107

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

Table 2. Selected Bond Lengths and Angles for the Platinum(II) Complexes *cis*-**1**, *cis*-**2**, and *trans*-**4**

	cis-**1**	*cis*-**2**	*trans*-**4**
Pt(1)−Cl(1)	2.3018(12)	2.3041(8)	2.2982(8)
Pt(1)−Cl(2)	2.3021(13)	2.3047(8)	2.3068(8)
Pt(1)−N(1)	2.020(4)	2.020(2)	2.020(3)
Pt(1)−N(3)	2.015(4)	2.014(2)	2.015(3)
N(1)−C(1)	1.254(7)	1.271(4)	1.272(4)
N(3)−C(6)	1.275(7)		
N(3)−C(8)		1.273(4)	
N(3)−C(18)			1.277(4)
Cl(1)−Pt(1)−Cl(2)	92.75(5)	91.94(3)	178.73(3)
N(1)−Pt(1)−N(3)	93.4(2)	90.67(10)	178.29(11)
Pt(1)−N(1)−C(1)	127.7(3)	127.9(2)	126.9(2)
Pt(1)−N(3)−C(6)	129.3(3)		
Pt(1)−N(3)−C(8)		128.8(2)	
Pt(1)−N(3)−C(18)			129.0(2)

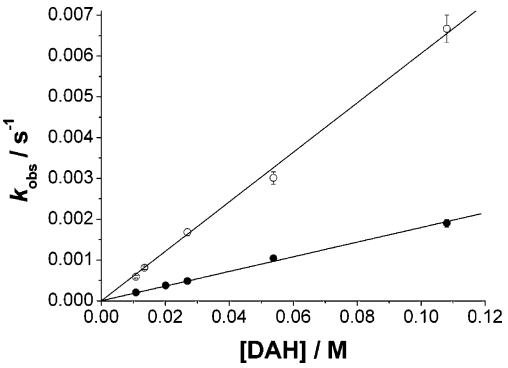

Figure 4. Pseudo-first-order rate constants k_{obs} as a function of [DAH] for reactions 1 (○) and 2 (●) at 40.0 and −20.0 °C, respectively, in $CDCl_3$ as solvent; [**I**] = [**II**] = 1.35×10^{-3} M.

material and the product. Complexes **I** and **II** react via eqs 1 and 2 (Scheme 2), respectively, which are again rather similar but the reactivity of **I** is significantly lower than that of **II**.

Major kinetic data for complexes **I** and **II** have been obtained at different temperatures, viz. −20.0 and 40.0 °C, respectively. Under such conditions, the reactions are complete in a matter of 0.5−1 h. A satisfactory pseudo-first-order behavior has been observed for both complexes in the presence of an excess of the hydroxylamine (p-$ClC_6H_4CH_2)_2$-NOH (DAH). A first order in complexes **I** and **II** holds for at least 3−5 half-lives. The dependences of pseudo-first-order rate constants k_{obs} against the concentration of DAH indicate a first order in the incoming nucleophile for **I** and **II** without any significant intercept (Figure 4). Thus, reactions 1 and 2 follow the same rate law 3.

$$k_{obs} = k_2[\mathrm{DAH}] \quad (3)$$

The second-order rate constants k_2 have been obtained at different temperatures (Table 3) and these data have been used for calculating the corresponding activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for reactions 1 and 2, which are also included in Table 3. The rate constants k_2 are unaffected by the presence of a large excess of free propionitrile. Indeed, the same values of k_2 have been obtained in the presence of 100-fold excess of EtCN relative to **I** or **II**. Free propionitrile does not react with DAH in chloroform even under harsh conditions (1 week at 45 °C).

In principle, reactions 1 and 2 could involve a reversible substitution of chloride by DAH followed by an intramolecular nucleophilic attack at the coordinated nitrile. Therefore, the effect of chloride on k_2 has been tested by the example of reaction 1 at 40 °C. Addition of $[Ph_3PCH_2Ph]Cl$ does not practically affect the rate constants and k_2 equals 0.77 ± 0.01, 0.73 ± 0.04, and 0.70 ± 0.03 M^{-1} s^{-1} at [Cl^-] = 0.0, 0.013, and 0.135 M, respectively. We could not measure the effect of chloride on the rate of reaction 2 due to the substitution of EtCN by chloride that occurs via eq 4.

$$\mathbf{II} + [Ph_3PCH_2Ph]Cl \rightarrow [Ph_3PCH_2Ph]_2[PtCl_6] + EtCN \quad (4)$$

Ligand substitution reaction 4 involves the Pt(IV) complex and a nucleophile (Cl^-). The observation that complex **II** reacts with chloride but complex **I** does not is in accordance with the fact that the Pt(IV) complex is more electrophilic and therefore the reactivity of **II** is also higher with respect

Scheme 2

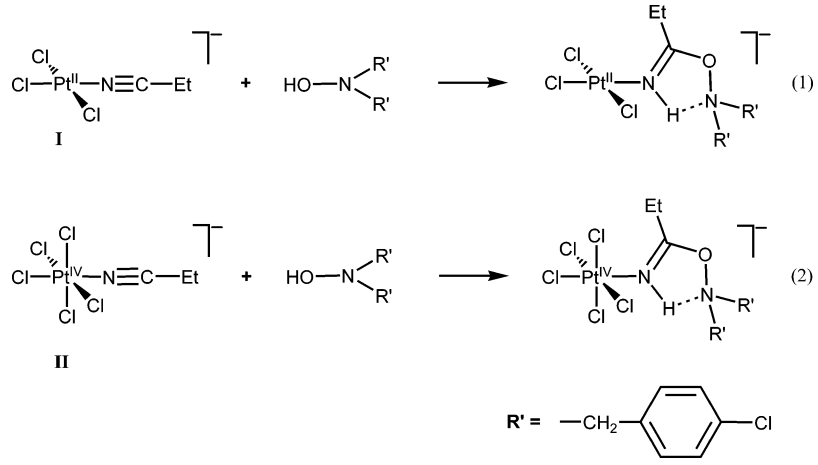

Table 3. Kinetic and Activation Parameters for Reactions 1 and 2 in $CDCl_3$

T/°C	[DAH]/M	k_{obs}/s^{-1}	k_2/M^{-1} s^{-1}	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J mol^{-1} K^{-1}
		Reaction 2			
−30.0	5.38×10^{-2}	$(8.1 \pm 0.4) \times 10^{-4}$	$(1.5 \pm 0.1) \times 10^{-2}$	56 ± 6	-47 ± 23
−20.0	1.08×10^{-2}	$(5.9 \pm 0.3) \times 10^{-4}$	$(6.1 \pm 0.4) \times 10^{-2}$		
	1.35×10^{-2}	$(8.1 \pm 0.4) \times 10^{-4}$			
	2.69×10^{-2}	$(1.7 \pm 0.1) \times 10^{-3}$			
	5.38×10^{-2}	$(3.0 \pm 0.2) \times 10^{-3}$ [a]			
	1.08×10^{-1}	$(6.7 \pm 0.3) \times 10^{-3}$			
−15.0	5.38×10^{-2}	$(4.1 \pm 0.4) \times 10^{-4}$	$(7.7 \pm 0.4) \times 10^{-2}$		
−10.0	5.38×10^{-2}	$(7.5 \pm 0.3) \times 10^{-3}$	$(1.4 \pm 0.1) \times 10^{-1}$		
		Reaction 1			
20.0	5.38×10^{-2}	$(1.1 \pm 0.2) \times 10^{-4}$	$(2.2 \pm 0.1) \times 10^{-3}$	74 ± 3	-41 ± 10
30.0	5.38×10^{-2}	$(3.5 \pm 0.4) \times 10^{-4}$	$(6.5 \pm 0.3) \times 10^{-3}$		
40.0	1.08×10^{-2}	$(2.1 \pm 0.1) \times 10^{-4}$	$(1.9 \pm 0.1) \times 10^{-2}$		
	2.01×10^{-2}	$(3.8 \pm 0.2) \times 10^{-4}$			
	2.69×10^{-2}	$(4.8 \pm 0.2) \times 10^{-4}$			
	5.38×10^{-2}	$(1.0 \pm 0.1) \times 10^{-3}$ [b]			
	1.08×10^{-1}	$(1.9 \pm 0.1) \times 10^{-3}$			
50.0	5.38×10^{-2}	$(2.1 \pm 0.2) \times 10^{-3}$	$(4.0 \pm 0.2) \times 10^{-2}$		

[a] $(3.5 \pm 0.2) \times 10^{-3}$ s^{-1} for $(PhCH_2)_2NOH$. [b] $(1.28 \pm 0.07) \times 10^{-3}$ s^{-1} for $(PhCH_2)_2NOH$.

to the hydroxylamine nucleophile DAH. Limited data obtained for $(PhCH_2)_2NOH$ as a nucleophile (see footnote to Table 3) indicate that this more nucleophilic hydroxylamine reacts somewhat faster as compared to $(p\text{-}ClC_6H_4CH_2)_2NOH$ (DAH), as could be anticipated.

The addition of hydroxylamines to nitriles coordinated to Pt(II) and Pt(IV) is a true nucleophilic reaction where the platinum centers enhance immensely the reactivity of propionitrile. The kinetic data suggest that it is always the coordinated nitrile that reacts with the hydroxylamine and the nucleophilic attack occurs from the bulk solution. Clear first-order kinetics in hydroxylamine for both Pt(II) and Pt(IV) complexes (Figure 4) and the absence of inhibition by added chloride agrees with the fact that hydroxylamine does not coordinate platinum(II) or (IV) before the addition across the C≡N bond. In other words, reactions 1 and 2 are true *inter*molecular processes. The negative values of entropies of activation $\Delta S^{\ddagger}$ (Table 3) agree with the bimolecular character of the reactions.[30,31] The more nucleophilic dibenzyl hydroxylamine reacts somewhat faster than DAH supporting the nucleophilic nature of the reactions.

The platinum(IV) complex **II** is notably more reactive than its platinum(II) counterpart **I**. The difference in the reactivity of compounds **II** and **I** leads to faster kinetics (k_2) in the former by a factor of 1.4×10^3 at 0 °C. The k_2 ratio was calculated by using the values of activation parameters from Table 3. Recent theoretical studies[32] suggest that although nitriles exhibit both weak σ-donor and π-acceptor properties, the σ-donor features prevail even for the Pt(II) complexes. An increase in the oxidation state of platinum from II to IV results in a stronger shift of the electron density from the ligand to the metal. Hence, the nitrile should be more electron-deficient in complex **II** and this facilitates the nucleophilic attack at the ligand bound to Pt(IV). Analysis

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of the frontier molecular orbitals of the dinitrile complexes *trans*-$[PtCl_2(NCMe)_2]$ and *trans*-$[PtCl_4(NCMe)_2]$[11,32] indicates that the energy of the empty π^*(CN) MO in the Pt(IV) complex is lower as compared with the Pt(II) species. Thus, the higher reactivity of the Pt(IV) species can also be accounted for in terms of the frontier orbital energy difference. Note the free energy of activation $\Delta G^{\ddagger}$ that can be calculated from the data in Table 3 is by 16 kJ mol^{-1} (at 0 °C) lower in reaction 2 involving the Pt(IV) species.

The general mechanism of addition of hydroxylamines to nitriles coordinated to Pt(II) and Pt(IV) complexes should involve the rate-limiting nucleophilic attack of the hydroxylamine oxygen at the *sp*-carbon of the C≡N group of coordinated nitrile followed by a fast proton migration. It is interesting to note that ligand substitution at Pt(II) and Pt(IV) centers generally occurs via different mechanisms, i.e., associative and dissociative, respectively.[31] Our study has shown that the kinetic features of reactions 1 and 2 are strikingly similar. This may indicate that ligand substitution is not involved in these processes, thus supporting the suggested mechanism.

Final Remarks

Qualitatively the activation effect of a metal center toward the nucleophlic attack at the coordinated RCN can be estimated by analyzing IR spectra of free and ligated nitriles. Thus, the ν(C≡N) stretching vibrations of (nitrile)Pt(II) complexes exhibit positive coordination shift values of $\Delta\nu = \nu(C{\equiv}N)_{coord} - \nu(C{\equiv}N)_{free} \approx 50$ cm^{-1} indicating[5] the increased electrophilic susceptibility of the nitrile carbon. Moreover, this shift is even more positive on going from platinum(II) to the relevant platinum(IV) species [e.g., ν(C≡N) 2314 and 2340 cm^{-1} for *trans*-$[PtCl_n(EtCN)_2]$[25,27] (n = 2, 4), respectively] and this comparison favors the higher activation of RCN, toward the nucleophilic attack, by a Pt(IV) center. In general, the nucleophilic additions to Pt(II)- and Pt(IV)-bound nitriles proceed under strictly different conditions[1,4,8,33] and this hampered the qualitative comparison of the activation effect by the two Pt metal centers.

In the current work, we discovered that the coupling between EtCN and R_2NOH proceeds in a similar way, albeit with substantially different rates, in the structurally related platinum(II) and platinum(IV) complexes $[Ph_3PCH_2Ph][PtCl_n(EtCN)]$ (n = 3, 5). This finding prompted further kinetic study and, eventually, allowed the *first quantitative comparison* of the activation effect of the Pt centers in different oxidation states toward RCN species. The actual activating effect of nitriles by Pt(IV) versus Pt(II) is 3 orders of magnitude when coordinated propionitrile reacts with $(p\text{-}ClC_6H_4CH_2)_2NOH$. This reactivity difference, on one hand, explains the previous preparative observations, i.e., (*i*) weak HO-nucleophiles such as oximes, under mild conditions, react with RCN in (nitrile)Pt(IV) complexes, whereas they are unreactive when treated with (nitrile) Pt(II) species;[11] (*ii*) alcohols[33] or water[3] react easily with (nitrile)Pt(IV) complexes without added OH^-, whereas these reactions with (nitrile)Pt(II) complexes require the addition of an alkali to perform the addition. On the other hand, the kinetic data also suggest that synthetic chemists could take advantage of the stronger electrophilic activation power of a Pt(IV) center of RCN ligands to form, upon addition followed by reduction, final (imine)Pt(II) complexes which otherwise would not be accessible.

Experimental Section

Materials and Instrumentation. Hydroxylamines were purchased from Aldrich. Solvents were obtained from commercial sources and used as received. C, H, and N elemental analyses were carried out by the Microanalytical Service of the Instituto Superior Técnico. For TLC, Merck UV 254 SiO_2-plates have been 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 JASCO FTS 3000MX instrument in KBr pellets. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were measured on a Varian UNITY 300 spectrometer at ambient temperature.

Synthetic Work. Addition of R_2NOH to $[PtCl_2(EtCN)_2]$. In a typical experiment, the isomerically pure *trans*-**III** (0.10 g, 0.266 mmol) [or a mixture of *cis/trans*-**III**] which contains, by NMR and TLC, ca. 80% of the cis isomer[25,26]] is dissolved in chloroform (5 mL) at 20−25 °C, the hydroxylamine (0.522 mmol) is added, and the reaction mixture is left to stand for 3 h at room temperature. The bright yellow solution is evaporated to dryness at room temperature under a flow of N_2 and the solid residue is washed with diethyl ether (five 3-mL portions) to remove the excess of the hydroxylamine. Yields are 95−90%, based on Pt. In the case of *trans*-**III** only the isomerically pure *trans*-$[PtCl_2\{NH{=}C(Et)ONR_2\}_2]$ was isolated, otherwise the mixture of *cis/trans* isomers was obtained. In the latter case, the isomers were separated by chromatography on SiO_2.

***trans*-$[PtCl_2\{NH{=}C(Et)ONMe_2\}_2]$ (*trans*-1).** Anal. Calcd for $C_{10}H_{24}N_4Cl_2O_2Pt$: C, 24.10; H, 4.85; N, 11.24%. Found: C, 24.05; H, 4.80; N, 11.00%. FAB-MS, *m*/*z*: 498 $[M]^+$, 463 $[M - Cl]^+$, 427 $[M - 2Cl]^+$. IR spectrum (selected bands), cm^{-1}: 3225 mw ν(N−H), 1661 s ν(C═N), 1438 s ν(C═C), 750 s δ(C−H). ^1H NMR spectrum in $CDCl_3$, δ: 1.37 (t, J = 7.5 Hz, 3*H*, CH_2*Me*), 2.76 (s, 6*H*, N*Me*), 2.92 (q, J = 7.5 Hz, 2*H*, C*H*$_2$Me), 8.05 (s, br, 1*H*, N*H*). $^{13}C\{^1H\}$ NMR spectrum in $CDCl_3$, δ: 10.2 (CH_3), 21.1 (CH_2)-(Et), 47.2 (Me, NMe), 176.5 (HN═C).

***cis*-$[PtCl_2\{NH{=}C(Et)ONMe_2\}_2]$ (*cis*-1).** Anal. Calcd for $C_{10}H_{24}N_4Cl_2O_2Pt$: C, 24.10; H, 4.85; N, 11.24%. Found: C, 24.00; H, 4.84; N, 11.20%. FAB-MS, *m*/*z*: 498 $[M]^+$, 463 $[M - Cl]^+$, 427 $[M - 2Cl]^+$. IR spectrum (selected bands), cm^{-1}: 3225 mw ν(N−H), 1661 s ν(C═N), 1438 s ν(C═C), 750 s δ(C−H). ^1H NMR spectrum in $CDCl_3$, δ: 1.27 (t, J = 7.5 Hz, 3*H*, CH_2*Me*), 2.73 (s, 6*H*, N*Me*), 2.92 (q, J = 7.5 Hz, 2*H*, C*H*$_2$Me), 8.15 (s, br, 1*H*, N*H*). $^{13}C\{^1H\}$ NMR spectrum in $CDCl_3$, δ: 10.2 (CH_3), 21.1 (CH_2)-(Et), 47.2 (Me, NMe), 176.5 (HN═C).

***trans*-$[PtCl_2\{NH{=}C(Et)ONEt_2\}_2]$ (*trans*-2).** Anal. Calcd for $C_{14}H_{32}N_4Cl_2O_2PPt$: C, 30.33; H, 5.82; N, 10.11%. Found: C, 30.40; H, 6.18; N, 9.97%. FAB-MS, *m*/*z*: 554 $[M]^+$, 519 $[M - Cl]^+$, 483 $[M - 2Cl]^+$. IR spectrum (selected bands), cm^{-1}: 3189 m−w ν(N−H), 1661 s ν(C═N), 1438 m ν(C═C). ^1H NMR spectrum in

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$CDCl_3$, δ: 1.01 (t, J = 7.5 Hz, 6*H*, NCH_2*Me*), 1.30 (t, J = 7.5 Hz, 3*H*, CH_2*Me*), 2.92−2.97 (m, 4*H*, NCH_2Me and 2*H*, CH_2Me), 8.14 (s, br, 1*H*, N*H*). $^{13}C\{^1H\}$ NMR in $CDCl_3$, δ: 10.2 (CH_3) and 26.4 (CH_2)(Et), 11.7 (CH_3) and 62.4 (CH_2)(NEt), 175.7 (HN=C).

***cis*-[PtCl$_2${NH=C(Et)ONEt$_2$}$_2$] (*cis*-2).** Anal. Calcd for $C_{14}H_{32}N_4Cl_2O_2PPt$: C, 30.33; H, 5.82; N, 10.11%. Found: C, 43.79; H, 4.31; N, 3.24%. FAB-MS, *m*/*z*: 554 $[M]^+$, 519 $[M - Cl]^+$, 483 $[M - 2Cl]^+$. IR spectrum (selected bands), cm^{-1}: 3189 m−w ν(N−H), 1661 s ν(C=N), 1438 m ν(C=C). ^1H NMR spectrum in $CDCl_3$, δ: 1.01 (t, J = 7.5 Hz, 6*H*, NCH_2*Me*), 1.30 (t, J = 7.5 Hz, 3*H*, CH_2*Me*), 2.92−2.97 (m, 4*H*, NCH_2Me and 2*H*, CH_2Me), 8.14 (s, br, 1*H*, N*H*). $^{13}C\{^1H\}$ NMR in $CDCl_3$, δ: 10.2 (CH_3) and 26.4 (CH_2)(Et), 11.7 (CH_3) and 62.4 (CH_2)(NEt), 175.7 (HN=C).

***trans*-[PtCl$_2${NH=C(Et)ON(CH$_2$Ph)$_2$}$_2$] (*trans*-3).** Anal. Calcd for $C_{34}H_{40}N_4Cl_2O_2Pt$: C, 50.87; H, 5.02; N, 6.98%. Found: C, 50.00; H, 5.02; N, 6.83%. FAB-MS, *m*/*z*: 641 $[M]^+$, 569 $[M - 2Cl]^+$. IR spectrum (selected bands), cm^{-1}: 3197 s ν(N−H), 1658 vs ν(C=N), 1435 m ν(C=C), 754 s δ(C−H). ^1H NMR spectrum in $CDCl_3$, δ: 1.02 (t, J = 7.5 Hz, 3*H*, CH_2*Me*), 2.75 (q, J = 7.5 Hz, 2*H*, CH_2Me), 3.98 and 4.06 (d, J = 13.2 Hz, 4*H*, CH_2Ph), 7.27−7.39 (m, 5*H*, C*H*, *Ph*), 8.10 (s, br, 1*H*, N*H*). $^{13}C\{^1H\}$ NMR in $CDCl_3$, δ: 10.0 (CH_3) and 25.8 (CH_2)(Et), 62.4 (CH_2, $NCH_2C_6H_5$), 128.3, 128.7, 129.7, and 134.0 (aryls), 174.0 (HN=C).

***cis*-[PtCl$_2${NH=C(Et)ON(CH$_2$Ph)$_2$}$_2$] (*cis*-3).** Anal. Calcd for $C_{34}H_{40}N_4Cl_2O_2Pt$: C, 50.87; H, 5.02; N, 6.98%. Found: C, 50.00; H, 5.02; N, 6.83%. FAB-MS, *m*/*z*: 641 $[M]^+$, 569 $[M - 2Cl]^+$. IR spectrum (selected bands), cm^{-1}: 3197 s ν(N−H), 1658 vs ν(C=N), 1435 m ν(C=C), 754 s δ(C−H). ^1H NMR spectrum in $CDCl_3$, δ: 0.86 (t, J = 7.5 Hz, 3*H*, CH_2*Me*), 1.93 (q, J = 7.5 Hz, 2*H*, CH_2Me), 3.94 and 4.02 (m, J = 12.6 Hz, 4*H*, CH_2Ph), 7.27−7.30 (m, 5*H*, Ph), 8.15 (s, br, 1*H*, N*H*). $^{13}C\{^1H\}$ NMR in $CDCl_3$, δ: 9.7 (CH_3) and 25.3 (CH_2)(Et), 61.8 (CH_2, $NCH_2C_6H_5$), 128.3, 128.7, 129.7, and 134.0 (aryls), 174.0 (HN=*C*).

***trans*-[PtCl$_2${NH=C(Et)ON(CH$_2$C$_6$H$_4$Cl-*p*)$_2$}$_2$] (*trans*-4).** Anal. Calcd for $C_{34}H_{36}N_4Cl_6O_2Pt$: C, 43.42; H, 3.86; N, 5.96%. Found: C, 43.24; H, 4.20; N, 5.89%. FAB-MS, *m*/*z*: 942 $[M + 2H]$, 867 $[M - 2Cl - H]$, 604 $[M - L + 2H]$. (eluent CH_2Cl_2). IR spectrum (selected bands), cm^{-1}: 3274 mw ν(N−H), 1661 s ν(C=N), 1433 s ν(C=C). ^1H NMR spectrum in $CDCl_3$, δ: 1.02 (t, J = 7.5 Hz, 3*H*, CH_2*Me*), 2.74 (q, J = 7.5 Hz, 2*H*, CH_2Me), 3.94 and 4.03 (d, J = 13.8 Hz, 4*H*, $CH_2C_6H_4$Cl-*p*), 7.22 and 7.35 (d, J = 7.5 Hz, 4*H*, aryl), 8.03 (s, br, 1*H*, N*H*).$^{13}C\{^1H\}$ NMR in $CDCl_3$, δ: 10.2 (CH_3) and 25.8 (CH_2)(Et), 61.8 (CH_2, $NCH_2C_6H_4$Cl-*p*), 128.5, 129.1, 131.3, 132.1, 132.3, and 134.4 (aryls), 174.2 (HN=C).

***cis*-[PtCl$_2${NH=C(Et)ON(CH$_2$C$_6$H$_4$Cl-*p*)$_2$}$_2$] (*cis*-4).** Anal. Calcd for $C_{34}H_{36}N_4Cl_6O_2Pt$: C, 43.42; H, 3.86; N, 5.96%. Found: C, 43.24; H, 4.20; N, 5.89%. FAB-MS, *m*/*z*: 942 $[M + 2H]^+$, 867 $[M - 2Cl - H]^+$, 604 $[M - L + 2H]^+$. IR spectrum (selected bands), cm^{-1}: 3274 mw ν(N−H), 1661 s ν(C=N), 1433 s ν(C=C). ^1H NMR spectrum in $CDCl_3$, δ: 0.94 (t, J = 7.5 Hz, 3*H*, CH_2*Me*), 2.14 (q, J = 7.5 Hz, 2*H*, CH_2Me), 3.96 (m, 4*H*, $CH_2C_6H_4$Cl-*p*), 7.21−7.36 (m, 4*H*, aryl), 8.51 (s, br, 1*H*, N*H*). $^{13}C\{^1H\}$ NMR in $CDCl_3$, δ: 9.8 (CH_3) and 25.6 (CH_2)(Et), 61.0 (CH_2, $NCH_2C_6H_4$-Cl-*p*), 128.8, 130.8, 131.2, 132.3, 132.4, and 134.3 (aryls), 173.3 (HN=*C*).

Addition of R_2NOH to [Ph$_3$PCH$_2$Ph][PtCl$_3$(EtCN)]. In a typical experiment, **I** (0.10 g, 0.140 mmol) is suspended in chloroform (10 mL) at 20−25 °C, the hydroxylamine (0.140 mmol) is added, and the reaction mixture is left to stand on vigorous stirring for 12 h at room temperature. The bright yellow-orange solution is evaporated to dryness under a flow of N_2 and the solid residue is washed with diethyl ether (five 3-mL portions) to remove the excess of the hydroxylamine. Yields are 80−90%, based on Pt.

[Ph$_3$PCH$_2$Ph][PtCl$_3${NH=C(Et)ONMe$_2$}] (5). Anal. Calcd for $C_{30}H_{34}N_2Cl_3OPPt$: C, 46.73; H, 4.44; N, 3.63%. Found: C, 46.53; H, 4.54; N, 3.43%. FAB^+-MS, *m*/*z*: 353 $[M_{cation}]$, 262 $[M_{cation} - CH_2Ph]$. FAB^- -MS, *m*/*z*: 417 $[M_{anion}]$, 347 $[M_{anion} - 2Cl]$. IR spectrum (selected bands), cm^{-1}: 3225 mw ν(N−H), 1652 s ν(C=N), 1438 s ν(C=C), 1111 s ν(P−C), 750 s δ(C−H). ^1H NMR spectrum in $CDCl_3$, δ: 1.14 (t, J = 7.5 Hz, 3*H*, CH_2*Me*), 2.82 (q, J = 7.5 Hz, 2*H*, CH_2Me), 3.09 (s, 3*H*, N*Me*), 4.91 (d, $^2J_{PH}$ = 13.8 Hz, 2*H*, PCH_2Ph), 6.97−7.29 and 7.53−7.74 (m, C*H*, *Ph*), 8.20 (s, br, 1*H*, N*H*). $^{13}C\{^1H\}$ NMR spectrum in $CDCl_3$, δ: 10.2 (*C*H_3), 21.1(*C*H_2)(Et), 30.8 (CH_2, $^1J_{PC}$ = 47.7 Hz, PCH_2Ph), 47.2 (Me, NMe), 116.6, 117.7, 126.7, 128.5, 128.8, 130.1, 130.2, 131.2, 134.1, and 135.0 (aryls), 176.5 (HN=*C*). $^{31}P\{^1H\}$ NMR in $CDCl_3$, δ: 23.2.

[Ph$_3$PCH$_2$Ph][PtCl$_3${NH=C(Et)ONEt$_2$}] (6). Anal. Calcd for $C_{32}H_{38}N_2Cl_3OPPt$: C, 48.10; H, 4.79; N, 3.51%. Found: C, 48.01; H, 4.78; N, 3.41%. FAB^+-MS, *m*/*z*: 353 $[M_{cation}]$, 262 $[M_{cation} - CH_2Ph]$. FAB^- -MS, *m*/*z*: 410 $[M_{anion} - Cl]$, 339 $[M_{anion} - 3Cl]$. IR spectrum (selected bands), cm^{-1}: 3220 m−w ν(N−H), 1663 s ν(C=N), 1437 s ν(C=C), 1111 s ν(P−C), 748 m δ(C−H). ^1H NMR spectrum in $CDCl_3$, δ: 1.14 (t, J = 7.5 Hz, 6*H*, NCH_2*Me*), 1.24 (t, J = 7.5 Hz, 3*H*, CH_2*Me*), 2.96 (q, J = 7.5 Hz, 4*H*, NCH_2Me), 3.11 (q, J = 7.5 Hz, 2*H*, CH_2Me), 5.00 (d, $^2J_{PH}$ = 13.5 Hz, 2*H*, PCH_2Ph), 7.05−7.82 (m, C*H*, Ph), 8.15 (s, br, 1*H*, N*H*). $^{13}C\{^1H\}$ NMR spectrum in $CDCl_3$, δ: 10.9 (CH_2*Me*), 11.7 (NCH_2*Me*), 24.1 (*C*H_2Me), 31.5 (CH_2, $^1J_{PC}$ = 47.6 Hz, P*C*H_2Ph), 52.9 (N*C*H_2Me), 116.8, 117.9, 128.4, 128.8, 130.4, 131.6, 134.4, 135.0 (*Ph*), 177.6 (HN=*C*). $^{31}P\{^1H\}$ NMR in $CDCl_3$, δ: 28.4.

[Ph$_3$PCH$_2$Ph][PtCl$_3${NH=C(Et)ON(CH$_2$Ph)$_2$}] (7). Anal. Calcd for $C_{42}H_{42}N_2Cl_3OPPt$: C, 54.64; H, 4.59; N, 3.03%. Found: C, 54.54; H, 4.57; N, 3.00%. FAB^+-MS, *m*/*z*: 353 $[M_{cation}]$, 262 $[M_{cation} - CH_2Ph]$. FAB^- -MS, *m*/*z*: 569 $[M_{anion}]$, 534 $[M_{anion} - Cl]$. IR spectrum (selected bands), cm^{-1}: 3222 mw ν(N−H), 1664 s ν(C=N), 1437 s ν(C=C), 1111 s ν(P−C), 749 s δ(C−H). ^1H NMR spectrum in $CDCl_3$, δ: 0.85 (t, J = 7.5 Hz, 3*H*, CH_2*Me*), 2.91 (q, J = 7.5 Hz, 2*H*, CH_2Me), 4.08 (s, 4*H*, NCH_2Ph), 5.00 (d, $^2J_{PH}$ = 13.5 Hz, 2*H*, PCH_2Ph), 7.04 (m, 2*H*, ortho), 7.15 (m, 2*H*) and 7.24 (m, 1*H*)(PCH_2*Ph*), 7.30−7.42 (m, 10*H*, NCH_2*Ph*), 7.58−7.70 (m, 12*H*) and 7.78 (m, 3H)(*Ph*), 8.20 (s, br, 1*H*, N*H*). $^{13}C\{^1H\}$ NMR in $CDCl_3$, δ: 10.5 (*C*H_3) and 24.0 (*C*H_2)(Et), 31.5 (CH_2, $^1J_{PC}$ = 47.7 Hz, P*C*H_2Ph), 61.4 (CH_2, N*C*H_2Ph), 117.5 (C_{ipso}, $^1J_{PC}$ = 86.1 Hz, Ph), 126.9 (C_{ipso}, $^2J_{PC}$ = 8.9 Hz, PCH_2*Ph*), 128.1 (CH, NCH_2*Ph*), 128.5 (CH_p, J_{PC} = 2.8 Hz, PCH_2*Ph*), 128.8 (CH, NCH_2*Ph*), 128.9 (CH_m, J_{PC} = 3.4 Hz, PCH_2*Ph*), 129.8 (CH, NCH_2*Ph*), 130.3 (CH, J_{PC} = 11.9 Hz, *Ph*), 131.6 (CH_o, J_{PC} = 5.5 Hz, PCH_2*Ph*), 133.6 (C_{ipso}, NCH_2*Ph*), 134.4 (CH, J_{PC} = 10.1 Hz, *Ph*), 135.0 (CH_p, J_{PC} = 2.8 Hz, *Ph*), 176.3 (HN=*C*). $^{31}P\{^1H\}$ NMR in $CDCl_3$, δ: 23.5.

[Ph$_3$PCH$_2$Ph][PtCl$_3${NH=C(Et)ON(CH$_2$C$_6$H$_4$Cl-*p*)$_2$}] (8). Anal. Calcd for $C_{42}H_{40}N_2Cl_5OPPt$: C, 50.85; H, 4.06; N, 2.82%. Found: C, 50.83; H, 4.04; N, 2.78%. FAB^+-MS, *m*/*z*: 353 $[M_{cation}]$, 262 $[M_{cation} - CH_2Ph]$. FAB^- -MS, *m*/*z*: 602 $[M_{anion}]$, 533 $[M_{anion} - 3Cl + H]$. IR spectrum (selected bands), cm^{-1}: 3204 mw ν(N−H), 1663 s ν(C=N), 1439 s ν(C=C), 1111 s ν(P−C), 750 m δ(C−H). ^1H NMR spectrum in $CDCl_3$, δ: 0.85 (t, J = 7.5 Hz, 3*H*, CH_2*Me*), 2.80 (q, J = 7.5 Hz, 2*H*, CH_2Me), 4.05 (s, 4*H*, $CH_2C_6H_4$-Cl-*p*), 5.00 (d, $^2J_{PH}$ = 13.5 Hz, 2*H*, PCH_2Ph), 7.07−7.82 and (m, C*H*, aryl), 8.15 (s, br, 1*H*, N*H*). $^{13}C\{^1H\}$ NMR in $CDCl_3$, δ: 11.5 (*C*H_3) and 24.5 (*C*H_2)(Et), 31.5 (CH_2, $^1J_{PC}$ = 47.7 Hz, P*C*H_2Ph), 62.0 (CH_2, $NCH_2C_6H_4$Cl-*p*), 117.3, 118.5, 127.3, 128.9,

129.5, 130.7, 130.9, 131.6, 132.1, 132.4, 134.8, 135.0 and 135.5 (aryls), 176.5 (HN=*C*). $^{31}P\{^1H\}$ NMR in $CDCl_3$, δ: 28.1.

Addition of R_2NOH to $[PtCl_4(EtCN)_2]$. In a typical experiment, isomerically pure *trans*-**IV**[27] (0.12 g, 0.266 mmol) [or a mixture of *cis/trans*-**IV** which contains, by NMR, ca. 60% of the *cis*-isomer[27]] is dissolved in chloroform (5 mL) at 20−25 °C, the hydroxylamine (0.522 mmol) is added, and the reaction mixture is left to stand for 15 min at room temperature. The bright yellow solution is evaporated to dryness at room temperature under a flow of N_2 and the solid residue is washed with diethyl ether (five 3-mL portions) to remove the excess of the hydroxylamine. Yields are 90−95%, based on Pt. In the cases of both *trans*-**IV** and a mixture of *cis/trans*-**IV**, only the isomerically pure *trans*-$[PtCl_4\{NH{=}C(Et)ONR_2\}_2]$ was isolated.

***trans*-$[PtCl_4\{NH{=}C(Et)ONMe_2\}_2]$ (*trans*-9).** Anal. Calcd for $C_{10}H_{24}N_4Cl_4O_2Pt$: C, 21.10; H, 4.25; N, 9.84%. Found: C, 21.02; H, 4.10; N, 9.69%. FAB-MS, *m*/*z*: 533 $[M - Cl]^+$, 498 $[M - 2Cl]^+$. IR spectrum (selected bands), cm^{-1}: 3225 mw ν(N−H), 1664 s ν(C=N), 1438 s ν(C=C), 750 s δ(C−H). ^1H NMR spectrum in $CDCl_3$, δ: 1.02 (t, J = 7.5 Hz, 3*H*, CH_2*Me*), 2.88 (s, 6*H*, N*Me*), 2.92 (q, J = 7.5 Hz, 2*H*, C*H*$_2$Me), 9.01 (s, br, 1*H*, N*H*). $^{13}C\{^1H\}$ NMR spectrum in $CDCl_3$, δ: 8.2 (CH_3), 20.1 (CH_2)(Et), 52.2 (Me, NMe), 174.5 (HN=C).

***trans*-$[PtCl_4\{NH{=}C(Et)ONEt_2\}_2]$ (*trans*-10).** Anal. Calcd for $C_{14}H_{32}N_4Cl_4O_2Pt$: C, 26.89; H, 5.16; N, 8.96%. Found: C, 26.44; H, 5.01; N, 8.82%. FAB-MS, *m*/*z*: 624 $[M]^+$, 554 $[M - 2Cl]^+$. IR spectrum (selected bands), cm^{-1}: 3220 m−w ν(N−H), 1665 s ν(C=N), 1438 m ν(C=C). ^1H NMR spectrum in $CDCl_3$, δ: 0.99 (t, J = 7.5 Hz, 6*H*, NCH_2*Me*), 1.20 (t, J = 7.5 Hz, 3*H*, CH_2*Me*), 2.88−3.02 (m, 4*H*, NC*H*$_2$Me and 2*H*, C*H*$_2$Me), 9.02 (s, br, 1*H*, N*H*). $^{13}C\{^1H\}$ NMR in $CDCl_3$, δ: 8.2 (CH_3) and 22.4 (CH_2)(Et), 11.6 (CH_3) and 61.4 (CH_2)(NEt), 174.2 (HN=C).

***trans*-$[PtCl_4\{NH{=}C(Et)ON(CH_2Ph)_2\}_2]$ (*trans*-11).** Anal. Calcd for $C_{34}H_{40}N_4Cl_4O_2Pt$: C, 46.75; H, 4.62; N, 6.41%. Found: C, 46.22; H, 4.60; N, 6.18%. FAB-MS, *m*/*z*: 873 $[M + H]^+$, 767 $[M - 3Cl]^+$. IR spectrum (selected bands), cm^{-1}: 3237 s ν(N−H), 1655 vs ν(C=N), 1435 m ν(C=C). ^1H NMR spectrum in $CDCl_3$, δ: 0.90 (t, J = 7.5 Hz, 3*H*, CH_2*Me*), 2.78 (q, J = 7.5 Hz, 2*H*, C*H*$_2$Me), 4.02−4.12 (m, 4*H*, C*H*$_2$Ph), 7.25−7.42 (m, 5*H*, C*H*, *Ph*), 8.92 (s, br, 1*H*, N*H*).$^{13}C\{^1H\}$ NMR in $CDCl_3$, δ: 7.0 (CH_3) and 23.8 (CH_2)(Et), 58.4 (CH_2, N*C*H$_2$C$_6$H$_5$), 128.0−134.0 (aryls), 173.0 (HN=C).

***trans*-$[PtCl_4\{NH{=}C(Et)ON(CH_2C_6H_4Cl\text{-}p)_2\}_2]$ (*trans*-12).** Anal. Calcd for $C_{34}H_{36}N_4Cl_8O_2Pt$: C, 40.38; H, 3.59; N, 5.54%. Found: C, 40.11; H, 3.44; N, 5.02%. FAB-MS, *m*/*z*: 941 $[M - 2Cl + H]$, 906 $[M - 3Cl + H]$. IR spectrum (selected bands), cm^{-1}: 3230 mw ν(N−H), 1660 s ν(C=N), 1433 s ν(C=C). ^1H NMR spectrum in $CDCl_3$, δ: 0.92 (t, J = 7.5 Hz, 3*H*, CH_2*Me*), 2.86 (quart, J = 7.5 Hz, 2*H*, C*H*$_2$Me), 4.04−4.14 (m, 4*H*, C*H*$_2$C$_6$H$_4$Cl-*p*), 7.31−7.38 (m, 4*H*, aryl), 9.03 (s, br, 1*H*, N*H*). $^{13}C\{^1H\}$ NMR in $CDCl_3$, δ: 6.2 (CH_3) and 19.8 (CH_2)(Et), 57.0 (CH_2, N*C*H$_2$C$_6$H$_4$Cl-*p*), 127.1−130.2 (aryls), 172.8 (HN=C).

Addition of R_2NOH to $[Ph_3PCH_2Ph][PtCl_5(EtCN)]$. In a typical experiment, **II** (0.10 g, 0.128 mmol) is dissolved in chloroform (10 mL) at 20−25 °C, the hydroxylamine (0.128 mmol) is added, and the reaction mixture is left to stand for 3 h at room temperature. The bright yellow solution is evaporated to dryness under a flow of N_2 and the solid residue is washed with diethyl ether (five 3-mL portions) to remove the excess of the hydroxylamine. Yields are 80−90%, based on Pt.

$[Ph_3PCH_2Ph][PtCl_5\{NH{=}C(Et)ONMe_2\}]$ (13). Anal. Calcd for $C_{30}H_{34}N_2Cl_5OPPt$: C, 42.80; H, 4.07; N, 3.33%. Found: C, 41.67; H, 4.07; N, 3.17%. FAB^+-MS, *m*/*z*: 353 $[M_{cation}]$, 262 $[M_{cation} - CH_2Ph]$. FAB^--MS, *m*/*z*: 489 $[M_{anion}]$, 417 $[M_{anion} - 2Cl]$, 373 $[PtCl_5]$. IR spectrum (selected bands), cm^{-1}: 3225 mw ν(N−H), 1655 s ν(C=N), 1438 s ν(C=C), 1111 s ν(P−C), 750 s δ(C−H). ^1H NMR spectrum in $CDCl_3$, δ: 1.14 (t, J = 7.5 Hz, 3*H*, CH_2*Me*), 2.98 (qu, J = 7.5 Hz, 2*H*, C*H*$_2$Me), 3.09 (s, 3*H*,N*Me*), 4.91 (d, $^2J_{PH}$ = 13.8 Hz, 2*H*, PC*H*$_2$Ph), 6.97−7.29 and 7.53−7.74 (m, C*H*, *Ph*), 8.78 (s, br, 1*H*, N*H*). $^{13}C\{^1H\}$ NMR spectrum in $CDCl_3$, δ: 10.2 (*C*H_3), 21.1(*C*H_2)(Et), 30.8 (CH_2, $^1J_{PC}$ = 47.7 Hz, P*C*H$_2$Ph), 47.2 (Me, NMe), 116.6, 117.7, 126.7, 128.5, 128.8, 130.1, 130.2, 131.2, 134.1, and 135.0 (aryls), 176.5 (HN=*C*). $^{31}P\{^1H\}$ NMR in $CDCl_3$, δ: 23.2.

$[Ph_3PCH_2Ph][PtCl_5\{NH{=}C(Et)ONEt_2\}]$ (14). Anal. Calcd for $C_{32}H_{38}N_2Cl_5OPPt$: C, 44.18; H, 4.40; N, 3.22%. Found: C, 43.79; H, 4.31; N, 3.24%. FAB^+-MS, *m*/*z*: 353 $[M_{cation}]$, 262 $[M_{cation} - CH_2Ph]$. FAB^--MS, *m*/*z*: 514 $[M_{anion} - H]$, 444 $[M_{anion} - 2Cl]$, 373 $[PtCl_5]$. IR spectrum (selected bands), cm^{-1}: 3220 m−w ν(N−H), 1663 s ν(C=N), 1437 s ν(C=C), 1111 s ν(P−C), 748 m δ(C−H). ^1H NMR spectrum in $CDCl_3$, δ: 1.14 (t, J = 7.5 Hz, 6*H*, NCH_2*Me*), 1.24 (t, J = 7.5 Hz, 3*H*, CH_2*Me*), 2.96 (q, J = 7.5 Hz, 4*H*, NC*H*$_2$Me), 3.13 (q, J = 7.5 Hz, 2*H*, C*H*$_2$Me), 5.00 (d, $^2J_{PH}$ = 13.5 Hz, 2*H*, PC*H*$_2$Ph), 7.05−7.82 (m, C*H*, Ph), 9.15 (s, br, 1*H*, N*H*). $^{13}C\{^1H\}$ NMR spectrum in $CDCl_3$, δ: 10.9 (CH_2*Me*), 11.7 (NCH_2*Me*), 24.1 (*C*H_2Me), 31.5 (CH_2, $^1J_{PC}$ = 47.6 Hz, P*C*H$_2$Ph), 52.9 (N*C*H$_2$Me), 116.8, 117.9, 128.4, 128.8, 130.4, 131.6, 134.4, 135.0 (*Ph*), 177.6 (HN=*C*). $^{31}P\{^1H\}$ NMR in $CDCl_3$, δ: 28.4.

$[Ph_3PCH_2Ph][PtCl_5\{NH{=}C(Et)ON(CH_2Ph)_2\}]$ (15). Anal. Calcd for $C_{42}H_{42}N_2Cl_5OPPt$: C, 50.74; H, 4.26; N, 2.82%. Found: C, 50.68; H, 4.22; N, 2.74%. FAB^+-MS, *m*/*z*: 353 $[M_{cation}]$, 262 $[M_{cation} - CH_2Ph]$. FAB^--MS, *m*/*z*: 641 $[M_{anion}]$, 569 $[M_{anion} - 2Cl]$. IR spectrum (selected bands), cm^{-1}: 3222 mw ν(N−H), 1664 s ν(C=N), 1437 s ν(C=C), 1111 s ν(P−C), 749 s δ(C−H). ^1H NMR spectrum in $CDCl_3$, δ: 0.85 (t, J = 7.5 Hz, 3*H*, CH_2*Me*), 2.91 (q, J = 7.5 Hz, 2*H*, C*H*$_2$Me), 4.08 (s, 4*H*, NC*H*$_2$Ph), 5.00 (d, $^2J_{PH}$ = 13.5 Hz, 2*H*, PC*H*$_2$Ph), 7.04 (m, 2*H*, ortho), 7.15 (m, 2*H*, meta) and 7.24 (m, 1*H*, para)(PCH_2*Ph*), 7.30−7.42 (m, 10*H*, NCH_2*Ph*), 7.58−7.70 (m, 12*H*, ortho + meta) and 7.78 (m, 3H, para)(*Ph*), 9.22 (s, br, 1*H*, N*H*). $^{13}C\{^1H\}$ NMR in $CDCl_3$, δ: 10.5 (*C*H_3) and 24.0 (*C*H_2)(Et), 31.5 (CH_2, $^1J_{PC}$ = 47.7 Hz, P*C*H$_2$Ph), 61.4 (CH_2, N*C*H$_2$Ph), 117.5 (C_{ipso}, $^1J_{PC}$ = 86.1 Hz, Ph), 126.9 (C_{ipso}, $^2J_{PC}$ = 8.9 Hz, PCH_2*Ph*), 128.1 (CH, NCH_2*Ph*), 128.5 (CH_p, J_{PC} = 2.8 Hz, PCH_2*Ph*), 128.8 (CH, NCH_2*Ph*), 128.9 (CH_m, J_{PC} = 3.4 Hz, PCH_2*Ph*), 129.8 (CH, NCH_2*Ph*), 130.3 (CH, J_{PC} = 11.9 Hz, *Ph*), 131.6 (CH_o, J_{PC} = 5.5 Hz, PCH_2*Ph*), 133.6 (C_{ipso}, NCH_2*Ph*), 134.4 (CH, J_{PC} = 10.1 Hz, *Ph*), 135.0 (CH_p, J_{PC} = 2.8 Hz, *Ph*), 176.3 (HN=*C*). $^{31}P\{^1H\}$ NMR in $CDCl_3$, δ: 23.5.

$[Ph_3PCH_2Ph][PtCl_5\{NH{=}C(Et)ON(CH_2C_6H_4Cl\text{-}p)_2\}]$ (16). Anal. Calcd for $C_{42}H_{40}N_2Cl_7OPPt$: C, 47.46; H, 3.79; N, 2.64%. Found: C, 47.49; H, 3.75; N, 2.60%. FAB^+-MS, *m*/*z*: 353 $[M_{cation}]$, 262 $[M_{cation} - CH_2Ph]$. FAB^--MS, *m*/*z*: 636 $[M_{anion} - 2Cl]$, 616 $[M_{anion} - 3Cl]$, 566 $[M_{anion} - 4Cl + H]$. IR spectrum (selected bands), cm^{-1}: 3204 mw ν(N−H), 1663 s ν(C=N), 1439 s ν(C=C), 1111 s ν(P−C), 750 m δ(C−H). ^1H NMR spectrum in $CDCl_3$, δ: 0.85 (t, J = 7.5 Hz, 3*H*, CH_2*Me*), 2.90 (q, J = 7.5 Hz, 2*H*, C*H*$_2$Me), 4.05 (s, 4*H*, C*H*$_2$C$_6$H$_4$Cl-*p*), 5.00 (d, $^2J_{PH}$ = 13.5 Hz, 2*H*, PC*H*$_2$Ph), 7.07−7.82 and (m, C*H*, aryl), 9.15 (s, br, 1*H*, N*H*). $^{13}C\{^1H\}$ NMR in $CDCl_3$, δ: 11.5 (*C*H_3) and 24.5 (*C*H_2)(Et), 31.5 (CH_2, $^1J_{PC}$ = 47.7 Hz, P*C*H$_2$Ph), 62.0 (CH_2, N*C*H$_2$C$_6$H$_4$Cl-*p*), 117.3, 118.5, 127.3, 128.9, 129.5, 130.7, 130.9, 131.6, 132.1, 132.4, 134.8, 135.0 and 135.5 (aryls), 176.5 (HN=*C*). $^{31}P\{^1H\}$ NMR in $CDCl_3$, δ: 28.1.

X-ray Structure Determinations. The X-ray diffraction data were collected with a Nonius KappaCCD diffractometer using Mo Kα radiation (λ = 0.71073 Å). Crystals were mounted in inert oil

within the cold gas stream of the diffractometer. The DenzoScalepack[34] or EvalCCD[35] programs packages were used for cell refinements and data reduction. Structures were solved by direct methods using the SHELXS or SIR-2002 program.[36,37] The structure *trans*-**4** was solved as a racemic mixture (ratio ca. 0.4/0.6) in the monoclinic space group $P2_1$. A multiscan absorption correction based on equivalent reflections (XPREP in SHELXTL v. 6.14)[38] was applied to data (T_{min}/T_{max} values were 0.1907/0.6272, 0.3219/0.4584, 0.08068/0.13409, and 0.15477/0.21243 for *cis*-**1**, *cis*-**2**, *trans*-**4**, and **15**, respectively). The structures were refined with SHELXL-97[39] and WinGX graphical user interface.[40] In *cis*-**1**, *cis*-**2**, and *trans*-**4**, the NH hydrogens were located from the difference Fourier map and refined isotropically (*cis*-**1** and *trans*-**4**) or were fixed (*cis*-**2**). All other hydrogens were placed in idealized position and constrained to ride on their parent atom. Crystallographic data are summarized in Table 1. Selected bond lengths and angles are shown in Table 2 and in the caption of Figure 3.

Kinetic Measurements. The kinetics of reactions 1 and 2 was studied in $CDCl_3$ using a Varian UNITY 300 NMR spectrometer equipped with an indirect detection probe and a thermostated module in the temperature range from −30 to 50 °C. The progress of reactions was monitored by integrating the ^{1}H NMR signals from the coordinated EtCN of $[Ph_3PCH_2Ph][PtCl_n(EtCN)]$ or signals of the Et group from the imino ligand of $[Ph_3PCH_2Ph][PtCl_n\{NH{=}C(Et)ON(CH_2C_6H_4Cl\text{-}p)_2\}]$. The pseudo-first-order conditions were ensured by using at least 8-fold excess of $(p\text{-}ClC_6H_4CH_2)_2NOH$ (DAH) with respect to $[Ph_3PCH_2Ph][PtCl_n(EtCN)]$. The reactions were initiated by mixing solutions of $[Ph_3PCH_2Ph][PtCl_n(EtCN)]$ and DAH in $CDCl_3$ to give the total solution volume 0.5 mL. Commonly used concentrations of $[Ph_3PCH_2Ph][PtCl_n(EtCN)]$ and DAH were 1.35×10^{-3} M and $(1.08-10.8) \times 10^{-2}$ M, respectively. The pseudo-first-order rate constants k_{obs} were calculated from the slope of linear plots $\ln(100/(100 - x))$ versus time where x (in %) is the conversion of the starting material to the product of the reaction. All k_{obs} rate constants throughout are the mean values of at least three measurements. The curve fit and all other calculations were performed using an Origin 6.1 package.

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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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