Inorg. Chem. **2006**, *45*, 2296–2306

Kinetic and Thermodynamic Aspects of the Regioselective Addition of Bifunctional Hydroxylaminooxime-type HO-Nucleophiles to Pt-Complexed Nitriles

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Received November 4, 2005

The coupling between coordinated propiononitriles in *trans*-[$PtCl_n(EtCN)_2$] ($n = 2$, 4) and the 1,2-hydroxylaminooximes $HON(H)CMe_2C(R)$═NOH (R = Ph **1**, Me **2**) proceeds smoothly in $CHCl_3$ at ca. 40–45 °C and gives *trans*-[$PtCl_n$-{NH═C(Et)ON(H)CMe_2C(R)═NOH}$_2$] ($n = 2$, R = Ph **5**, Me **6**; $n = 4$, R = Ph **7**, Me **8**) in 80–85% isolated yields. The reaction is highly regioselective, and both spectroscopic (IR; FAB^+-MS; 1D ^1H, $^{13}C\{^1H\}$, and ^{195}Pt NMR; and 2D ^1H,^{13}C HMQC, ^1H,^{13}C HMBC, and ^1H,^{15}N HMQC NMR) and X-ray data for **6**–**8** suggest that the addition proceeds exclusively via the hydroxylamine moiety of the 1,2-hydroxylaminooxime species; the existence of an oxime group remote from the nucleophile was also confirmed. Heating of **6** in air leads to its conversion to the unusual nitrosoalkane complex [$PtCl_2${HON═C(Me)C(Me)$_2$N═O}] (**9**), whereas in the case of **5**, only the metal-free salt [$H_3NC(Me)_2C(Ph)$═$NOH]_2(NO_3)Cl\cdot H_2O$ (**10**) was isolated. To compare the kinetic aspects and trends in the addition of both types of nucleophiles (oximes and hydroxylamines; for the latter, see our recent work: *Inorg. Chem.* **2005**, *44*, 2944) to coordinated nitriles, a kinetic study of the addition of HON═$C(CH_2Ph)_2$ to [Ph_3PCH_2-Ph][$PtCl_5$(EtCN)] (**11**) to give [Ph_3PCH_2Ph][$PtCl_5${NH═C(Et)ON═$C(CH_2Ph)_2$}] (**12**) was performed. The calculated rate constant k_2 of 3.9×10^{-6} M^{-1} s^{-1} at –20 °C for the addition of the oxime indicates that the hydroxylamine is, by a factor 1.7×10^4, more reactive toward the addition to nitriles than the oxime. Results of the synthetic, kinetic, and theoretical (at the B3LYP level of theory) studies have demonstrated that the high regioselectivity of the reactions of the 1,2-hydroxylaminooximes with ligated nitriles is both kinetically and thermodynamically controlled.

Introduction

Nucleophilic addition to metal-activated RC≡N species is one of the frontier areas of current research on organonitriles, and this topic has been the subject of comprehensive reviews,[1−3] including recent surveys.[4−6] In general, the interest in conversions of nitriles at metal centers stems from the following possibilities: first, to use nitriles as synthons

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10.1021/ic051909r CCC: $33.50
Published on Web 01/31/2006

for the preparation of compounds with a broad spectrum of applications (e.g., phthalocyanines[7]); second, to provide environmentally friendly metal-catalyzed hydrolytic transformations of RCN species to amides (e.g., of industrial and pharmacological significance[4]); and third, to synthesize, via the nucleophilic addition, diverse imino complexes (e.g., exhibiting antitumor properties[8]). Regarding the creation of a C−O bond due to metal-mediated nitrile−nucleophile coupling, the analysis of experimental material collected to date[1−6] shows that the largest number of works in this direction have been focused on the hydration of RCN species,[9] and reactions with alcohols,[10] whereas coupling with HON-type nucleophiles is still a scarcely explored area.

Following our ongoing project investigating various reactivity modes of complexed organonitriles (i.e., nucleophilic[1−2] and electrophilic[1−3,11] additions and [2 + 3] dipolar cycloadditions[12]), we extended our previous works on the metal-mediated hydroxylamine−nitrile[13,14] and oxime−nitrile[15−22] couplings to such combined bifunctional HO-nucleophiles,

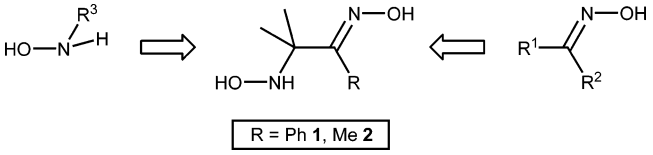

Figure 1.

i.e., 1,2-hydroxylaminooximes (see boxed compounds in Figure 1; IUPAC names 2-hydroxyamino-2-methyl-1-phenylpropan-1-one oxime, **1**, and 3-hydroxyamino-3-methylbutan-2-one oxime, **2**), where the N atoms of the HON functional groups are in sp^3 and sp^2 hybridization, respectively. The distinct hybridization should determine different nucleophilic properties of the HO moieties of the hydroxylaminooxime species.

This project, utilizing the model Pt-based system, was driven primarily by the necessity to shed light on the recently discovered Ni^{II}/HON-nucleophile-promoted conversion of *o*-phthalonitriles (**I**, Scheme 1) to nickel(II) phthalocyanines (**II**).[23,24] In the case of HON-nucleophiles such as oximes, this reaction proceeds (route A) via the formation of an intermediate complex (**III**) (generated by the double nucleophilic addition to a cyano carbon), which, in turn, reacts further with 2 equiv of *o*-phthalonitriles to form NiPcs (route B). The employment of $HONR_2$ species as alternative HON-nucleophiles (route C) enhances the reactivity to such a degree that the tetramerization proceeds rapidly in a single pot and the intermediate similar to **III** could not be detected. The difference in promoting abilities of oximes and dialkylhydroxylamines toward the formation of phthalocyanines should be rationalized, and this warrants a separate investigation.

Further interests in the project are at least three-fold: (i) to study the regioselectivity of the addition of **1** and **2** and to verify preferences in the C−O bond formation; (ii) to investigate, by theoretical methods, thermodynamic aspects of the regioselectivity of the addition; and (iii) to study quantitatively the relative nucleophilicities of oximes and hydroxylamines toward RCN species bound to a Pt center in order to understand kinetic aspects and trends in their addition to coordinated nitriles. The scenario of our work, described in this article, follows these lines.

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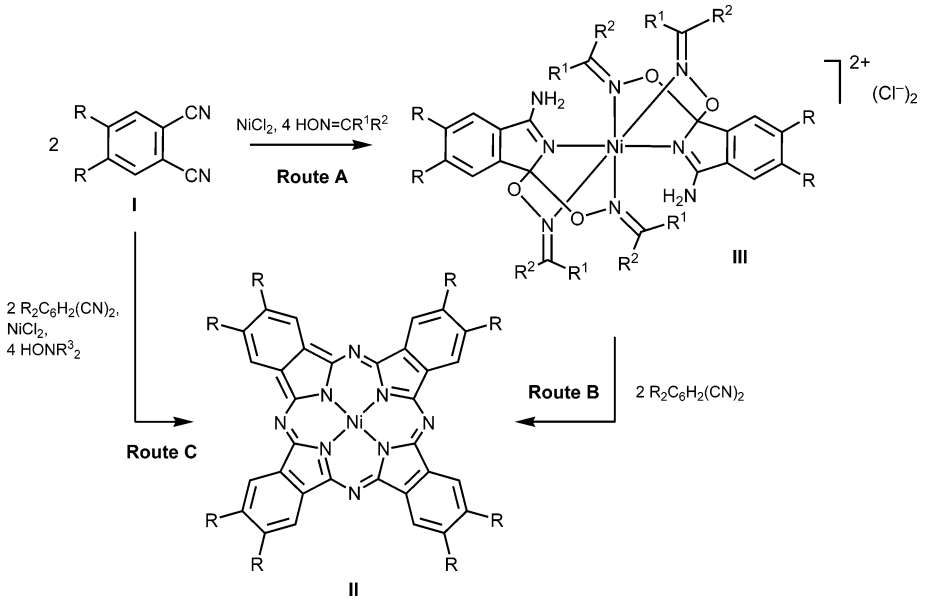
Scheme 1



Results and Discussion

Platinum-Mediated Coupling of Nitriles with 1,2-Hydroxylaminooximes. Despite certain progress in metal-mediated nitrile−nucleophile coupling, relatively few investigations have been carried out with the addition of potentially *bifunctional nucleophiles* to the nitrile C atom. Among the latter, attention should be drawn to the coupling between metal-complexed nitriles and bifunctional nucleophiles bearing the same (e.g., diphosphines,[25] dioximes,[17,26] and diamines[27]) and different (amino alcohols,[28] salicylaldoximes,[20] mixed sulfimide/sulfides,[29] hydroxy/phosphines,[30] and oxime/hydrazones[31]) nucleophilic sites. 1,2-Hydroxylaminooximes (**1** and **2**) are bifunctional HO-nucleophiles insofar as both N and O atoms from the hydroxylamine NHOH moiety and O atom from the oxime C═NOH group exhibit nucleophilic properties;[13−22] their reactions *with* and the regioselectivity of their addition *to* complexed nitriles have not been studied to date.

We have now found that the coupling between Pt-bound nitriles in **3** and **4** and 1,2-hydroxylaminooximes HON(H)-$CMe_2C(R)$═NOH, with R = Ph (**1**), Me (**2**) (in the synthetic experiment, **2** was used as the monoacetate salt, **2**·$MeCO_2H$), proceeds smoothly in $CHCl_3$ at ca. 40−45 °C via routes E and F, Scheme 2, and the subsequent workup provides the new Pt^{II} and Pt^{IV}-imino species *trans*-[$PtCl_n${NH═C(Et)ON(H)$CMe_2C(R)$═NOH}$_2$] (n = 2, R = Ph **5**, Me **6**; n = 4, R = Ph **7**, Me **8**) in good isolated yields (80−85%). The reaction is highly regioselective, and both spectroscopic and X-ray data (see later) suggest that the addition proceeds exclusively via the hydroxylamine moiety of the 1,2-hydroxylaminooxime species.

It is well-known that alkyl hydroxylamines are much stronger N-bases than oximes, e.g., protonation of the N atom of oximes occurs at the Hammet acidity (H_0) range from −1.75 to +0.61,[32] whereas for MeNHOH, the pK_a is 5.96 in water.[33] This significant difference in basicity allows the protonation of 1,2-hydroxylaminooximes to occur exclusively at the hydroxylamino group, leaving the oxime functionality intact. We attempted to control the addition of the 1,2-hydroxylaminooxime species to complexed nitriles and performed the reaction of **3** and **4** with **2**·$MeCO_2H$ (or with **2**·$MeCO_2H$ in the presence of added CF_3CO_2H in the amount of 1 mmol). In doing so, we observed that, although protonation of the hydroxylamine function provokes a significant decrease of the reactivity of this nucleophilic center, the reaction still remains highly regioselective and the addition proceeds exclusively via the same hydroxylamine moiety.

It is worth noting that the coupling of propiononitrile in **3** or **4** with **1** or **2**·$MeCO_2H$ is metal-mediated insofar as the reaction of free EtCN with 1,2-hydroxylaminooximes in $CHCl_3$ does not occur under the same conditions for even 2 days.

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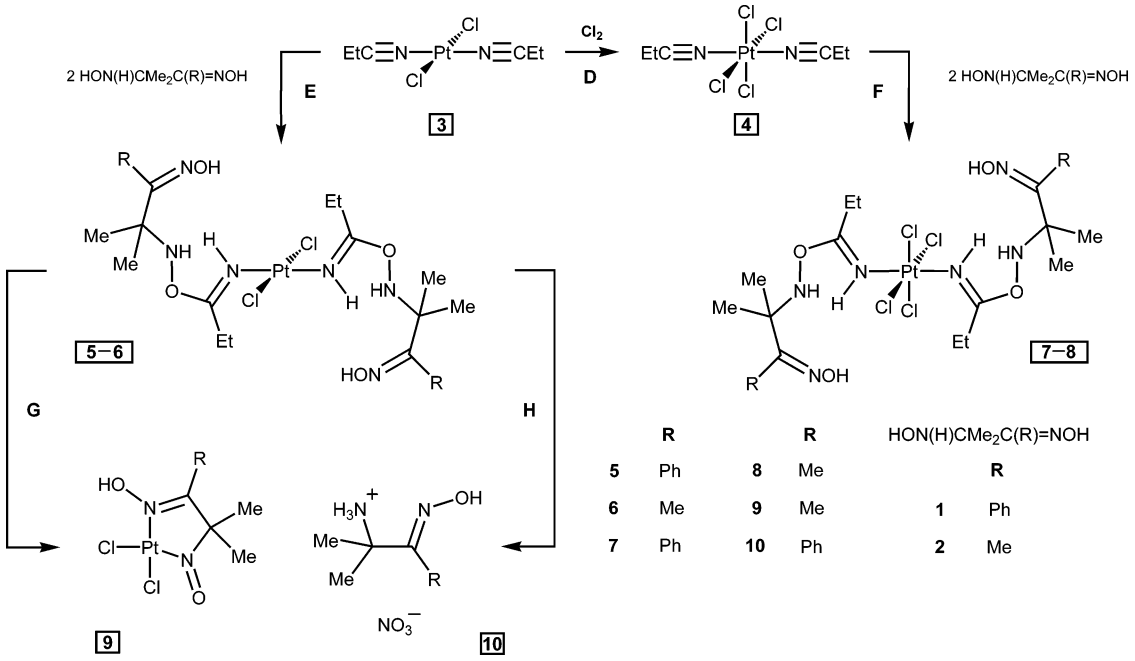
Scheme 2



Characterization of Imino Complexes 5−8. Compounds **5**−**8** gave satisfactory C, H, and N elemental analyses. Their FAB-MS, IR, and 1D (^{1}H, ^{13}C{^{1}H}, and ^{195}Pt) and 2D (^{1}H,^{13}C HMQC, ^{1}H,^{13}C HMBC, and ^{1}H,^{15}N HMQC) NMR spectra are in good agreement with the proposed structures of Pt^{II} and Pt^{IV} complexes with the newly formed imino ligands HN═C(Et)ON(H)CMe$_2$C(R)═NOH, the latter derived from the regioselective nitrile−hydroxylamine coupling of the 1,2-hydroxylaminooximes.

The FAB$^+$-MS spectra of **5**−**8** display molecular ion peaks and/or a characteristic fragmentation for [PtCl$_n$(imine)$_2$] compounds, corresponding to the loss of Cl's from the molecular ion, viz., [M − *n*Cl]$^+$; these data agree well with those observed for the previously characterized platinum imino complexes.[13−15,17−22] In the IR spectra, **5**−**8** give no bands from ν(C≡N) stretching vibrations in the range between 2400 and 2270 cm^{-1} {such bands appear at 2340 cm^{-1} (vs) for *trans*-[PtCl$_4$(EtCN)$_2$][34] and 2314 cm^{-1} (m) for *trans*-[PtCl$_2$(EtCN)$_2$][35]} but show one (for **5**, **7**, **8**) or two (for **6**) intense bands in the range of 1660−1595 cm^{-1} assigned to ν(C═N) of the newly formed imino group C═NH and the free oxime group C═NOH from the HN═CEtON(H)CMe$_2$C(R)═NOH ligand; these data match well with those for similar complexes derived from the addition of "simple" oximes, e.g., [PtCl$_n${NH═C(Me)ON═CR^{1}R^2}$_2$],[15,17,18,20] or dialkyl- and dibenzylhydroxylamines, e.g., [PtCl$_n${NH═C(Et)ONR^3}$_2$],[14] to Pt-bound nitriles.

The addition of the 1,2-hydroxylaminooximes **1** and **2** to the nitrile platinum(II) and -(IV) complexes *trans*-[PtCl$_2$(EtCN)$_2$] and *trans*-[PtCl$_4$(EtCN)$_2$], respectively, was monitored by ^{1}H, ^{13}C, ^{15}N, and ^{195}Pt NMR spectroscopy, and selected data are presented in Table 1. The oxidation state of the metal center and the coupling of hydroxylamine versus oxime moieties can best be judged on the basis of significant shift differences and two-dimensional heteronuclear correlated NMR techniques.

Table 1. Selected NMR Chemical Shifts for Complexes **5**−**8**

	^{1}H		^{13}C		^{195}Pt
complex	Pt−NH	N−OH	Pt−N═C	C═NOH	
5	8.18	9.84	175.6	159.9	−2027
6	8.16	10.68	177.0	157.9	−2031
7	9.14	9.39	179.5	160.8	−153
8	9.06	10.81	179.5	157.1	−92

Complexes **5**−**8** display a single broad ^{195}Pt resonance signal, typical for a Pt^{II}Cl$_2$N$_2$ or Pt^{IV}Cl$_4$N$_2$ coordination environment, with half-height line widths between 700 and 800 Hz, suggesting that only one type of imino complex was formed in the reactions. The chemical shifts for the platinum(II) complexes were found at −2027 and −2031 ppm for **5** and **6**, respectively, whereas for platinum(IV) complexes, the change in the oxidation state of the metal center is reflected by a significant downfield shift of about 2000 ppm (−153 and −92 ppm for **7** and **8**, respectively), and these values correspond well to those for related species, i.e., [PtCl$_n${NH═C(Me)ON═CR^{1}R^2}$_2$] (n = 2, −2060 ± 30 ppm;[36] n = 4, −120 ± 40 ppm[15,18]), [PtCl$_n${NH═C(Me)-ONR$^3_2$}$_2$] (n = 2, −2035 ± 15 ppm;[36] n = 4, −160 ± 10 ppm[13]), and [PtCl$_n${NH═C(Et)OR^4}$_2$] (n = 2, −1935 ± 30 ppm;[10,37] n = 4, −100 ± 70 ppm[10,37]).

The ^{1}H NMR spectra of the Pt^{II} complexes **5** and **6** display a broad peak in the range of δ 8.10−8.20 ppm assigned to the imine proton Pt−NH, involved in intramolecular hydrogen bonding (observed also in the solid-state molecular

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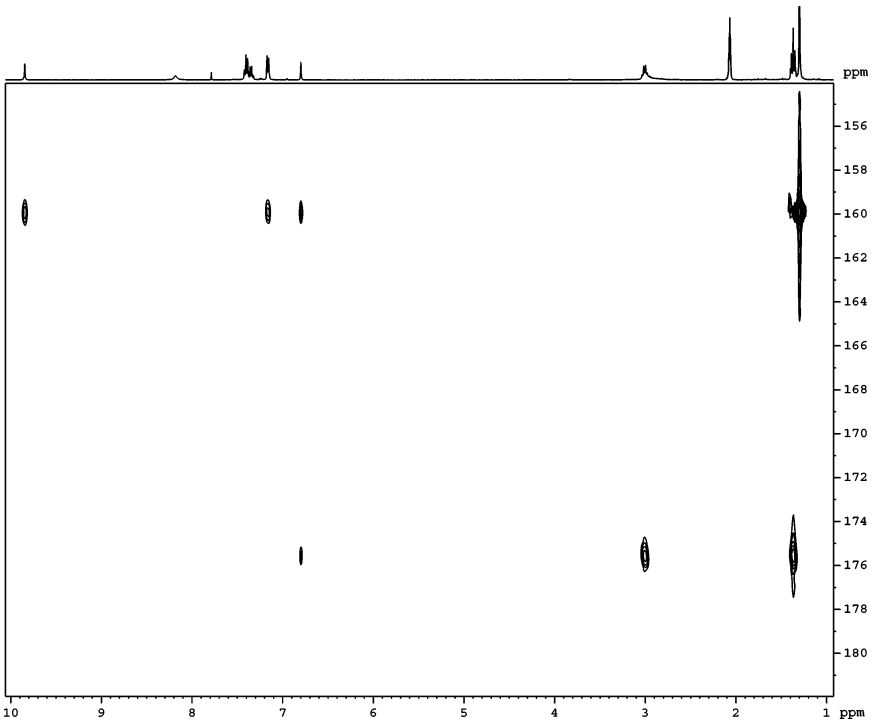

Figure 2. Downfield $^{1}H,^{13}C$ HMBC NMR spectrum of **5** in DMSO-d_6.

structures; see later), whereas for the Pt^{IV} complexes **7** and **8**, a downfield shift of about 1 ppm of the corresponding signal was detected [δ 9.05−9.15 ppm]. These observations are in a good agreement with NMR spectroscopic data for similar platinum imino complexes, viz., $[PtCl_n\{NH{=}C(Et)ONR^3{}_2\}_2]$ ($n = 2, 4$; R^3 = Me, Et, CH_2Ph, $CH_2C_6H_4Cl$-*p*).[14] In the $^{1}H,^{15}N$ HMQC experiment, two resonances from ^{15}N with protons directly bound to a N atom were found. The signal at 83−95 ppm was assigned to the imine Pt−NH nitrogen signal, whereas the other (143−151 ppm) corresponds to the NH signal from the hydroxylamine moiety.

Addition of the 1,2-hydroxylaminooximes **1** and **2** to a coordinated nitrile is accompanied by a change of the ^{13}C chemical shift of the quaternary carbon atom from the nitrile to the imino group (C≡N to C═N). The C═NH imine ^{13}C signals were found to resonate in the δ range of 175−180 ppm and are shifted by approximately 60 ppm to lower field in comparison to the starting platinum nitrile complexes (i.e., 119 ppm for C≡N from *trans*-$[PtCl_4(EtCN)_2]$[34]).

The ^{1}H and ^{13}C signal assignments were performed unequivocally by interpretation of gradient-enhanced two-dimensional $^{1}H,^{13}C$ HMQC and $^{1}H,^{13}C$ HMBC NMR spectra. Especially the long-range shift correlation experiments via $^{2}J_{H,C}$ and $^{3}J_{H,C}$ coupling were found to be of high value, because they allowed the detection of the quaternary carbon atoms and the determination of whether the hydroxylamine or the oxime functionality was added to the coordinated nitrile.

Thus, for example, in the $^{1}H,^{13}C$ HMBC NMR spectrum of **5** (Figure 2), the ^{13}C signal of the coordinated imine carbon atom was detected at 175.6 ppm and assigned through the shift correlation peaks with both the CH_3 and the CH_2 protons from the ethyl residue. A further cross-peak of C═N with the O−NH proton clearly confirms that the addition reaction

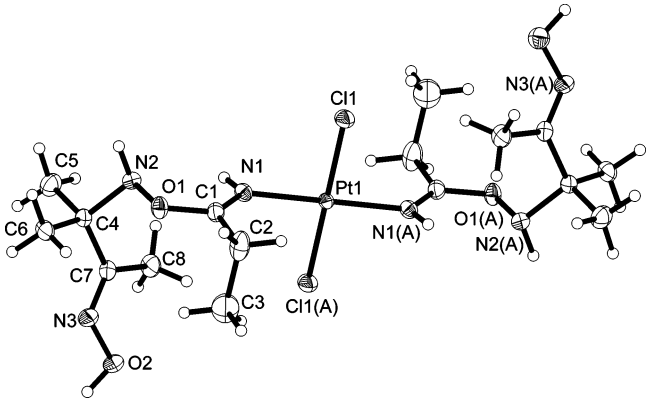

Figure 3. Thermal ellipsoid view of complex **6** with atomic numbering scheme. Thermal ellipsoids are drawn at 50% probability.

proceeds via the hydroxylamine group. Furthermore, coupling from this proton to the dimethyl-substituted carbon atom at 62.4 ppm was observed (not shown). The $C(CH_3)_2$ protons, as well as the ortho protons of the phenyl group (Me in case of **6** and **8**), the O−NH proton, and the oxime (NOH) proton display a correlation (via $^{3}J_{H,C}$ coupling) to the HO−N═C quaternary atom, which resonates at 159.9 ppm. These NMR spectroscopic features were also found in complexes **6**−**8**, consequently leading to a full assignment of ^{1}H and ^{13}C chemical shifts and confirming that the nucleophilic addition to nitriles, ligated to the Pt centers, proceeds exclusively via the hydroxylamine moiety of the 1,2-hydroxylaminooxime species **1** and **2**.

The structures of **6**−**8** were determined by single-crystal X-ray diffraction analysis (Figures 3−5, Tables 2 and 3), and it was established that (i) in **6**−**8**, the existence of the pendant oxime group C═N−OH was detected, and this observation, in addition to the NMR spectroscopic data in solution (see above), indicates that the 1,2-hydroxylami-

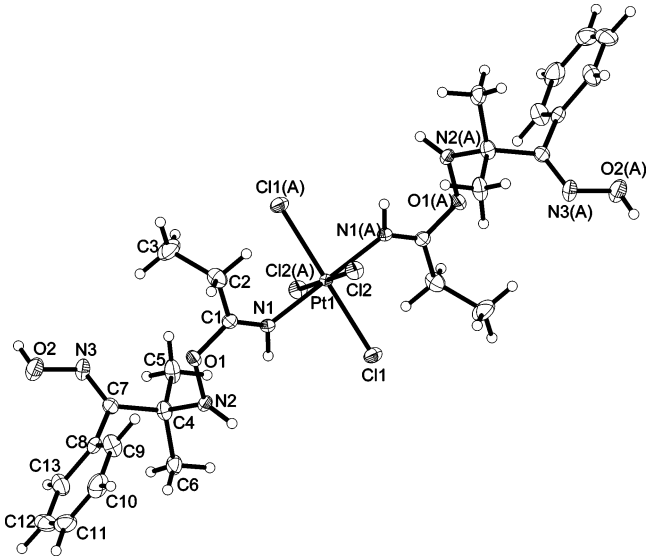

Figure 4. Thermal ellipsoid view of complex **7** with atomic numbering scheme. Thermal ellipsoids are drawn at 50% probability.

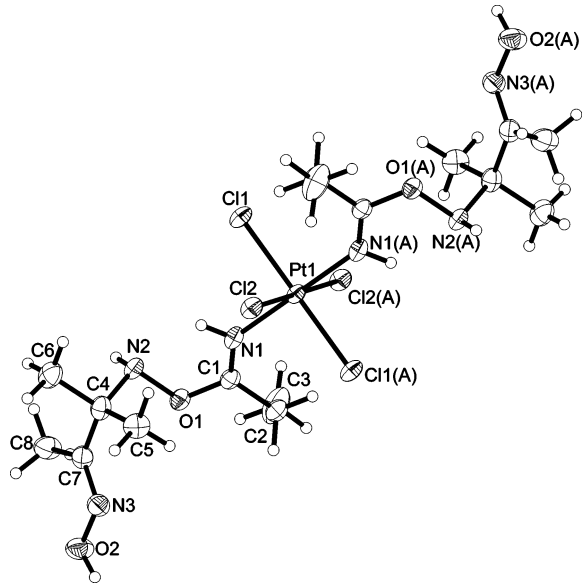

Figure 5. Thermal ellipsoid view of complex **8**·(C_7H_8) with atomic numbering scheme. Thermal ellipsoids are drawn at 50% probability. The toluene molecule has been omitted for clarity.

nooximes react with Pt^{II}- and Pt^{IV}-bound nitriles exclusively via the hydroxylamine moiety; (ii) all of the imino ligands are mutually trans and are in the *E* configuration; and (iii) all bond lengths and angles are not unusual and are within the expected limits.[38]

Theoretical Studies of Thermodynamic Aspects of the Regioselectivity of the Coupling. The results of both synthetic and kinetic work (see later) clearly demonstrate that the high regioselectivity of the nucleophilic addition of the bifunctional hydroxylaminooximes to the complexed nitriles should be explained by kinetic reasons. However, there is another factor, i.e., thermodynamics, that might

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Table 2. Crystallographic Data for **6**, **7**, **8**·(C_7H_8), and **9**

	6	**7**	**8**·(C_7H_8)	**9**
empirical formula	$C_{16}H_{34}Cl_2N_6O_4Pt$	$C_{26}H_{38}Cl_4N_6O_4Pt$	$C_{23}H_{42}Cl_4N_6O_4Pt$	$C_5H_{10}Cl_2N_2O_2Pt$
Fw	640.48	835.51	803.52	396.14
temp (K)	120(2)	120(2)	120(2)	120(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073
cryst syst	monoclinic	monoclinic	triclinic	triclinic
Space group	$P2_1/n$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a (Å)	7.6006(2)	9.8206(6)	7.2923(2)	8.9309(3)
b (Å)	15.4326(6)	15.7599(10)	9.0813(4)	9.0528(3)
c (Å)	10.1530(3)	10.5418(10)	13.2633(6)	13.2321(6)
α (deg)	90	90	77.931(2)	99.276(2)
β (deg)	99.141(2)	97.395(7)	85.591(3)	106.497(2)
γ (deg)	90	90	73.284(3)	100.964(2)
V (Å^3)	1175.79(7)	1618.0(2)	822.50(6)	980.38(6)
Z	2	2	1	4
r_{calc} (Mg/m^3)	1.809	1.715	1.622	2.684
μ(Mo Ka) (mm^{-1})	6.227	4.707	4.626	14.820
R_{int}	0.0389	0.0427	0.0456	0.0730
R1[a] ($I \geq 2s$)	0.0272	0.0241	0.0305	0.0481
wR2[b] ($I \geq 2s$)	0.0685	0.0397	0.0725	0.1090

[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 3. Selected Bond Lengths (Å) and Angles (deg) for **6**, **7**, **8**·(C_7H_8), and **9**

	6	**7**	**8**·(C_7H_8)	**9A**	**9B**
Pt1−Cl1	2.3008(7)	2.3042(7)	2.3203(8)	2.287(3)	2.301(3)
Pt1−Cl2		2.3087(9)	2.3186(8)	2.288(3)	2.290(3)
Pt1−N1	2.013(3)	2.013(3)	2.014(3)	1.927(10)	1.916(11)
Pt1−N2				2.009(10)	1.989(9)
N1−C1	1.265(4)	1.265(4)	1.274(5)	1.568(14)	1.541(16)
N1−O1				1.186(13)	1.206(15)
N2−O2				1.382(13)	1.371(13)
C1−O1	1.351(4)	1.348(4)	1.349(4)		
O1−N2	1.465(3)	1.444(3)	1.467(4)		
N2−C4	1.496(4)	1.476(4)	1.478(5)	1.271(15)	1.292(15)
C7−N3	1.281(4)	1.264(4)	1.279(5)		
N3−O2	1.426(3)	1.406(4)	1.411(5)		
Cl1−Pt1−Cl2			91.11(3)	90.62(11)	92.47(12)
Cl1−Pt1−N1	90.74(7)	85.18(8)	85.18(9)	172.7(3)	172.3(3)
C1−O1−N2	113.1(2)	113.5(2)	112.0(3)		
C7−N3−O2	110.6(2)	111.1(3)	112.9(3)		
N1−Pt1−N2				80.8(4)	80.7(4)
O1−N1−C1				116.0(10)	115.8(11)
O2−N2−C4				118.2(10)	116.9(9)

significantly affect the reactivity. To investigate whether the kinetic and thermodynamic characteristics of these processes are coherent or opposite, quantum chemical calculations of the possible products of the reactions of free acetonitrile MeCN and the four ligated nitriles *trans*-[$PtCl_n(NCMe)_2$] [$n = 2$ (**T1**), 4 (**T2**)] and [$PtCl_m(NCMe)$]$^-$ [$m = 3$ (**T3**), 5 (**T4**)] with the model bifunctional nucleophile HON=$CHCH_2$-NHOH were performed at the B3LYP level of theory.

An inspection of the energies of the calculated structures NH=C(Me)ON(H)CH_2CH=NOH (**H5**), *trans*-[$PtCl_n${NH=C(Me)ON(H)CH_2CH=NOH}$_2$] [$n = 2$ (**H6**), 4 (**H7**)], [$PtCl_m${NH=C(Me)ON(H)CH_2CH=NOH}]$^-$ [$m = 3$ (**H8**), 5 (**H9**)], NH=C(Me)ON=$CHCH_2$N(H)OH (**O5**), *trans*-[$PtCl_n${NH=C(Me)ON=$CHCH_2$N(H)OH}$_2$] [$n = 2$ (**O6**), 4 (**O7**)], and [$PtCl_m${NH=C(Me)ON=$CHCH_2$N(H)OH}]$^-$ [$m = 3$ (**O8**), 5 (**O9**)] leads to the following conclusions (see Supporting Information for the table with the absolute energies). First, the products of the addition by the hydroxylamine site (**H5**−**H9**) are more stable than the corresponding

Table 4. Reaction Energies (in kcal/mol) for the Formation of the Products **H/O5**−**H/O9** upon Addition of HON(H)CH_2C(H)═NOH to Nitriles[a]

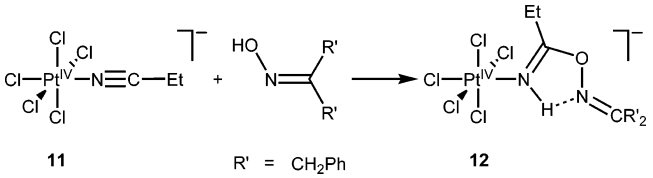
	ΔE	ΔH	ΔG
5H	−14.69 (−13.21)	−12.50	−0.21 (+1.26)
6H	−54.98 (−49.04)	−49.75	−20.86 (−14.92)
7H	−67.62 (−62.72)	−63.03	−33.11 (−28.22)
8H	−23.85 (−21.24)	−21.39	−6.76 (−4.15)
9H	−30.62 (−29.12)	−28.16	−13.63 (−12.13)
5O	−12.97 (−11.35)	−10.95	+1.08 (+2.70)
6O	−48.78 (−42.53)	−44.03	−16.74 (−10.49)
7O	−61.81 (−56.03)	−56.38	−29.58 (−23.80)
8O	−19.90 (−18.05)	−17.63	−4.30 (−2.45)
9O	−27.19 (−25.05)	−24.89	−10.35 (−8.21)

[a] Energies corrected for the solvent effect are in parentheses.

oxime addition complexes (**O5**−**O9**), by 1.44, 4.43, 4.42, 1.70, and 3.92 kcal/mol, respectively, in terms of Gibbs free energy in solution (ΔG_s), although, in some cases, this difference is small. Hence, there is a direct correlation between the kinetically and thermodynamically preferred products of the reactions. Second, all of the reactions are exothermic and exoergonic, except the addition to free MeCN (Table 4). The ΔG magnitudes are significantly lower, in absolute values, than ΔH because of a strong decrease of the entropy upon addition. The endoergonic character of the reactions with free MeCN accounts for the experimentally observed spontaneous splitting of the imino species, e.g., HN═C(Et)ON═C(Me)C(Me)(═O),[21] to the parent nitrile and dione monoxime, whereas the corresponding platinum species *trans*-[$PtCl_2${NH═C(Et)ON═C(Me)C(Me)(═O)}$_2$] are stable.[21] Third, the coordination of MeCN by platinum results in significant increases of $|\Delta H|$ and $|\Delta G|$. The change of the oxidation state of the metal center has a markedly greater effect on the reaction energies (by 6−8 kcal/mol per ligand) than the variation of the overall charge of the complex moiety (by 2−4 kcal/mol per ligand). Thus, the exothermic and exoergonic character of the reactions increases along the sequence MeCN ≪ **T3** (Pt^{II}, anionic complex) < **T1** (Pt^{II}, neutral complex) < **T4** (Pt^{IV}, anionic complex) < **T2** (Pt^{IV}, neutral complex). This trend perfectly correlates with both kinetic data (ref 14 and this work) and qualitative synthetic results that show the enhancement of the reactivity according to the same trend. Fourth, consideration of the effects of the solvent leads to a decrease of the reaction energies (in absolute values) in comparison to gas-phase calculations because of the higher stabilization, in solution, of the reactant's level than the product's level.

Kinetics of Nucleophilic Addition of 1,3-Diphenylpropan-2-one Oxime to Pt^{IV}-Bound Propiononitrile. Despite significant achievements in *synthetic* approaches to metal-mediated additions to RCN ligands, the existing knowledge about actual *reactivity* of incoming nucleophiles is rather rudimentary. Therefore, we recently launched systematic kinetic and mechanistic studies of nucleophilic additions to nitriles at Pt^{II} and Pt^{IV} centers. In particular, we have demonstrated that the nucleophilic addition of dibenzylhydroxylamines $HONR_2$ (R = CH_2Ph and $CH_2C_6H_4$Cl-*p*) to N≡CEt coordinated to Pt^{II} and Pt^{IV} follows clean second-order kinetics and the reactivity of Pt^{IV} complexes is 10^3 times higher than the reactivity of the corresponding Pt^{II} species.[14] These reactions can be considered as standards in investigations of the reactivity of other incoming nucleophiles.

Scheme 3



Here, we report kinetic data for the addition of 1,3-diphenylpropan-2-one oxime, HON═C(CH_2Ph)$_2$, to the Pt^{IV} complex [Ph_3PCH_2Ph][$PtCl_5$(EtCN)] (**11**) to give [Ph_3PCH_2-Ph][$PtCl_5${NH═C(Et)ON═C(CH_2Ph)$_2$}] (**12**; for its characterization, see the Experimental Section) in order to compare rate constants with those for the addition of the relevant hydroxylamines $HONR_2$ (R = CH_2Ph and $CH_2C_6H_4$Cl-*p*)[14] and, subsequently, to verify kinetic aspects and trends in the addition of both types of nucleophiles to coordinated nitriles. Complex **11** was chosen for this study because the Pt^{IV} center provides a substantial electrophilic activation of the nitrile toward even very weak nucleophiles[19] and, in addition, the coupling between oximes and Pt^{II} complexes does not proceed at all.[14]

Initially, some structural features of the *O*-nucleophiles hydroxylamines and oximes appear similar, but in fact, the N═C double bond in oximes could noticeably reduce their nucleophilic reactivity by making the nucleophilic center electron-poorer. Note that these nucleophilic addition reactions proceed in dichloromethane or chloroform as the solvent, and therefore, neutral uncharged forms of both hydroxylamines and oximes should be considered as reactive species.

The kinetics of the reaction depicted in Scheme 3 was studied by ^{1}H NMR spectroscopy under conditions very similar to those used for the reaction with HON(CH_2Ph)$_2$ and HON($CH_2C_6H_4$Cl-*p*)$_2$.[14] The majority of runs were performed at 50 °C, where the reaction is complete within 0.5−1 h. In the presence of 8−80-fold excesses of the oxime, a satisfactory pseudo-first-order behavior was observed for complex **11**. The values of pseudo-first-order rate constants k_{obs} showed no variation for at least 3−5 half-lives. The dependence of k_{obs} on oxime concentration is linear without any significant intercept (Figure 6). Therefore, $k_{obs} = k_2$[oxime], implying that the kinetic features of the additions of hydroxylamines and oximes match nicely.

The second-order rate constants k_2 were obtained at 40, 50, 55, and 60 °C (Table 5) and used for calculating the corresponding activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, which are included in Table 6. The rate constants k_2 are unaffected by excess free propiononitrile. The same values of k_2 were obtained in the presence of a 100-fold excess of EtCN relative to **11**. Furthermore, free propiononitrile does not react with the oxime in chloroform for 1 week at 45 °C.

The results obtained in this and previous[14] works clearly indicate that the reactivity of hydroxylamines is significantly higher than that of oximes. The activation parameters in Table 6 allow for the calculation of the rate constant k_2 as

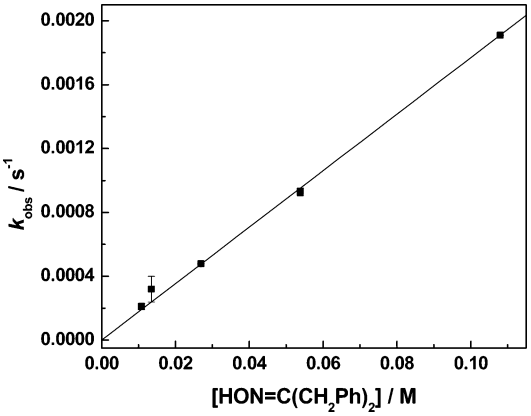


Figure 6. Pseudo-first-order rate constants k_{obs} as a function of oxime concentration for reaction depicted in Scheme 3: 50 °C, $CDCl_3$ solvent, [**11**] = 1.35×10^{-3} M.

Table 5. Rate Constants for the Reaction Depicted in Scheme 3 (in $CDCl_3$)

T (°C)	[oxime] (M)	k_{obs} (s^{-1})	k_2 (M^{-1} s^{-1})
40.0	2.69×10^{-2}	$(2.3 \pm 0.4) \times 10^{-4}$	$(8.8 \pm 0.5) \times 10^{-3}$
	1.08×10^{-2}	$(2.1 \pm 0.2) \times 10^{-4}$	
	1.35×10^{-2}	$(3.2 \pm 0.8) \times 10^{-4}$	$(1.8 \pm 0.1) \times 10^{-2}$
50.0	2.69×10^{-2}	$(4.8 \pm 0.2) \times 10^{-4}$	
	5.38×10^{-2}	$(9.3 \pm 0.4) \times 10^{-4}$	
	1.08×10^{-1}	$(1.9 \pm 0.1) \times 10^{-3}$	
55.0	2.69×10^{-2}	$(8.6 \pm 0.4) \times 10^{-4}$	$(3.3 \pm 0.2) \times 10^{-2}$
60.0	2.69×10^{-2}	$(1.6 \pm 0.3) \times 10^{-3}$	$(6.3 \pm 0.3) \times 10^{-2}$

Table 6. Activation Parameters for Reactions of **11** with Different Nucleophiles in $CDCl_3$

incoming nucleophile	$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta S^{\ddagger}$ (J mol^{-1} K^{-1})	ref
HON(CH$_2$C$_6$H$_4$Cl-*p*)$_2$	56 ± 6	-47 ± 23	14
HON=C(CH$_2$Ph)$_2$	81 ± 10	-27 ± 31	this work

3.9×10^{-6} M^{-1} s^{-1} at −20 °C. Measured at this temperature, the rate constant for HON(CH$_2$C$_6$H$_4$Cl-*p*)$_2$ equals 6.5×10^{-2} M^{-1} s^{-1}.[14] Hence, the hydroxylamine is a factor of 1.7×10^4 more reactive than the oxime. Inspection of Table 6 suggests that the significantly lower enthalpy of activation, $\Delta H^{\ddagger}$, accounts for this difference. The entropies of activation, $\Delta S^{\ddagger}$, are negative, similar, and typical of clean second-order reactions.[39,40]

There is no doubt that the HO-nucleophilicity of hydroxylamines is substantially higher than that of oximes. It is very likely that the lone-pair electrons of oxygen are significantly delocalized over the O−N=C moiety of the oxime. As a result, the highest occupied molecular orbital (HOMO) of oximes is lower in its energy than that of hydroxylamines (by 0.38 eV for HON=CMe$_2$ and HONMe$_2$ at the B3LYP/6-31G* level of theory), providing the slower nucleophilic attack for the former reagent.

Further Conversions of 5 and 6. When the syntheses of **5** and **6** (Scheme 2) were performed in air under prolonged heating (45 °C, 12 h) followed by slow evaporation of the solution for 1 day, the reactions resulted in the formation of crystals of **9** and **10** along with the starting materials and yet unidentified noncrystalline decomposition species. Authentic crystals of **9** were also obtained by vapor diffusion of diethyl ether into a DMF solution of **6** for 1 week at room temperature. X-ray determinations show that decomposition of **6** (route G) leads to, in particular, the unusual nitrosoalkane complex [PtCl$_2${HON=C(Me)C(Me)$_2$N=O}] (**9**), whereas in the case of **5** (route H), we succeeded in isolating and identifying the metal-free species [H$_3$NC(Me)$_2$C(Ph)=NOH]$_2$(NO$_3$)Cl·H$_2$O (**10**) (for the X-ray structure of this salt, see the Supporting Information), which possibly originates from the disproportionation of the hydroxylamine functionality[41] to afford the amine group and NO_3^-; compound **10** is known from the literature.[42]

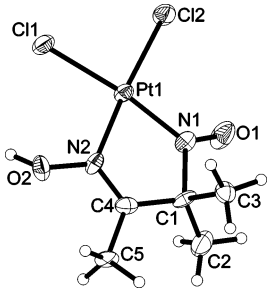


Figure 7. Thermal ellipsoid view of complex **9** with atomic numbering scheme. Thermal ellipsoids are drawn at 50% probability. The asymmetric unit contained two independent molecules. The second molecule has been omitted for clarity.

In the IR spectrum of **9**, there are two strong bands at 1658 cm^{-1} assigned to ν(C=N) of the oxime group C=NOH and at 1547 cm^{-1} due to ν(N=O) from the nitroso group of the newly formed ligand. In the X-ray structure of **9** (see Figure 7), the ligand HON=C(Me)C(Me)$_2$N=O is coordinated to the Pt(II) center by both the oxime and nitroso nitrogens, forming a five-membered chelate ring similar to that observed in related platinum chelates of the type [PtCl$_2$(NN)].[43] The measured N=O bond distance from the nitroso fragment is 1.206(15) Å, and this value agrees well with that for the relevant platinum nitrosoalkane complexes, i.e., *trans*-[PtCl$_2${Me$_3$C(N=O)}$_2$] [1.21(1) Å][44] and [PtCl$_2${N(=O)CR$_2$ONCR$_2$}] (R = Me, C$_5$H$_{10}$) (1.21−1.24 Å).[43]

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It is worth mentioning that, even though oxidations of 1,2-hydroxylaminooxime species involving metal centers to afford nitrosoalkane complexes are known,[45−47] the formation of a (nitrosoalkane)platinum(II) complex by route G (Scheme 2) is the first example of this kind in platinum chemistry. Moreover, (nitrosoalkane)platinum(II) complexes are so far quite rare, and the known examples include only *trans*-[$PtCl_2${$Me_3C(\underline{N}{=}O)$}$_2$][44] and [$PtCl_2${$\underline{N}(=O)CR_2O\underline{N}CR_2$}] (R = Me, C_5H_{10}).[43] It is anticipated that the reaction of 1,2-hydroxylaminooximes with Pt^{II} precursors, in air, might constitute an entry to these complexes, and this project is underway in our group.

Final Remarks. In synthetic experiments, it has been demonstrated that the 1,2-hydroxylaminooximes, i.e., reagents bearing both hydroxylamine and oxime HO moieties, react readily with both Pt^{II}- and Pt^{IV}-ligated EtCN to achieve, with a high degree of regioselectivity, the product of hydroxylamine-site addition to the nitrile group. This reaction represents an unusual reactivity pattern for 1,2-hydroxylaminooximes, which were previously employed mostly as sequestering reagents[48] for various metal centers.

In complete accord with the synthetic work, the kinetic study revealed that *N*,*N*-disubstituted hydroxylamines, as compared to the structurally related oxime species, are ca. 10^4-fold better nucleophiles toward Pt^{IV}-bound EtCN. Moreover, the computational study explicitly shows that the platinum-mediated nitrile−hydroxylamine coupling gives products that are more thermodynamically stable than those derived from the nitrile−oxime coupling. The verified kinetic and thermodynamic aspects of the metal-mediated nitrile−hydroxylamine and nitrile−oxime coupling make highly unfavorable the mechanism involving the addition of 1,2-hydroxylaminooximes to RCN ligands via the oxime site followed by isomerization of [M]−N(H)=C(R)ON=C−CN(H)OH species to achieve the appropriate [M]−N(H)=C(R)ON(H)C−C=NOH-type complexes.

All the more important is that the obtained results shed light on the mechanism and driving forces of the recently discovered mild protocol for syntheses of metal-containing and metal-free phthalocyanines from *o*-phthalonitriles;[23,24] the basic reaction (Scheme 1) involves application, as promoters, of such HON-nucleophiles as oximes[23] (routes A and B) or *N*,*N*-substituted hydroxylamines[23,49] (route C). In fact, the cyclotetramerization of *o*-phthalonitriles **I** to yield phthalocyanines **II** requires a two-electron reduction and the donation of two protons from a promoter.[7] From this perspective, it is clear that substantially higher tetramerization rates in the case of hydroxylamines than in the case of oximes can be explained by both better nucleophilic properties toward the nitrile group (this work) and higher reducing abilities (ref 50) of the former compared to the latter.

Experimental Section

Materials and Instrumentation. The preparations of the nitrile platinum(II) and platinum(IV) complexes *trans*-[$PtCl_n(EtCN)_2$] (*n* = 2, **3**;[35,51] *n* = 4, **4**[34]) and [Ph_3PCH_2Ph][$PtCl_5(EtCN)$] (**11**)[19] were reported previously. 1,2-Hydroxylaminooximes **1** and **2**·$MeCO_2H$ and HON=$C(CH_2Ph)_2$ (1,3-diphenylpropan-2-one oxime) were synthesized in accord with the published procedures.[52] 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 thin-layer chromatography (TLC), Merck UV 254 SiO_2 plates were used. FAB^+ and 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. 1D NMR experiments, i.e., ^1H, $^{13}C\{^1H\}$, and ^{195}Pt, and 2D NMR correlation experiments, i.e., ^1H,^{13}C HMQC, ^1H,^{13}C HMBC, and ^1H,^{15}N HMQC, were performed on Bruker Avance DPX 400 (UltraShield Magnet) and Varian UNITY 300 spectrometers at ambient temperature. ^{195}Pt NMR chemical shifts are given relative to $K_2[PtCl_6]$ (0.0 ppm), and ^{15}N NMR chemical shifts are relative to NH_4Cl (0.0 ppm).

X-ray Structure Determinations. X-ray diffraction data were collected with a Nonius KappaCCD diffractometer using Mo Kα radiation ($\lambda = 0.71073$ Å). Crystals were mounted in inert oil within a cold gas stream of the diffractometer. The Denzo-Scalepack[53] [**6**, **8**·(C_7H_8), **9**, **10**] or EvalCCD[54] (**7**) program packages were used for cell refinements and data reduction. Structures were solved by direct methods using the SHELXS-97 or SIR97 programs.[55,56] A multiscan absorption correction based on equivalent reflections

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{XPREP in SHELXTL[57] version 6.14-1 [**6**, **8**·(C_7H_8), **10**] or SADABS version 2.10 (**7**)}[58] or analytical absorption correction (de Meullenaer and Tompa)[59] was applied to data [T_{min}/T_{max} values were 0.2539/0.6103, 0.4381/0.7622, 0.2982/0.7259, 0.2470/0.6327, and 0.9572/0.9855 for **6**, **7**, **8**·(C_7H_8), **9**, and **10**, respectively]. The structures were refined with SHELXL-97[60] and the WinGX graphical user interface.[61] Structure **9** contained two independent molecules in the asymmetric unit. In **6**, **9**, and **10**, the OH, H_2O, and NH hydrogens were located from difference Fourier maps but not refined. The methyl groups of the toluene solvent in **8**·(C_7H_8) were disordered over two sites with equal occupancies of 0.5. In **7**, the OH hydrogen was located from the difference Fourier map and refined isotropically. In **8**·(C_7H_8), OH and NH hydrogens were located from the difference Fourier map and modeled with isotropic displacement parameters and distance constraints (0.85 Å). Other hydrogens were placed in idealized positions and constrained to ride on their parent atoms. The crystallographic details for **6**−**9** are summarized in Table 2, and selected bond lengths and angles are reported in Table 3. The crystallographic details of **10** are given as Supporting Information.

Computational Details. The full geometry optimization of all structures was carried out in Cartesian coordinates using the Gaussian 98[62] program package at the DFT level of theory. The calculations were performed using Becke's three-parameter hybrid exchange functional[63] in combination with the gradient-corrected correlation functional of Lee, Yang, and Parr[64] (B3LYP). A quasirelativistic Stuttgart pseudopotential described 60 core electrons, and the appropriate contracted basis set (8s7p6d)/[6s5p3d][65] for the platinum atom and the 6-31G* basis set for other atoms were used. The combination of the B3LYP functional and the mentioned basis set was found to be a quite reasonable approximation for the investigation of properties of transition metal complexes,[66−68] including platinum species,[12,66] taking into account the low computational cost of this method and the fact that the results obtained at the B3LYP level agree well with those calculated using higher correlated methods.

The Hessian matrix was calculated analytically for all optimized structures to verify the location of correct minima (no "imaginary" frequencies) and to estimate the zero-point-energy (ZPE) correction and thermodynamic parameters; the latter were calculated at 25 °C. The reaction energies (ΔE) and reaction enthalpies and Gibbs free energies (ΔH and ΔG) were calculated as the differences in energy of the product and sum of the energies of the reactants. Solvent effects were taken into account at the single-point calculations based on the gas-phase equilibrium geometries by using the polarizable continuum model[69] in the CPCM version[70] with $CHCl_3$ as a solvent. The Gibbs free energies in solution (G_s) were estimated by addition of the ZPE, thermal, and entropic contributions taken from the gas-phase calculations (δG_g) to the single-point CPCM-SCF energy (E_s).

The experimental X-ray structures of *trans*-[$PtCl_n${NH═C(Et)-ONHCMe$_2$C(Me)═NOH}$_2$] (n = 2, 4) (current work), [Ph_3PCH_2-Ph][$PtCl_5${NH═C(Et)ON(CH_2Ph)$_2$}],[14] [Ph_3PCH_2Ph][$PtCl_5${NH═C(Et)ON═C(C_9H_{16})}],[19] *trans*-[$PtCl_2${NH═C(Me)ON═CMe$_2$}$_2$],[36] and *trans*-[$PtCl_4${NH═C(Me)ON═C(Me)C(Me)═NOH}$_2$][17] were chosen as the starting geometries for the optimization. The equilibrium geometries and the main calculated bond lengths of **H/O5**−**H/O9** are in reasonable agreement with the experimental data. The maximum deviations of the theoretical and experimental parameters are 0.1 and 0.05 Å for the Pt−Cl and Pt−N bonds, respectively, whereas the difference for the other bonds does not exceed 0.03 Å, often falling within the 3σ interval of the X-ray data.

Kinetic Measurements. The kinetics of the reaction depicted in Scheme 3 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 40 to 60 °C. The progress of the reactions was monitored by integrating the ^{1}H NMR signals from the coordinated EtCN of **11** or signals of the Et group from the imino ligand of [Ph_3PCH_2Ph][$PtCl_5${NH═C(Et)-ON═C(CH_2Ph)$_2$}] (for its complete characterization, see later). The pseudo-first-order conditions were ensured by using at least an 8-fold excess of HON═C(CH_2Ph)$_2$ (DBO) with respect to **11**. The reactions were initiated by mixing solutions of **11** and DBO in $CDCl_3$ to give the total solution volume of 0.5 mL. Commonly used concentrations of **11** and DBO were 1.35×10^{-3} 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 of ln[100/(100 − x)] versus time where x (in percent) 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 the Origin 6.1 package.

Synthetic Work. Addition of HON(H)CMe$_2$C(R)═NOH to [$PtCl_n$(EtCN)$_2$]. In a typical experiment, **3** or **4** (0.1 mmol) was dissolved in chloroform (5 mL) at 20−25 °C, the corresponding 1,2-hydroxylaminooxime **1** or **2**·$MeCO_2H$ (0.2 mmol) was added, and the reaction mixture was heated at 40 °C for ca. 15 min. In the cases of **5** and **7**, the bright yellow solution was evaporated to dryness at room temperature under a flow of N_2, and the solid residue was washed with cold chloroform (1 mL) and pentane (five 3-mL portions) to remove the unreacted reagents. In the cases of **6** and **8**, the bright yellow precipitate formed was washed with cold chloroform (1 mL) and ether (five 1-mL portions) to remove the unreacted reagents. Yields were 80−85%, based on Pt.

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***trans*-[PtCl$_2${NH=C(Et)ON(H)CMe$_2$C(Ph)=NOH}$_2$] (5).** Anal. Calcd for $C_{26}H_{38}N_6Cl_2O_4Pt$: C, 40.84; H, 5.01; N, 10.99%. Found: C, 40.70; H, 4.84; N, 10.87%. FAB$^+$-MS, *m*/*z*: 764 [M]$^+$, 692 [M − 2Cl − H]$^+$. IR spectrum (selected bands), cm^{-1}: 3180 mw ν(N−H), 1663 s ν(C=N). ^{1}H NMR spectrum in CDCl$_3$/DMSO-d_6 (9:1), δ: 1.30 (s, 6*H*, NC*Me*$_2$), 1.37 (t, *J* = 7.2 Hz, 3*H*, CH$_2$*Me*), 3.02 (quart, *J* = 7.2 Hz, 2*H*, C*H*$_2$Me), 6.76 (s, 1H, ONH), 7.16−7.40 (m, 5*H*, Ph), 8.18 (s, br, 1*H*, N*H*), 9.84 (s, 1H, NOH). ^{13}C{^{1}H} NMR spectrum in CDCl$_3$/DMSO-d_6 (9:1) (through direct ^{13}C{^{1}H} observation and ^{1}H,^{13}C HMQC, and ^{1}H,^{13}C HMBC experiments), δ: 10.5 (CH$_3$) and 26.4 (CH$_2$)(Et), 23.5 (NC*Me*$_2$), 62.4 (N*C*Me$_2$), 126.3−131.5 (Ph), 159.9 (ON=C), 175.6 (HN=C). ^{15}N NMR spectrum in CDCl$_3$/DMSO-d_6 (9:1) (through ^{1}H,^{15}N HMQC experiment), δ: 93.1 (HN=C), 143.8 (ONH). ^{195}Pt NMR spectrum in CDCl$_3$/DMSO-d_6 (9:1), δ: −2031 (800 Hz).

***trans*-[PtCl$_2${NH=C(Et)ON(H)CMe$_2$C(Me)=NOH}$_2$] (6).** Anal. Calcd for $C_{16}H_{34}N_6Cl_2O_4Pt$: C, 30.01; H, 5.35; N, 13.12%. Found: C, 29.42; H, 5.03; N, 12.56%. FAB$^+$-MS, *m*/*z*: 604 [M − Cl − H]$^+$, 569 [M − 2Cl]$^+$. IR spectrum (selected bands), cm^{-1}: 3189 m−w ν(N−H), 1660 s and 1595 m ν(C=N). ^{1}H NMR spectrum in DMSO-d_6, δ: 1.20 (t, *J* = 7.2 Hz, 3*H*, CH$_2$*Me*), 1.24 (s, 6*H*, NC*Me*$_2$), 1.80 (s, 3*H*, N=CMe), 2.85 (quart, *J* = 7.2 Hz, 2*H*, C*H*$_2$Me), 5.70 (s, 1H, ONH), 8.16 (s, br, 1*H*, N*H*), 10.68 (s, 1H, NOH). ^{13}C{^{1}H} NMR spectrum in DMSO-d_6 (through direct ^{13}C{^{1}H} observation and ^{1}H,^{13}C HMQC, and ^{1}H,^{13}C HMBC experiments), δ: 10.3 (CH$_3$) and 26.8 (CH$_2$)(Et), 10.2 (N=C*Me*), 23.2 (NC*Me*$_2$), 62.4 (N*C*Me$_2$), 157.9 (ON=C), 177.0 (HN=C). We were unable to perform the ^{15}N NMR measurements due to instability of the compound in DMSO-d_6. ^{195}Pt NMR spectrum in DMSO-d_6, δ: −2027 (800 Hz).

***trans*-[PtCl$_4${NH=C(Et)ON(H)CMe$_2$C(Ph)=NOH}$_2$] (7).** Anal. Calcd for $C_{26}H_{38}N_6Cl_4O_4Pt$: C, 37.38; H, 4.58; N, 10.06%. Found: C, 37.29; H, 4.85; N, 9.61%. FAB$^+$-MS, *m*/*z*: 835 [M + H]$^+$, 765 [M − 2Cl + H]$^+$. IR spectrum (selected bands), cm^{-1}: 3197 s ν(N−H), 1652 vs ν(C=N). ^{1}H NMR spectrum in CDCl$_3$/DMSO-d_6 (9:1), δ: 1.25 (t, *J* = 7.2 Hz, 3*H*, CH$_2$*Me*), 1.30 (s, 6*H*, NC*Me*$_2$), 3.42 (quart, *J* = 7.2 Hz, 2*H*, C*H*$_2$Me), 6.66 (s, 1H, ONH), 7.12−7.40 (m, 5*H*, Ph), 9.14 (s, br, 1*H*, N*H*), 9.39 (s, 1H, NOH). ^{13}C{^{1}H} NMR spectrum in CDCl$_3$/DMSO-d_6 (9:1) (through direct ^{13}C{^{1}H} observation and ^{1}H,^{13}C HMQC, and ^{1}H,^{13}C HMBC experiments), δ: 10.9 (CH$_3$) and 24.7 (CH$_2$)(Et), 23.4 (NC*Me*$_2$), 62.9 (N*C*Me$_2$), 127.4−131.0 (Ph), 160.8 (ON=C), 179.5 (HN=C). ^{15}N NMR spectrum in CDCl$_3$/DMSO-d_6 (9:1) (through ^{1}H,^{15}N HMQC experiment), δ: 85.3 (HN=C), 145.6 (ONH). ^{195}Pt NMR spectrum in CDCl$_3$/DMSO-d_6 (9:1), δ: −153 (700 Hz).

***trans*-[PtCl$_4${NH=C(Et)ON(H)CMe$_2$C(Me)=NOH}$_2$] (8).** Anal. Calcd for $C_{16}H_{34}N_6Cl_4O_4Pt$: C, 27.01; H, 4.82; N, 11.81%. Found: C, 27.51; H, 4.84; N, 10.79%. FAB$^+$-MS, *m*/*z*: 710 [M]$^+$, 641 [M − 2Cl + H]$^+$. IR spectrum (selected bands), cm^{-1}: 3232 mw ν(N−H), 1657 s ν(C=N). ^{1}H NMR spectrum in DMSO-d_6, δ: 1.11 (t, *J* = 7.5 Hz, 3*H*, CH$_2$*Me*), 1.23 (s, 6*H*, NCMe$_2$), 1.79 (s, 3*H*, N=CMe), 2.95 (quart, *J* = 7.2 Hz, 2*H*, C*H*$_2$Me), 8.45 (s, 1H, ONH), 9.06 (s + d, $^2J_{PtH}$ ca. 35 Hz, 1*H*, N*H*), 10.81 (s, 1H, C=NOH). ^{13}C{^{1}H} NMR spectrum in DMSO-d_6 (through direct ^{13}C{^{1}H} observation and ^{1}H,^{13}C HMQC, and ^{1}H,^{13}C HMBC experiments), δ: 10.5 (N=C*Me*), 11.4 (CH$_3$) and 24.8 (CH$_2$)(Et), 23.3 (Me, NC*Me*$_2$), 62.8 (N*C*Me$_2$), 157.1 (ON=C), 179.5 (HN=C). ^{15}N NMR spectrum in DMSO-d_6 (through ^{1}H,^{15}N HMQC experiment), δ: 83.9 (HN=C), 151.1 (ONH). ^{195}Pt NMR spectrum in DMSO-d_6, δ: −92 (750 Hz).

Further Conversions of 5 and 6. Prolonged heating of **5** and **6** (45 °C, 12 h) obtained in situ (see above), followed by slow evaporation of the solution for 1 day, results in the formation of crystals of **10** and **9** along with the unreacted starting material and yet unidentified noncrystalline decomposition species. Authentic crystals of **9** were also obtained by vapor diffusion of diethyl ether into a DMF solution of **6** for 1 week at room temperature.

[PtCl$_2${HON=C(Me)C(Me)$_2$N=O}] (9). Anal. Calcd for $C_5H_{10}N_2Cl_2O_2Pt$: C, 15.16; H, 2.54; N, 7.07%. Found: C, 15.00; H, 2.34; N, 6.80%. IR spectrum (selected bands), cm^{-1}: 3238 mw ν(O−H), 1658 s ν(C=N), 1547 s ν(N=O). ^{1}H NMR spectrum in DMSO-d_6, δ: 1.20 (s, 6*H*, NCMe$_2$), 1.84 (s, 3*H*, N=CMe).

Synthesis of [Ph$_3$PCH$_2$Ph][PtCl$_5${NH=C(Et)ON=C(CH$_2$Ph)$_2$}] (12) was performed analogously to that described for [Ph$_3$PCH$_2$Ph][PtCl$_5${NH=C(Et)ON=CMe$_2$}].[19] The yield was 85%. Anal. Calcd for $C_{43}H_{42}N_2Cl_5OPPt$: C, 51.33; H, 4.21; N, 2.78%. Found: C, 52.33; H, 4.17; N, 2.60%. FAB$^-$-MS, *m*/*z*: 581 [M − 2Cl]$^-$, 373 [PtCl$_5$]$^-$. IR spectrum (selected bands), cm^{-1}: 3228 mw ν(N−H), 1656 s ν(C=N). ^{1}H NMR spectrum in CDCl$_3$, δ: 1.30 (t, *J* = 7.5 Hz, 3*H*, CH$_2$*Me*), 2.33 (quart, *J* = 7.2 Hz, 2*H*, C*H*$_2$Me), 3.73 (s, 4*H*, N=CCH$_2$), 5.34 (s, 4*H*, PCH$_2$Ph), 7.01−7.63 (m, 30*H*, Ph) 9.12 (s, 1*H*, NH). ^{13}C{^{1}H} NMR spectrum in CDCl$_3$ (through direct ^{13}C{^{1}H} observation), δ: 10.6 (CH$_3$) and 25.3 (CH$_2$)(Et), 32.6 (CH$_2$, $^1J_{PC}$ = 44.0, P*C*H$_2$Ph), 39.4 (CH$_2$, N*C*H$_2$Ph$_2$), 126.6−136.5 (Ph), 168.7 (N=C), 177.0 (HN=C). We were unable to perform the ^{15}N NMR measurements because of the rather poor solubility of the compound in CDCl$_3$ and instability in DMSO-d_6. ^{195}Pt NMR spectrum in CDCl$_3$, δ: −6 (290 Hz).

Acknowledgment. This work was partially supported by the Fundação para a Ciência e a Tecnologia (FCT), Portugal, and its POCTI program (POCTI/QUI/43415/2001 project) (FEDER funded). K.V.L. and M.L.K. express gratitude to FCT and the POCTI program (FEDER funded), Portugal, for fellowships (Grants SFRH/BD/10464/2002 and BPD/16369/98//BPD/5558/2001). The authors thank NATO for the Collaborative Linkage Grant PST.CLG.979289. V.Yu.K. is very much obliged to the Russian Fund for Basic Research (Grants 06-03-32065 and 05-03-32140), the Scientific Council of the President of the Russian Federation (Grant MK-1040.2005.3), the POCTI program (FEDER funded) (Cientista Convidado/Professor at the Instituto Superior Técnico, Portugal), the Academy of Finland for support of the cooperation with the University of Joensuu, and ISSEP for the Soros Professorship. M.L.K. thanks the Russian Fund for Basic Research for a grant (05-03-32504), M.G. thanks the Austrian Science Fund (FWF), M.H. thanks the Academy of Finland, and E.V.T. and V.I.O. thank Bruker for financial support of their studies. The authors also thank Dr. N.A. Bokach for experimental assistance and Dr. P.F. Kelly for valuable suggestions.

Supporting Information Available: General view of the equilibrium geometries, bond lengths, total energies, enthalpies, free Gibbs energies, entropies, and Cartesian coordinates of the calculated structures; Tables S1−S6 listing crystallographic data, atomic coordinates, bond lengths and bond angles, anisotropic displacement parameters, hydrogen coordinates and isotropic displacement parameters, and torsion angles. X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC051909R