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Theoretical Study of Nucleophilic Addition of Amines to Organic Nitriles

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Abstract—The mechanism of nucleophilic addition of a series of amines to acetonitrile MeC≡N both free and activated in a platinum complex *trans*-[$PtCl_2$(N ≡CMe)$_2$] was studied in detail by the theoretical methods of quantum chemistry. The influence of the nature of a particular nucleophile on the mechanism, kinetic and thermodynamic characteristics of the processes was elucidated. These reactions proceed according to a concerted highly synchronous mechanism that includes formation of 6-membered transition state consisting of the nitrile, amine, and water molecules. Hydrazine, aliphatic amines, and methylendiamine exhibit the highest reactivity from both kinetic and a thermodynamic viewpoint, while aromatic amines and amidine are the most inert.

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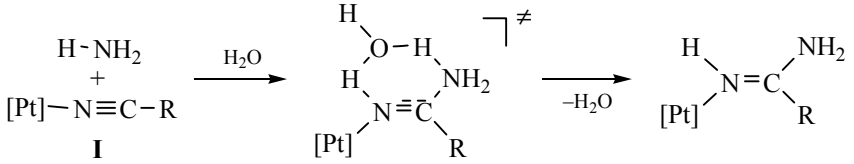
INTRODUCTION

The nucleophilic addition to organic nitriles RCN is a promising method for the one-step synthesis of various compounds possessing important industrial and pharmacological properties, for example, amides (including acrylamide and nicotinamide), iminoesters and amidines [1–6]. The latter are traditionally obtained using the Pinner reaction, which includes interaction of RC≡N with R'OH or R'SH in the presence of HX (X = Cl, Br) and ammonia or amine. However, the inertness of alkyl nitriles in these processes prevents the widespread use of RCN in synthetic practice.

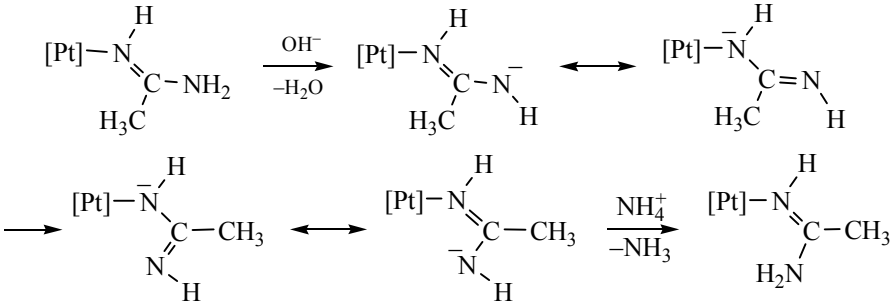
One of the most promising and actively studied in recent years means of RCN activation is the coordination with a Lewis acid. It was shown that the complexation of nitriles with platinum is an effective way of their activation toward nucleophilic addition and cycloaddition [3, 7–16]. Despite the importance of the reaction of nitriles with amines, there are only a few publications that discuss the possible mechanism of these processes [17, 18]. Previously [19] we published the results of a detailed theoretical study of reaction mechanism of nucleophilic addition of ammonia to the nitrile RC≡N, both free and activated in a platinum complex *trans*-[$PtCl_2$(N≡CMe)$_2$] (**I**), leading to the formation of amidines. It was shown that this reaction proceeded as a successive formation of the orientation complex, the 6-membered cyclic transition state, and the final reaction product, the amidine in *E*-conformation (Scheme 1). The water contained in the solvent plays a role of the process promoter. Also the mechanism of *E–Z* isomerization of the reaction product was investigated, which includes the deprotonation of the amino group nitrogen atom, the change in the conformation of the coordinated ligand followed by the protonation of the nitrogen atom (Scheme 2).

However, there are other, more traditional in organic chemistry ways to modify the reactivity of compounds, namely, varying substituents in the molecules of the reactants. Thus, the theoretical calculations of cycloaddition of nitrones RCH=N(Me)O to acetonitrile MeCN showed that, depending on the nature of R (R = H, Me, *p*-C_6H_4Me, *p*-C_6H_4OMe), a change in the Gibbs free activation energy reaches 6.4 kcal mol^{-1}, which corresponds to 5.2×10^4 times change in the reaction rate [20].

Scheme 1.

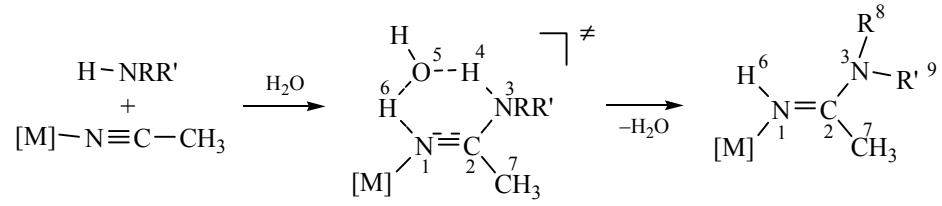


Scheme 2.



In order to explore this method of modifying the reagents reactivity we undertook a theoretical study of the influence of nucleophile nature (NH_2Me, $NHMe_2$, NH_2Ph, $NHPh_2$, NHMePh, NH_2 CH_2 NH_2, NH_2 NH_2, NH_2OH and NH_2–C(Me)=NH) on the particular reaction mechanism, kinetic and thermodynamic characteristics of reactions of nucleophilic addition of these nucleophiles to nitriles, both free and coordinated to Pt^{II} in the complex *trans*-$[PtCl_2(N{\equiv}CMe)_2]$ (Scheme 3). To simplify the calculations, the nucleophilic addition to only one of the coordinated MeCN molecules is considered. In the case of bifunctional nucleophiles NH_2OH and NH_2–C(Me)=NH we discuss only the reaction with the amino group. The obtained results are presented in this publication that is a continuation of a series of the reactivity studies of coordinated nitriles [21–33], including the reactions of nucleophilic addition [21–27].

Scheme 3.



[M] = none; {$PtCl_2(NCMe)$}

R = H; R' = Me
R = R' = Me
R = H; R' = Ph
R = R' = Ph
R = Me; R' = Ph
R = H; R' = CH_2NH_2
R = H; R' = NH_2
R = H; R' = OH
R = H; R' = C(Me)=NH

Details of Calculations

Full geometry optimization of all structures and transition states was performed in Cartesian coordinates using density functional method by means of the program package Gaussian-98 [34]. In the calculations was used the three-parametric hybrid exchange Becke functional [35] in conjunction with the Lee, Yang and Parr correlation functional [36] (B3LYP). Previously we showed that this approach is optimal for the study of the cycloaddition reactions of organonitriles [20, 30–33]. In considering electronic structure of the platinum complexes, in order to take into account relativistic effects, for the platinum atom the Stuttgart quasi-relativistic pseudo-potential was used, approximating 60 inner shell electrons, and a

corresponding set of grouped basis functions (8s7p6d)/[6s5p3d] [37]. For the other atoms, at the geometry optimization the valence-split basis set of standard Gaussian functions 6-31G* is employed including the polarization d-functions on the atoms of elements of the second and third periods with the exponents 0.8 for the carbon, oxygen and nitrogen atoms and 0.75 for chlorine. This basis is denoted further as 6-31G*, despite the use of another set for Pt atom. For all compounds the restrictions by symmetry were not imposed.

The Hessian matrices were calculated analytically, each structure corresponds either to a minimum on the potential energy surface, or to a saddle point of the first-order transition state. Thermodynamic functions were determined for standard conditions (pressure 1 atm and temperature 298.15 K). Effective atomic charges and Wiberg bond indices [38] were determined by the method of natural bond orbitals (NBO) [39].

To estimate the effects of solvation, we calculated the total energy (E_s) of all structures using the polarization continuum model [40] in CPCM version [41] (solvent CH_2Cl_2) on the basis of equilibrium gas-phase geometry in the CPCM-B3LYP/6-31+ G*//gas-B3LYP/6-31G* approximation. The value of entropy for the solution (S_s) was calculated in accordance with the procedure described in [42, 43] using the equations:

$$\Delta S_1 = R\ln V^s_{m,liq}/V_{m,gas}, \quad (1)$$

$$\Delta S_2 = R\ln V^o_m/V^s_{m,liq}, \quad (2)$$

$$\alpha = \frac{S^{o,s}_{liq} - (S^{o,s}_{gas} + R\ln V^s_{m,liq}/V_{m,gas})}{(S^{o,s}_{gas} + R\ln V^s_{m,liq}/V_{m,gas})}, \quad (3)$$

$$S_s = S_g + \Delta S_{sol} = S_g + [\Delta S_1 + \alpha(S_g + \Delta S_1) + \Delta S_2]$$

$$= S_g + [(-14.3 \text{ cal mol}^{-1} \text{ K}^{-1}) - 0.46(S_g - 14.3 \text{ cal mol}^{-1} \text{ K}^{-1}) + 7.98 \text{ cal mol}^{-1} \text{ K}^{-1}], \quad (4)$$

where S_g is gas-phase entropy of the solute, ΔS_{sol} is solvation entropy, $S^{0,s}_{liq}$, $S^{0,s}_{gas}$, and $V^s_{m,liq}$ are standard entropies and molar volume of water for liquid and gaseous phase, $V^s_{m,gas}$ is the molar volume of ideal gas at 25°C, V^0_m is molar volume of standard solution (1000 ml mol^{-1}). The enthalpy and Gibbs free energy in solution (H_s and G_s) were calculated as:

$$H_s = E_s(6\text{-}31{+}G^*) + H_g(6\text{-}31G^*) - E_g(6\text{-}31{+}G^*), \quad (5)$$

$$G_s = H_s - TS_s, \quad (6)$$

where E_s is the total energy in solution, E_g and H_g are gas-phase total energy and enthalpy, calculated in the respective basis.

Quantitative estimation of the degree of the cycloaddition synchronicity was carried out using formula (7) [46–49]:

$$S_W = 1 - \frac{\sum_{i=1}^{n} \frac{|\delta B_i - \delta B_{av}|}{\delta B_{av}}}{2n-2}, \quad (7)$$

where n is the number of bonds directly involved in the reaction (for the processes considered in this study n = 6). δB_i is the relative variation of Wiberg coefficients for ith bond in the transition state (TS), calculated with the Eq. (8):

$$\delta B_i = \frac{B_i^{TS} - B_i^R}{B_i^P - B_i^R}, \quad (8)$$

where the indices P, R and TS correspond to the product, reactants and transition state, respectively. The average variation δB_{av} is determined from the relation (9):

$$\delta B_{av} = n^{-1} \sum_{i=1}^{n} \delta B_i. \quad (9)$$

Thus, for a fully synchronous process S_W = 1, for completely asynchronous S_W = 0.

RESULTS AND DISCUSSION

The equilibrium geometry of the reaction products. In line with the experimental data [1, 2] and previous theoretical studies [19], addition of ammonia or amines to the Pt^{II} nitrile complexes leads to the formation of amidines in *E*-configuration (Scheme 1), which then, depending on the nature of the nucleophile, may isomerize to the corresponding *Z*-isomer (Scheme 2). Possible mechanisms for this isomerization have been discussed earlier and, therefore, in this work are not considered. The main equilibrium structural parameters for model products of nucleophilic addition of amines to MeCN and to the complex *trans*-[$PtCl_2(NCMe)_2$] (**I**), namely, for compounds HN=C(Me)NRR' (L1–L9) and *trans*-[$PtCl_2$(HN=C(Me)NRR')(NCMe)] (**II–X**), as well as the calculated transition states TSL1–TSL9 and TS1–TS9, are shown in Table. 1. General view of the equilibrium structures is depicted in Fig. 1. The structure of the initial complex **I** has been discussed previously [23], but the main calculated bond lengths are also given in Table 1 for comparison.

The main calculated bond lengths in **II** are in good agreement with experimental data for the *trans*-

Table 1. The calculated principal bond lengths (Å) in compounds **I–X** and L1–L9, and in the transition states TS1–TS9 and TSL1–TSL9

Bond	**I** [29]	**II**	**III**	**IV**	**V**	**VI**	**VII**	**VIII**	**IX**	**X**
Pt–Cl	2.369	2.372.	2.372.	2.368.	2.370.	2.371.	2.371.	2.372.	2.364.	2.370.
		2.375	2.374	1.379	2.377	2.377	2.377	2.376	2.381	2.373
$Pt–N^1$	1.963	2.025	2.025	2.021	2.018	2.023	2.023	2.023	2.021	2.025
N^1C^2	1.152	1.303	1.305	1.297	1.299	1.303	1.304	1.299	1.293	1.293
C^2C^7	1.455	1.501	1.505	1.503	1.505	1.505	1.503	1.500	1.499	1.504
C^2N^3		1.360	1.365	1.367	1.381	1.369	1.352	1.360	1.366	1.380
N^3X^8		1.456	1.460		1.436	1.465	1.459	1.397	1.392	1.420
N^3C^9			1.460	1.424	1.442	1.438				
Bond	L1	L2	L3	L4	L5	L6	L7	L8	L9	
N^1C^2	1.285	1.286	1.279	1.280	1.282	1.283	1.282	1.277	1.277	
C^2C^7	1.511	1.515	1.512	1.514	1.514	1.512	1.510	1.509	1.514	
C^2N^3	1.390	1.396	1.401	1.417	1.410	1.397	1.394	1.404	1.409	
N^3X^8	1.455	1.454		1.432	1.463	1.447	1.407	1.406	1.405	
N^3C^9		1.457	1.408	1.429	1.424					
Bond	TS1	TS2	TS3	TS4	TS5	TS6	TS7	TS8	TS9	
Pt–Cl	2.373.	2.374.	2.371.	2.368.	2.373.	2.375.	2.373.	2.370.	2.371.	
	2.384	2.383	2.387	2.386	2.383	2.385	2.384	2.392	2.387	
N^1C^2	1.260	1.262	1.258	1.259	1.260	1.263	1.261	1.259	1.255	
C^2N^3	1.516	1.515	1.528	1.538	1.532	1.504	1.512	1.508	1.538	
N^3H^4	1.245	1.228	1.258	1.218	1.227	1.255	1.258	1.303	1.255	
H^4O^5	1.279	1.296	1.270	1.309	1.300	1.278	1.266	1.223	1.276	
O^5H^6	1.156	1.186	1.123	1.161	1.167	1.157	1.140	1.092	1.101	
$N^1 H^6$	1.377	1.337	1.429	1.367	1.357	1.383	1.406	1.497	1.469	
Bond	TSL1	TSL2	TSL3	TSL4	TSL5	TSL6	TSL7	TSL8	TSL9	
$N^1 C^2$	1.227	1.229	1.218	1.209	1.220	1.230	1.229	1.226	1.210	
$C^2 N^3$	1.669	1.671	1.762	1.910	1.763	1.654	1.657	1.667	1.847	
N^3H^4	1.135	1.124	1.161	1.220	1.144	1.119	1.117	1.171	1.220	
H^4O^5	1.437	1.456	1.382	1.294	1.410	1.477	1.469	1.372	1.295	
O^5H^6	1.236	1.246	1.279	1.317	1.297	1.244	1.229	1.212	1.277	
N^1H^6	1.291	1.282	1.243	1.204	1.226	1.289	1.301	1.319	1.241	

$[PtCl_2(HN=C(Me)NHMe)_2]$ [44]. Calculated bond lengths Pt–Cl and C^2N^3 are overestimated compared with the experimental data by 0.06 and 0.03 Å, respectively. The maximum difference between theoretical and experimental values for the lengths of other bonds not exceeds 0.01 Å. A good agreement is observed between the calculated values for complex **3** and the experimental data for the compound *trans*-$[PtCl_2(HN=C(Me)N(Me)(Bu\text{-}t)(NCMe)]$ [45]. The maximum difference is 0.08 and 0.03 Å for Pt–Cl and Pt–N bonds and not higher than 0.02 Å for the other bonds. Addition of amines to the complex **I** affects the most noticeably the length of the double bond N^1C^2, increasing it by 0.141–0.153 Å. The respective bond order decreases from 2.69 in **I** to 1.56–1.63 in **II–X**. Bond lengths $Pt–N^1$ and $C^2–C^7$ also increase by 0.055–0.162 Å and 0.044–0.050 Å, respectively, in going from **I** to **II–X**. The fragment $N^1C^2C^7$ becomes not linear, with the PtN^1C^2 and $N^1C^2C^7$ angles 130°–133° and 120°–123°, respectively.

For the series of reaction products **II–X**, the bond N^1C^2 is of maximum length for the alkyl and dialkylamine derivatives **II, III, VI,** and **VII**, whereas the minimum length is found for the products of nucleophilic addition of hydroxylamine and amidine, **IX** and **X**. The bond length C^2N^3 is even more varied, being minimal for dialkylamine and alkyl derivatives **II, III, VII**, and the product of hydrazine nucleophilic

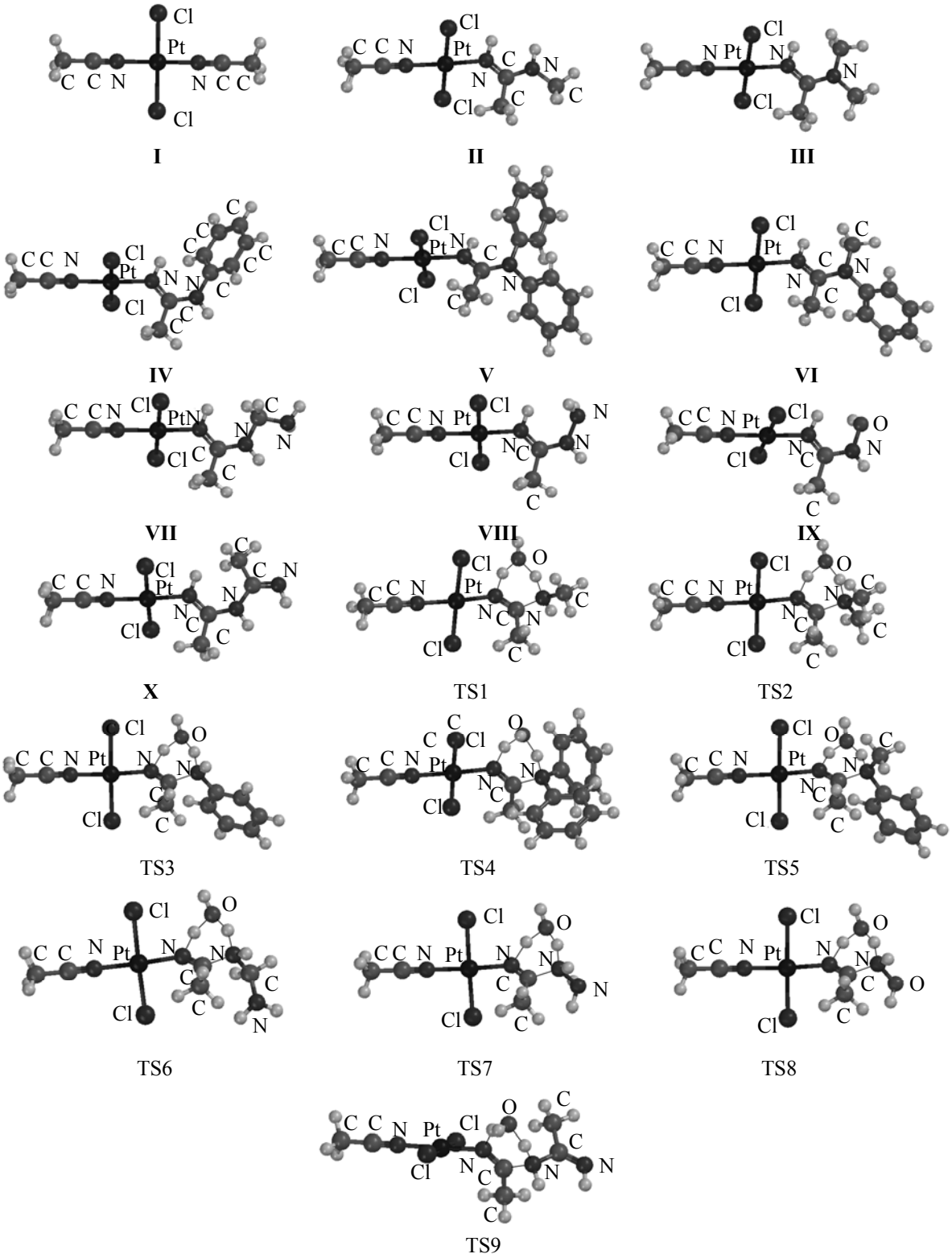


Fig. 1. General view of the equilibrium geometry of complexes **I–X** and transition states TS1–TS9.

addition **VIII** and maximal for the addition products of diphenylamine and amidine, **V** and **X**, respectively.

Transition states and the reaction mechanism. As shown earlier, the most energetically preferable mechanism for the ammonia addition to nitriles includes the formation of 6-membered transition state, containing nitrile molecule, ammonia (or amine), and water. For all the reactions of amines with acetonitrile MeCN and complex **I**, investigated in this work, were localized transition states of the same type (TSL1–TSL9 and TS1–TS9).

An important characteristic of the concereted reaction mechanism is the degree of the process synchronism. To quantify the degree of synchronism the following criteria are usually used: (1) The relative length of two new contacts in the corresponding transition states (if we consider H_2O–amine dimer as a molecule of one reactant). However, in practice, this criterion can be applied only to the reactions where interact the atoms of the same species. (2) The relative values of the Wiberg coefficients for these contacts. This test provides more reliable information, since Wiberg coefficients are less sensitive to the nature of atoms than the internuclear distance. (3) The most reliable criterion of the degree of the process synchronicity is S_y parameter taking into account the change of all bonds directly involved in the reaction (see Details of the calculation).

Analysis of these criteria (Tables 2 and 3) led us to the following conclusions. First, the mechanism of all reactions of the nucleophilic addition to free nitrile is characterized by a high degree of synchronicity. Indeed, although for each of the transition states TSL1–TSL9 the difference in the internuclear distances C^2N^3 and N^1H^6 is significant (0.348–0.706 Å), and the difference in the Wiberg coefficients reaches 0.04–0.26, the calculated values of S_y are equal to 0.86–0.94. Second, coordination of nitrile in the complex **I** does not substantially change the process synchronicity. The S_y parameter decreases slightly in the case of the reactions with phenylamine, diphenylamine, hydroxylamine, and amidine, and virtually remains unchanged or even slightly increases in the other reactions (Table 3). This pattern of changes in synchronism of the reactions of nucleophilic addition differs from that for the cycloaddition reactions of nitrile, where the coordination of RCN by a metal (Pt or Pd) leads to a substantial decrease in the synchronism [20, 29–33].

Activation energy. Localization of the transition states on the potential energy surfaces allowed an estimation of the "electronic" activation energy (E_{ag}), which is numerically equal to the activation enthalpy at 0 K, and allowed to find enthalpy and Gibbs free activation energy at 298.15 K ($\Delta H_g^{\neq}$ and $\Delta G_g^{\neq}$, respectively, Table 4). Analyzing these data we conclude the following. First, the activation barriers to the nucleophilic addition to free acetonitrile have high values for the gas phase (39–50 kcal mol^{-1} in the ΔG_g scale). Second, the coordination of acrylonitrile in complex **I** leads to a significant reduction in the activation energy, to 18–35 kcal mol^{-1}, which corresponds to 1.0×10^{11}–2.5×10^{15} times increase in the reaction rate. Third, the reactivity of the nucleophile in the reaction with noncoordinated MeCN decreases in the series: $NH_2NH_2 > NH_2Me \sim NHMe_2 > NH_2CH_2NH_2 > NH_2Ph > NHMePh \sim NH_2OH > NH_2C(Me)=NH > NHPh_2$. In the case of nucleophilic adition to complex **I**, methylenediamine becomes more reactive than methylamine, whereas the reactivity of other nucleophiles is not changed. Thus, the most reactive in the reactions of nucleophilic addition to nitriles are hydrazine and aliphatic mono- and diamines, while the most inert are aromatic amines, amidine, and hydroxylamine. Fourth, the coordination of nitriles decreases considerably the activation barrier in the reactions involving the more reactive amines (NH_2NH_2, $NH_2CH_2NH_2$, NH_2Me, or $NHMe_2$) and less significantly in the reactions with rather inert nucleophiles ($NH_2CMe=NH$ and $NHPh_2$). However, even for the two latter the activation of nitriles by the coordination by platinum is sufficient for the reaction to occur. Fifth, the activation energy E_a and the $\Delta H^{\neq}$ for some reactions with an activated nitrile have negative values, indicating that the transition state corresponds to lower energy level compared with the reactants. This is due to the formation in the first stage of the reaction of the orientational complex where the molecules of the amine, H_2O, and *trans*-$[PtCl_2(N{\equiv}CMe)_2]$ are connected by van der Waals interactions mainly of dipole-dipole nature. The existence of orientation complexes was predicted for a number of nucleophilic reactions [3, 27] and cycloaddition [20, 29–32] to nitriles.

Energy effects of the reactions. Analysis of the calculated energy effects of the reactions for the gas phase (ΔE_g, ΔH_g and ΔG_g) led us to the following conclusions. First, the reactions with free acetonitrile are characterized by the small negative ΔH_g value. The values of ΔG_g are small negative for some nucleo-

Table 2. Wiberg indices (WI) for amines, H_2O, MeCN, compounds L1–L9, **I**–**X**, and transition states TSL1–TSL9, TS1–TS9

WI	TSL1	TSL2	TSL3	TSL4	TSL5	TSL6	TSL7	TSL8	TSL9
N^1C^2	2.229	2.225	2.279	2.339	2.269	2.211	2.216	2.230	2.334
C^2N^3	0.660	0.652	0.566	0.448	0.564	0.675	0.667	0.661	0.494
N^3H^4	0.515	0.503	0.482	0.403	0.478	0.535	0.538	0.483	0.428
H^4O^5	0.242	0.237	0.268	0.327	0.260	0.222	0.224	0.272	0.318
O^5H^6	0.353	0.347	0.320	0.288	0.307	0.351	0.359	0.370	0.318
N^1H^6	0.424	0.432	0.457	0.484	0.472	0.429	0.418	0.401	0.453
WI	L1	L2	L3	L4	L5	L6	L7	L8	L9
N^1C^2	1.798	1.796	1.826	1.837	1.825	1.806	1.807	1.837	1.841
$C^2N(3)$	1.119	1.099	1.075	1.032	1.057	1.108	1.109	1.089	1.057
N^1H^6	0.857	0.851	0.840	0.839	0.839	0.852	0.849	0.834	0.842
WI	TS1	TS2	TS3	TS4	TS5	TS6	TS7	TS8	TS9
N^1C^2	1.922	1.914	1.932	1.929	1.924	1.902	1.911	1.916	1.945
C^2N^3	0.867	0.857	0.842	0.821	0.830	0.882	0.868	0.879	0.827
N^3H^4	0.403	0.393	0.387	0.392	0.389	0.397	0.393	0.362	0.392
H^4O^5	0.335	0.332	0.341	0.321	0.329	0.338	0.344	0.369	0.336
O^5H^6	0.410	0.386	0.440	0.405	0.400	0.411	0.424	0.469	0.460
N^1H^6	0.318	0.347	0.283	0.325	0.330	0.318	0.301	0.242	0.256
WI	**II**	**III**	**IV**	**V**	**VI**	**VII**	**VIII**	**IX**	**X**
N^1C^2	1.574	1.567	1.593	1.603	1.575	1.555	1.575	1.608	1.626
C^2N^3	1.229	1.215	1.195	1.148	1.194	1.250	1.224	1.202	1.152
N^1H^6	0.797	0.792	0.782	0.781	0.792	0.795	0.789	0.774	0.782
WI	NH_2Me	$NHMe_2$	NH_2Ph	$NHPh_2$	NHMePh	$(NH_2)_2CH_2$	NH_2NH_2	NH_2OH	$NH_2C(Me)NH$
N^3H^4	0.849	0.830	0.828	0.796	0.810	0.846	0.854	0.854	0.820
WI	H_2O	MeCN	**I**						
O^5H^6	0.784								
N^1C^2		2.911	2.689						

philes and small positive for others. Second, the coordination of nitrile leads to a significant decrease in the energy effects of the reaction. As a result, all the processes are exoergonic and substantially exothermic, although for the reactions with $NH_2C(Me)=NH$ and $NHPh_2$ the negative ΔG_g value is less than 2 kcal mol^{-1} (–0.7 and –1.6 kcal mol^{-1}, respectively). Thus, the binding of nitriles in the complexes provides both kinetic and thermodynamic activation of substrates. Third, exoergonic and exothermic nature of the reaction decreases in the series of nucleophiles NH_2NH_2 > $NH_2CH_2NH_2$ > NH_2Me > NH_2OH ~ $NHMe_2$ > NH_2Ph > $NH_2C(Me)=NH$ > NHMePh > $NHPh_2$ for the nucleophilic addition to MeCN and in the sequence NH_2NH_2 > $NH_2CH_2NH_2$ > NH_2Me > $NHMe_2$ ~ NH_2OH > NH_2Ph ~ NHMePh > $NHPh_2$ > $NH_2C(Me)=NH$ for the nucleophilic addition to **I**. Fourth, there is a definite correlation between the value of activation energy and the energy effect of reaction: in general, the higher the activation barrier, the more positive (less negative) energy effect (Fig. 2).

Solvation effects. The reactions of nucleophilic addition of ammonia and amines to nitriles are usually performed in CH_2Cl_2 solution [5]. To account for the solvation effects and to analyze their influence on the

energy characteristics of the processes, we calculated the polarization energy in the CPCM version of the continuum model (solvent CH_2Cl_2). The effect of solvation leads to an increase in E_a and $\Delta H^{\ddagger}$ (by 1.3–9.5 kcal mol^{-1}, respectively) due to a higher stabilization of the reactants level (strongly polar molecules) as compared with the levels of transition states. The influence of the solvation on the energy effects of the processes is more complicated. For the reactions with NH_2Me and NH_2OH, the solvation increases the exothermic nature of the process, whereas in other cases, ΔH becomes less negative (more positive). The values of $\Delta G^{\ddagger}$ and ΔG for the solution is substantially lower than for the gas phase due to the less negative values of $\Delta S^{\ddagger}$ and ΔS in the condensed system as compared with the gas phase (see Details of the calculation).

Table 3. Synchronicity of nucleophilic addition of amines to MeCN and complex **I**

Amine	S_W	
	MeCN	**I**
NH_2Me	0.89	0.88
$NHMe_2$	0.88	0.89
NH_2Ph	0.90	0.87
$NHPh_2$	0.92	0.87
NHMePh	0.89	0.89
$NH_2CH_2NH_2$	0.86	0.88
NH_2NH_2	0.87	0.88
NH_2OH	0.90	0.84
$NH_2C(Me)NH$	0.94	0.85

Table 4. Activation parameters (E_a, $\Delta H^{\neq}$ and $\Delta G^{\neq}$), and energy effects (ΔE, ΔH and ΔG) of the studied reactions (in kcal mol^{-1})[a]

Amine	MeCN			**I**		
	E_a	$\Delta H^{\neq}$	$\Delta G^{\neq}$	E_a	$\Delta H^{\neq}$	$\Delta G^{\neq}$
NH_2Me	18.5 (20.1)	18.0 (19.6)	41.3 (32.3)	–3.6 (–0.0)	–3.8 (–0.2)	21.1 (13.4)
$NHMe_2$	18.2 (21.2)	17.8 (20.9)	41.3 (33.7)	–4.2 (1.5)	–4.5 (1.3)	21.9 (15.7)
NH_2Ph	22.2 (26.3)	21.4 (25.4)	44.9 (38.3)	2.5 (8.3)	2.4 (8.2)	27.7 (22.0)
$NHPh_2$	26.8 (34.5)	25.3 (33.0)	50.0 (46.5)	9.1 (18.6)	8.5 (18.1)	35.5 (32.8)
NHMePh	23.2 (28.6)	22.4 (27.7)	46.2 (40.8)	3.7 (11.3)	3.2 (10.9)	29.0 (25.0)
$NH_2CH_2NH_2$	19.1 (20.9)	18.9 (20.7)	42.2 (33.5)	–5.2 (–0.4)	–5.4 (–0.6)	20.0 (13.3)
NH_2NH_2	15.6 (19.3)	15.2 (18.9)	38.8 (31.7)	–6.7 (–1.3)	–7.1 (–1.7)	18.0 (12.0)
NH_2OH	24.7 (26.0)	23.2 (24.5)	46.3 (37.1)	2.9 (6.7)	1.7 (5.5)	28.7 (20.3)
$NH_2C(Me)NH$	25.6 (31.7)	24.2 (30.3)	47.7 (43.1)	7.7 (14.6)	6.8 (13.7)	34.7 (28.9)
Amine	ΔE	ΔH	ΔG	ΔE	ΔH	ΔG
NH_2Me	–11.0 (–11.8)	–8.8 (–9.6)	3.3 (–3.0)	–27.2 (–28.2)	–25.2 (–26.2)	–10.0 (–17.9)
$NHMe_2$	–9.9 (–9.4)	–7.6 (–7.1)	4.8 (–0.3)	–26.5 (–24.8)	–23.6 (–21.9)	–9.9 (–14.5)
NH_2Ph	–8.4 (–7.3)	–6.0 (–5.0)	6.3 (1.7)	–23.9 (–20.9)	–21.7 (–18.7)	–5.9 (–10.1)
$NHPh_2$	–3.3 (–0.2)	–1.3 (1.8)	11.6 (8.9)	–19.6 (–13.3)	–17.7 (–11.5)	–1.6 (–2.7)
NHMePh	–4.5 (–2.8)	–2.3 (–0.6)	10.6 (6.5)	–21.7 (–17.9)	–19.0 (–15.2)	–5.2 (–7.7)
$NH_2CH_2NH_2$	–11.9 (–11.8)	–9.6 (–9.6)	2.3 (–3.1)	–29.3 (–29.1)	–26.6 (–26.4)	–13.8 (–19.4)
NH_2NH_2	–17.1 (–16.4)	–15.0 (–14.4)	–2.4 (–7.5)	–33.3 (–31.7)	–30.9 (–29.3)	–16.8 (–21.6)
NH_2OH	–9.4 (–10.4)	–7.7 (–8.6)	4.6 (–1.9)	–24.3 (–24.5)	–22.2 (–22.4)	–8.4 (–14.8)
$NH_2C(Me)NH$	–5.3 (–3.3)	–2.8 (–0.9)	9.2 (5.7)	–18.0 (–14.1)	–15.7 (–11.8)	–0.7 (–3.7)

[a] The energies obtained with accounting for the solvation effects are given in parentheses.

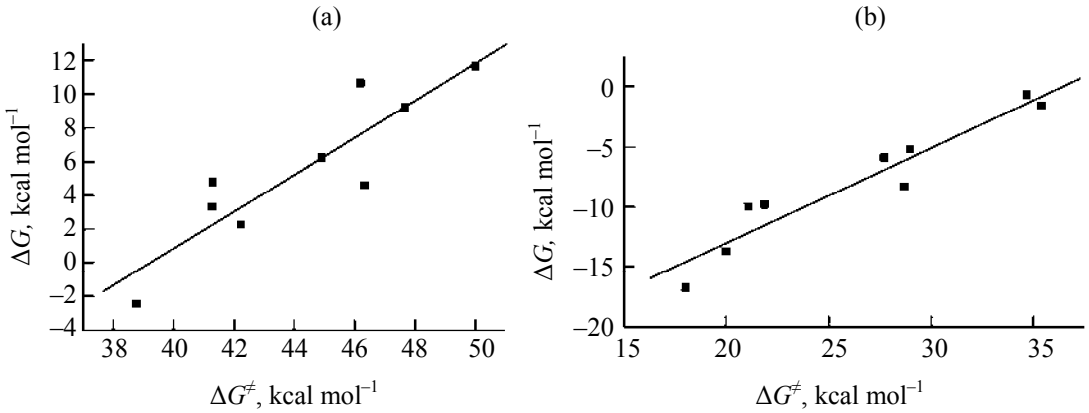


Fig. 2. Relationship between the activation energy (E_a) and the energy effect (ΔE) of the reactions of nucleophilic addition to (a) MeCN and (b) complex **I**.

CONCLUSIONS

In this paper we presented the results of theoretical study of reactions of nucleophilic addition of a series of amines to the organonitriles, both free and activated in *trans*-$[PtCl_2(N{\equiv}CMe)_2]$ complex. The reactions proceed along the concerted one-step mechanism that includes formation of 6-membered transition state including the molecules of the nitrile, amine, and water. Water acts as a promoter of these processes, stabilizing the transition state by formation of 6-membered cyclic structures. Reaction mechanism has a high degree of synchronism, even in the case of nucleophilic addition to the coordinated nitriles.

The reaction with free MeCN have a high activation barrier (32–46 kcal mol^{-1} in the ΔG_s scale) and the Gibbs free energy of reaction is close to zero. However, coordination of nitrile by platinum(II) leads to a significant decrease in the activation energy and increase in the the exothermic and exogenic nature of the reaction, which ensures the effective proceeing of the process even in the case of the most inert amines. Hydrazine, aliphatic amines, and methylendiamine exhibit the highest reactivity in the reactions of nucleophilic addition to nitriles both from kinetic and thermodynamic points of view, while the most inert are aromatic amines and amidine.

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