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Study of the reactivity of organonickel sigma-complexes towards nitriles

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The reactivity of organonickel sigma-complexes of type [NiBr(Ar)(bpy)], where Ar = 2,6-dimethylphenyl (Xyl), 2,4,6-trimethylphenyl (Mes), 2,4,6-triisopropylphenyl (Tipp), 2,4,6-tricyclohexylphenyl (Tchp), bpy = 2,2´-bipyridine, towards nitriles (acetonitrile, propionitrile, chloroacetonitrile, benzonitrile) has been investigated. This reaction leads to imines by formation of new carbon—carbon bond between aromatic fragment and nitrile group C≡N.

Key words: 2,2´-bipyridine, imines, organonickel sigma-complexes, nitriles, mass spectrometry, X-ray analysis, electrosynthesis.

The use of transition metal complexes in catalytic conversion of organic compounds is one of the most promising directions of development in modern chemistry.[1] Organometallic sigma-complexes are main intermediates of catalytic processes involving organic substrates. Application of nickel complexes as catalysts for coupling reactions, leading to the formation of organic and organophosphorus compounds, is actual and of practical demand due to availability and relatively low cost of nickel derivatives.[2] Particular attention has recently been given to processes based on the use of highly reactive organometallic intermediates, representing the products of the reaction of organic substrate with an active form of the metal complex catalyst.[3] Such active particles in the processes of homo- and cross-coupling involving organic halides are organonickel sigma-complexes, which could be stabilized and isolated in pure form by using *ortho*-substituted aromatic halides.[4] The substituents in the *ortho*-positions of aromatic ring, sigma-bonded with nickel atom, restrict free rotation around sigma metal-carbon bond and shield the axial positions of metal center.[5] However, at present almost no data on the reactivity of organonickel sigma-complexes towards unsaturated compounds, in particular, to nitriles, are available. At the same time, the processes of activation and functionalization of organic derivatives containing carbon-nitrogen multiple bonds in the coordination sphere of the transition metal complexes have been studied in some detail.[6—12]

The aim of this work is to investigate the reactivity of organonickel sigma-complexes of the type [NiBr(Ar)(bpy)] (Ar is 2,6-di- or 2,4,6-tri-substsituted phenyl, bpy is 2,2´-bipyridine) towards nitriles.

Results and Discussion

The series of organonickel sigma-complexes **1—4** of the composition [NiBr(Ar)(bpy)] (Ar is 2,6-dimethylphenyl (Xyl), 2,4,6-trimethylphenyl (Mes), 2,4,6-triisopropylphenyl (Tipp), 2,4,6-tricyclohexylphenyl (Tchp)) were prepared according to earlier developed procedure,[13—15] which includes oxidative addition of electrochemically generated [Ni^0(bpy)] complexes to corresponding aromatic bromides (Scheme 1).

First, it has been experimentally established that by dissolving of sigma-complex **2** in acetonitrile in the absence of intentionally added reagents, capable to decoordinate bromide anion from the coordination sphere of nickel, the reaction of complex **2** with the solvent (MeCN) molecules proceeds sufficiently slow (8 h). That can be judged by the change of the solution color from intensive red to greenish-yellow. This color change is associated with a cleavage of aryl moiety sigma-bonded to the nickel atom. The aryl moiety is a ligand of strong field, and it ensures the realization of low-spin state (16e-complex, dsp^2-hybridization) of the metal center.[2] This is followed by the formation of new carbon-carbon bond between the aryl moiety and carbon atom of the nitrile group C≡N.

It was established previously[16] that DMF molecules are capable to substitute the bromide anion in the coor-

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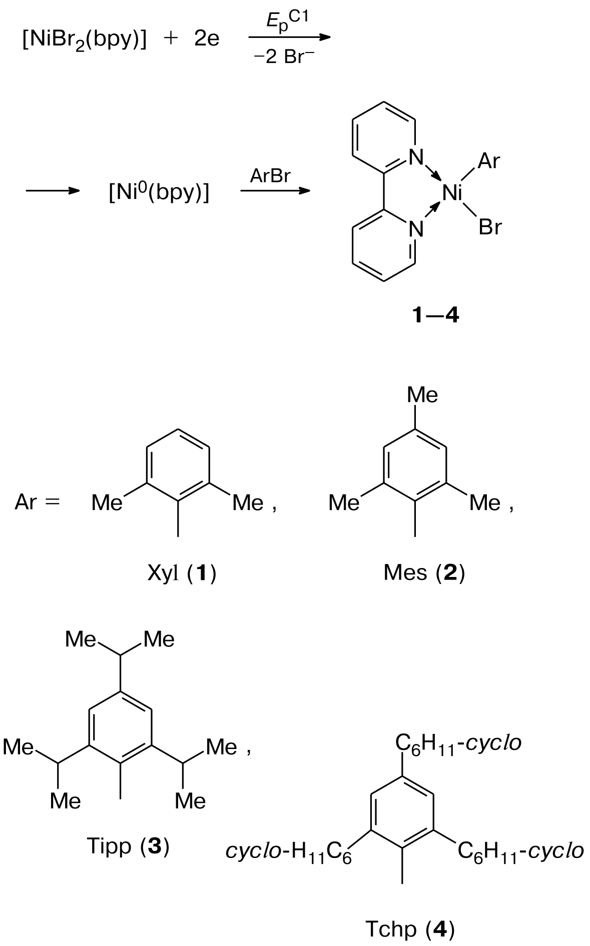
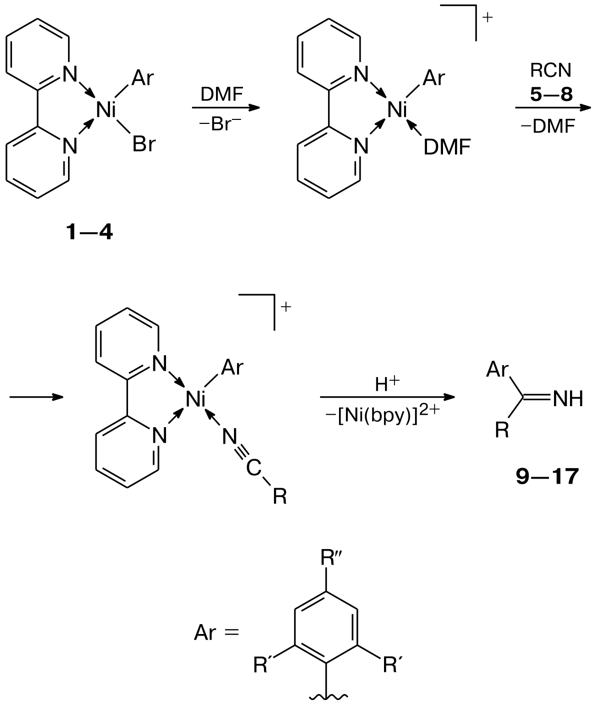
Scheme 1



dination sphere of organonickel sigma-complexes with the formation of cationic complexes which, in turn, can undergo the reaction of ligand exchange with the molecules of nitriles. Therefore, it was decided to investigate the interaction of the complex **2** with acetonitrile in the presence of small amounts of DMF. It turned out that in this case the solution color change is much faster (30 min) than in the absence of DMF. This result is of interest because the use of DMF as a solvent for the reaction of imines production can allow one to optimize the whole process with the transition of the conditions to one-pot synthesis. This is because the electrochemical generation of organonickel sigma-complexes **1—4** is also successfully carried out in DMF.[13—15] In this case the isolation and purification in the intermediate steps is not required. It should be noted that as bromine consuming reagent boron trifluoride diethyl etherate ($BF_3 \cdot Et_2O$) can be used instead of DMF. This allows one to perform the reaction of imines production in nonpolar organic solvents such as benzene, facilitating their separation due to the precipitation of inorganic nickel complexes.

Further study of the reactivity of the organonickel sigma-complexes **1—4** towards acetonitrile, propionitrile, chloroacetonitrile, and benzonitrile (Scheme 2) was carried out in DMF—nitrile system, most interesting for us in terms of the optimization of the overall process. As a result of all conducted experiments it was established that the interaction of complexes **1—4** with nitriles **5—8** in the presence of DMF leads to the formation of imines **9—17** in the solution (see Scheme 2, Table 1). It should be noted that the final step of the protonation proceeds as the results of the presence of water traces in the process.

Scheme 2



The formation of imines **9—17** in the solution was proved by gas chromato-mass spectrometry. It was found

Table 1. Products of interaction of obtained from organonickel sigma-complexes **1—4** with nitriles **5—8**

σ-Complex	R′	R″	Nitrile (R)			
			5 (Me)	**6** (Et)	**7** (CH_2Cl)	**8** (Ph)
1	Me	H	**9**	—*	—*	**10**
2	Me	Me	**11**	**12**	**13**	**14**
3	Pr^i	Pr^i	**15**	—*	—*	**16**
4	*cyclo*-C_6H_{11}	*cyclo*-C_6H_{11}	**17**	—*	—*	—*

* Not found.

that the reaction of organonickel sigma-complex **2** with all nitriles used in this work yields the corresponding imines **11—14** as the result of addition of Mes-fragment of original organonickel sigma-complex to the C≡N bond of nitrile molecule. Along the signal of molecular ions with *m/z* 161 (**11**), *m/z* 175 (**12**), *m/z* 195 (**13**), and *m/z* 223 (**14**) the peaks with *m/z* 146, corresponding to fragment ions of composition $[\mathrm{MesC{=}NH}]^+$ (or $[\mathrm{C_{10}H_{12}N}]^+$), forming at the elimination of Me, Et, CH_2Cl, and Ph groups from molecular ions of compounds **11—14**, respectively, were detected in the mass spectra of imine series **11—14** (Fig. 1). These compounds have the same aryl fragment (Mes), but different substituents R. It should be also noted that the peaks with *m/z* 160, corresponding to ions $[\mathrm{M - CH_3}]^+$ and $[\mathrm{M - Cl}]^+$, respectively, are registered in the mass spectra of compounds **12** and **13**.

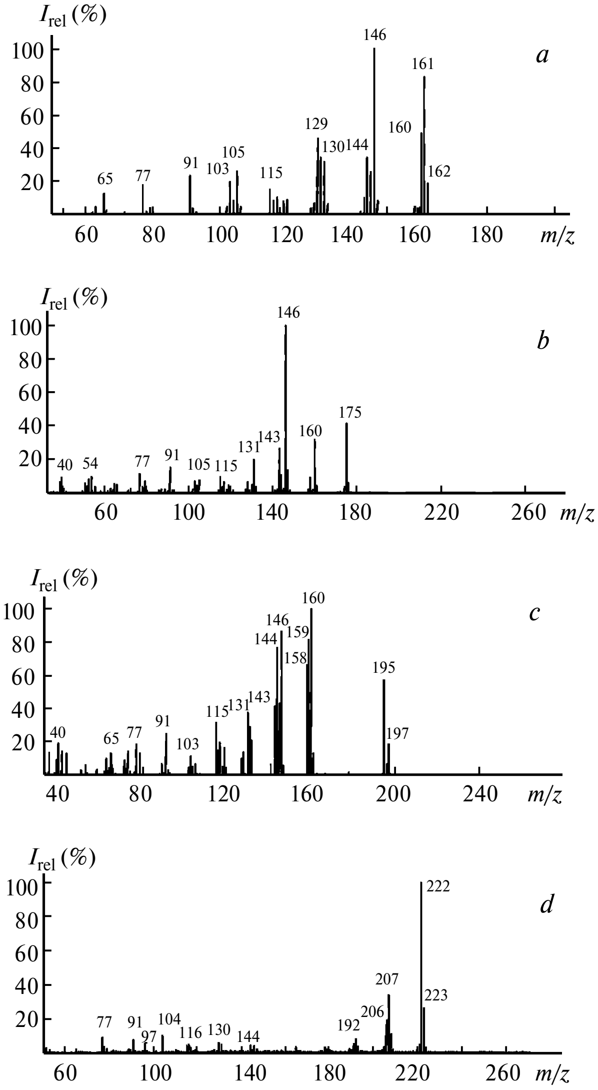
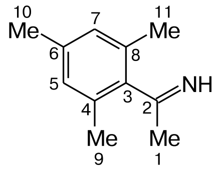


Fig. 1. Mass spectra of imine **11** (*a*), **12** (*b*), **13** (*c*), and **14** (*d*), obtained from organonickel sigma-complex **2**.

Similar behavior was also registered for the imines **9** (*m/z* 147), **10** (*m/z* 209), **15** (*m/z* 245), **16** (*m/z* 307), and **17** (*m/z* 364 $[\mathrm{M - H}]^+$). Thus, one may conclude that the characteristic fragmentation processes for the obtained imines are the cleavage of α- and β-bonds towards sp^2-hybridized carbon atom of the imine moiety. The cleavage of the NH-group under experimental conditions does not occur. This fragmentation pattern of the molecular ion confirms the structure of the obtained compounds.

Similar data were obtained for almost all combinations of organonickel sigma-complex—nitrile. A particularity of the mass spectra of compounds with phenyl substituent (the imines **10**, **14,** and **16**) is the presence of more intense peaks of ions $[\mathrm{M - H}]^+$ compared with the peaks of the molecular ion. An analysis of mass spectral database NIST 11[17] and other literature data[18] have shown that the experimentally obtained results reflecting the fragmentation mechanism of the imines molecules under conditions of mass spectrometry are in good agreement with known data obtained previously for the nitrogen-containing compounds.

To prove the structure and sequence of bonding of the atoms in the molecules of the synthesized compounds it has been attempted to isolate one of the imine obtained in the solution. The imine **11,** formed in the reaction of organonickel complex **2** with acetonitrile, was chosen as a model compound. The isolation was performed by column chromatography using ethyl acetate as eluent. As a result, it was succeeded to isolate the imine **11** with 32% yield.



11

The imine hydrochloride **11** crystals were obtained by prolonged storage (over 7 days) of the isolated imine **11** in the chloroform solution and slow evaporation of the solvent. The structure of crystals was confirmed by X-ray analysis (Fig. 2, Table 2).

Performing the reaction of organonickel sigma-complex **2** with acetonitrile at temperature 75—80 °C leads to

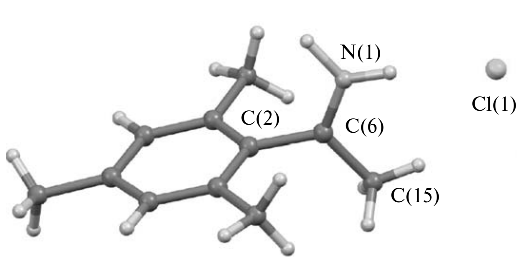
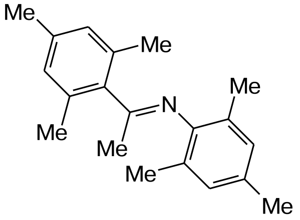


Fig. 2. Crystal structure of imine hydrochloride **11**.

Table 2. Selected bond lengths (*d*) and valence angles (ω) in compound **11**

Bond	*d*/Å	Angle	ω/degree
C(6)—N(1)	1.273(3)	N(1)—C(6)—C(2)	120.3(2)
C(6)—C(15)	1.489(4)	N(1)—C(6)—C(15)	119.9(2)
C(2)—C(6)	1.490(3)	C(2)—C(6)—C(15)	119.8(2)

the formation of compound **18** in solution. This compound represent the product of the addition of the second mesityl fragment by nitrogen atom of imine **11**. The signals with *m*/*z* 279 and *m*/*z* 264, corresponding to molecular ion $[M]^+$ and the ion $[M - CH_3]^+$, formed in the process of cleavage of methyl group in the condition of experiment, are detected in the mass spectrum of compound **18** (Fig. 3).



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The preparation of some imines described in this study (**9**—**12**, **14**, and **16**)[19—25] and reaction of organonickel sigma-complexes with acetonitrile[26] are known in the literature. However, in all described cases the processes occur under extreme conditions with the use of inflammable media and involving magnesium and lithium organic reagents, including derivatives obtained from relatively expensive alkyl iodides. Moreover, the formation of the imines in the reactions involving organonickel sigma-complexes requires the use of highly toxic reagents, such as thallium tetrafluoroborate ($TlBF_4$).[26] The method developed here for production of asymmetrical imines in the reaction of the nitriles with the organonickel sigma-complexes allows one to avoid completely the use of flammable media, unstable and toxic reagents.

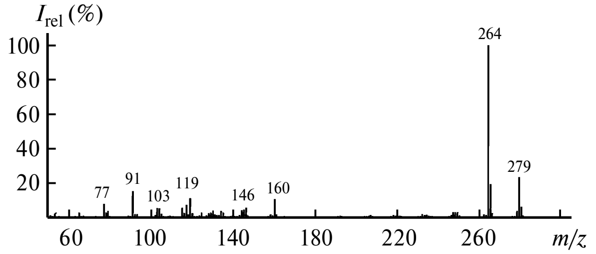

Fig. 3. Mass spectra of compound **18**, obtained from organonickel sigma-complex **2** and acetonitrile.

Thus, in this study we have shown that the interaction of the organonickel sigma-complexes with the nitriles results in the formation of the imines of the composition R(Ar)C=NH (Ar is 2,6-di- or 2,4,6-trisubstituted phenyl) containing aromatic moiety from the initial organonickel sigma-complex. The obtained results is one of the first examples of the use of electrochemically generated organonickel sigma-complexes as substrates in organic synthesis. These results expand the range of possibilities for the synthetic application of organometallic compounds of this type.

Experimental

Experiments related to the preparation of the initial reagents and preparative electrolysis were carried out under an inert atmosphere (nitrogen) using standard Schlenk technique.

Electron ionisation (EI) mass spectra were obtained using gas chromato-mass spectrometry with DFS Thermo Electron Corporation (USA) instrument at electron ionization energy of 70 eV, temperature of the ion source of 250 °C. Capillary column ID-BPX5 (analogue of DB-5MS) of SGE company with the length of 60 m and diameter of 0.32 mm was used. The chromatographic conditions were following: the flow rate of carrier gas (Helium) was 2 mL min^{-1}, injector temperature was 250 °C, initial thermostate temperature was 160 °C (1 min), heating rate was 20 deg min^{-1}, final thermostate temperature was 280 °C (15 min). The data treatment was performed using XCalibur software. ^1H and ^{13}C NMR spectra were registered using high resolution spectrometer Bruker Avance III 400 at room temperature (25 °C). IR spectra in the range of 4000—400 cm^{-1} were measured using Tensor-27 (Bruker) spectrometer with optical resolution of 4 cm^{-1} and accumulation of 32 scans. The samples for registration of IR spectra were prepared as thin layer between two KBr substrates. The centrifugation using OPN-3.02 (TNK Dastan, Kyrgyzstan) centrifuge at rotation rate of 1000 min^{-1} was used for the separation of low dispersity precipitates from the reaction mixture. The column filled with the silica gel (0.60—0.200 mm, 60 Å) was used for performing column chromatography, eluent was ethyl acetate.

Imine hydrochloride **11** crystal of suitable for X-ray analysis quality was isolated by crystallization of obtained compound in the chloroform, the crystals were colorless. Crystals ($C_{11}H_{16}N^+ \cdot Cl^-$, $M = 197.70$) were monoclinic, at 296 K $a = 11.469(2)$, $b = 8.3584(16)$, $c = 13.328(3)$ Å, $\beta = 114.814(5)°$, $V = 1159.7(4)$ Å^3, $Z = 4$, space group $P2_1/n$, $d_{calc} = 1.132$ g cm^{-3}, $\mu = 0.288$ mm^{-1}, $F(000) = 424$. Cell parameters and experimental data were obtained at $T = 296$ K using automatic diffractometer Bruker Smart APEX II CCD (λ(Mo-K_α) = 0.71073 Å, ω-scanning), $2\theta < 56°$, $R_{int} = 0.047$. 14573 reflections were measured, from them 2738 were independent, the number of observed reflections with $I > 2\sigma(I)$ was 1885. The structure was resolved by direct method using SIR[27] program and refined by full-matrix least square method using SHELXL97 program.[28] The hydrogen atoms were calculated geometrically and refined using a riding model. Hydrogen atoms of NH_2-group were identified from the series of electron density and refined in isotropic approximation on the final stage of refinement. All calculations were performed using program WinGX,[29] the final values of divergence factors were $R = 0.0572$, $wR_2 = 0.1699$, GOOF = 1.04, the number of parameters specified was 130. The analysis of intermolecular interactions was performed using PLATON program.[30] The figures were prepared in the program MERCURY.[31] Crystallographic data of the structure of **11** were deposited into Cambridge structural database (http://www.ccdc.cam.ac.uk; deposit number CCDC 1470168).

Dimethylformamide was purified by triple vacuum distillation with intermediate drying over calcium hydride (10 g L^{-1}) and was stored in the nitrogen atmosphere. Acetonitrile was purified by triple distillation in inert atmosphere with addition of small amount of potassium permanganate. Ethyl acetate was purified by subsequent distillation over phosphor pentoxide (P_2O_5), then potassium carbonate (K_2CO_3) to remove acidic admixtures. Organic substrates, namely chloroacetonitrile (Alfa Aeser), propionitrile, benzonitrile, and 2,2´-bipyridine (Sigma-Aldrich) were used as received. Complex [$NiBr_2$(bpy)], used for preparation of organonickel sigma-complexes, was prepared from nickel(II) bromide and 2,2´-bipyridine as described earlier.[32] Organonickel sigma-complexes **1—4** were prepared according to earlier published procedures[13—15] in the electrolyzer of the periodic loading, without separation of the anodic and cathodic areas, equipped with sacrificial nickel anode.[33]

Interaction of complex [NiBr(Mes)(bpy)] (2) with acetonitrile (5). Method *A*. The working solution was prepared by dissolving of 180 mg (0.43 mmol) of complex [NiBr(Mes)(bpy)] in 11 mL of acetonitrile at room temperature. The solution was stirred for 8 h. During the reaction, simultaneously with the change in color of the solution from bright red to greenish-yellow fine precipitate formation occurred in the reaction mixture. The precipitate was separated by centrifugation. Decanted solution was evaporated at water pump vacuum at a bath temperature of 30 °C. The resulting residue was chromatographed using silica gel column with ethyl acetate as eluent. Two fractions were obtained. TLC (Sorbfil, eluent was ethyl acetate): $R_f = 0.82$ (mass spectra peaks *m/z* 264 and 279) and $R_f = 0.50$ (mass spectra peak *m/z* 162.1). The yield of the imine **11** was 21 mg (32%). To determine the composition and structure of the obtained product the following methods were used: gas chromato-mass spectrometry, ^{1}H and ^{13}C NMR spectroscopy, IR spectroscopy.

1-(2,4,6-Trimethylphenyl)ethanimine (CH_3(Mes)C=NH) (11). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 2.21 (s, 6 H, C(9)Me, C(11)Me); 2.24 (s, 3 H, C(10)Me); 2.35 (s, 3 H, C(1)Me); 6.91 (s, 2 H, C(5)H, C(7)H). ^{13}C NMR (100.6 MHz, $CDCl_3$, δ): 20.57 (C(1)Me); 23.70 (2, C(9)Me, C(11)Me); 29.72 (C(10)Me); 129.03 (C(3)); 129.11 (2, C(5), C(7)); 136.29 (C(6)); 137.90 (2, C(4), C(8)); 147.93 (C(2) CN). MS (EI, 70 eV, t_R = 4.72 min), *m/z* (I_{rel} (%)): 161 $[M]^+$ (82), 160 (54), 146 $[M - CH_3]^+$ (100), 145 (25), 144 (35), 131 (35), 130 (37), 129 (42), 105 (26), 91 (25), 77 (22). IR (neat), ν/cm^{-1} 3251 (N—H); 2923, 2854 (CH_3); 1641 (N=C); 1611 ($C=C_{arom}$).

Method *B*. The working solution was prepared by dissolving of 83 mg (0.2 mmol) of complex [NiBr(Mes)(bpy)] in 2 mL of acetonitrile at room temperature. Then 2—3 drops of DMF were added to the solution. After stirring for 30 min the obtained reaction mixture was analyzed without additional treatment by gas chromato-mass spectroscopy.

Method *C*. The working solution was prepared by dissolving of 83 mg (0.2 mmol) of complex [NiBr(Mes)(bpy)] in 20 mL of benzene at room temperature. The 21 μL (0.4 mmol) of acetonitrile was added to the solution. Afterwards, 49 μL (0.4 mmol) of boron trifluoride diethyl etherate ($BF_3 \cdot Et_2O$) was added and immediate discoloration of solution was observed. After stirring for 30 min the formed turquoise precipitate was separated by filtration and the filtrate was analyzed by gas chromato-mass spectroscopy.

Interaction of complexes 1—4 with nitriles 5—8. The interaction was carried out using method ***B***. Complexes [NiBr(Ar)(bpy)], where Ar = Xyl (80 mg), Mes (83 mg), Tipp (100 mg), and Tchp (124 mg), and nitriles (MeCN, EtCN, $ClCH_2CN$, and PhCN) were used as starting compounds. The obtained reaction mixture was analyzed by gas chromato-mass spectroscopy without additional treatment. Retention times (t_R) and *m/z* peaks values, detected in EI mass spectra of the obtained compounds are represented below.

1-(2,6-Dimethylphenyl)ethanimine (CH_3(Xyl)C=NH) (9). MS (EI, 70 eV, t_R = 6.80 min), *m/z* (I_{rel} (%)): 147 $[M]^+$ (58), 133 $[M - CH_3]^+$ (44), 129 (33), 115 (42), 105 (27), 91 (51), 77 (40), 65 (23).

1-(2,6-Dimethylphenyl)-1-phenylmethanimine (Ph(Xyl)C=NH) (10). MS (EI, 70 eV, t_R = 6.15 min), *m/z* (I_{rel} (%)): 209 $[M]^+$ (25), 208 $[M - H]^+$ (100), 194 (11), 193 (28), 121 (13), 105 (23), 77 (49).

1-(2,4,6-Trimethylphenyl)ethanimine (CH_3(Mes)C=NH) (11). MS (EI, 70 eV, t_R = 4.72 min), *m/z* (I_{rel} (%)): 161 $[M]^+$ (80), 160 (52), 146 $[M - CH_3]^+$ (100), 145 (26), 144 (37), 131 (33), 130 (36), 129 (43), 105 (24), 91 (23), 77 (20).

1-(2,4,6-Trimethylphenyl)propanimine (C_2H_5(Mes)C=NH) (12). MS (EI, 70 eV, t_R = 6.23 min), *m/z* (I_{rel} (%)): 175 $[M]^+$ (41), 160 $[M - CH_3]^+$ (31), 146 $[M - C_2H_5]^+$ (100), 143 (26), 131 (20), 91 (15).

1-(2,4,6-Trimethylphenyl)-2-chloroethanimine ($ClCH_2$(Mes)C=NH) (13). MS (EI, 70 eV, t_R = 6.90 min) *m/z* (I_{rel} (%)): 195 $[M]^+$ (57), 160 $[M - Cl]^+$ (100), 159 (81), 158 (66), 146 $[M - CH_2Cl]^+$ (86), 145 (43), 144 (76), 143 (41), 130 (37), 115 (32), 91 (25), 77 (19).

1-(2,4,6-Trimethylphenyl)-1-phenylmethanimine (Ph(Mes)C=NH) (14). MS (EI, 70 eV, t_R = 6.75 min), *m/z* (I_{rel} (%)): 223 $[M]^+$ (26), 222 $[M - H]^+$ (100), 208 (11), 207 (34), 206 (18), 192 (7), 104 (10), 91 (7), 77 (8).

1-(2,4,6-Triisopropylphenyl)ethanimine (CH_3(Tipp)C=NH) (15). MS (EI, 70 eV, t_R = 7.42 min), *m/z* (I_{rel} (%)): 245 $[M]^+$ (21), 231 (27), 230 $[M - CH_3]^+$ (100), 229 (29), 214 (42), 186 (16), 172 (13), 157 (12), 143 (15), 129 (14).

1-(2,4,6-Triisopropylphenyl)-1-phenylmethanimine (Ph(Tipp)C=NH) (16). MS (EI, 70 eV, t_R = 6.89 min), *m/z* (I_{rel} (%)): 308 (15), 307 $[M]^+$ (63), 306 $[M - H]^+$ (100), 292 (19), 291 (23), 276 (14), 275 (24), 247 (19), 233 (15), 232 (15), 230 (18), 218 (9), 104 (19), 91 (12).

1-(2,4,6-Tricyclohexylphenyl)ethanimine (CH_3(Tchp)C=NH) (17). MS (EI, 70 eV, t_R = 13.10 min), *m/z* (I_{rel} (%)): 364 $[M - H]^+$ (9), 350 $[M - CH_3]^+$ (100), 348 (51), 333 (21), 308 (9), 265 (23), 183 (20).

***N*, 1-Bis(2,4,6-trimethylphenyl)ethanimine (CH_3(Mes)C=NMes) (18).** MS (EI, 70 eV, t_R = 8.14 min), *m/z* (I_{rel} (%)): 279 $[M]^+$ (23), 264 $[M - CH_3]^+$ (100), 160 (11), 146 (7), 119 (11), 103 (7), 91 (15), 77 (8).

Preparation of imine hydrochloride 11. Under long (more than 7 days) storage of 21 mg of isolated using method ***A*** imine **11** in chloroform solution (5 mL) and slow evaporation of solvent, small amount of imine hydrochloride **11** was obtained. Its molecular structure was determined by single crystal X-ray analysis (see Fig. 2). Found (%): C, 66.71; H, 8.57; N, 6.98. $C_{11}ClH_{16}N$. Calculated (%): C, 66.83; H, 8.16; N, 7.08.

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