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Facile Ni(II)/Ketoxime-Mediated Conversion of Organonitriles into Imidoylamidine Ligands. Synthesis of Imidoylamidines and Acetyl Amides

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Treatment of alkyl nitriles with $NiX_2 \cdot 6H_2O$ (X = Cl, NO_3) and 2-propanone oxime, followed by (X = Cl) addition of [*i*-Pr_4N](NO_3) for precipitation of the product, resulted in the formation of amidinium nitrates [$RC(=NH_2)NH_2$](NO_3) (R = Me, Et, *n*-Pr). The reaction went to another direction with $NiX_2 \cdot 2H_2O$, i.e., the reaction between neat RCN (R = Me, Et, *n*-Pr, *i*-Pr, *n*-Bu, CH_2Cl, $CH_2C_6H_4OMe$-*p*) and $NiCl_2 \cdot 2H_2O$/2-propanone oxime (other ketoximes can also be used) gave the (imidoylamidine)Ni(II) complexes $[Ni\{\underline{N}(H)=C(R)NHC(R)=\underline{N}H\}_2]^{2+}$ (**1**$^{2+}$–**7**$^{2+}$). The latter were isolated in good yields (65–91%) as the bis-chloride salts **1**·Cl_2–**6**·Cl_2 and the mixed salt **7**·(Cl)(*p*-$MeOC_6H_4CH_2CO_2$). Remarkably, the latter transformation does not proceed at all if $NiCl_2 \cdot 2H_2O$ or the ketoxime are taken alone. Liberation of imidoylamidines was performed for one alkyl-containing complex [**2**·Cl_2] and one benzyl-containing complex [**7**·(Cl)(*p*-$MeOC_6H_4CH_2CO_2$)], by (i) addition of $HBF_4 \cdot Et_2O$ to the acetonitrile solution of the complexes to yield [N(H)=C(R)NHC(R)=NH]·$2HBF_4$ (R = Et **8** and R = $CH_2C_6H_4OMe$-*p* **9**) or (ii) substitution for ethanediamine (en) with following precipitation of the complex $[Ni(en)_3]Cl_2$ with formation of free N(H)=C(R)NHC(R)=NH (R = Et **10** and R = $CH_2C_6H_4OMe$-*p* **11**). In contrast to the liberation in nonaqueous media, treatment of **2**·Cl_2 and **7**·(Cl)(*p*-$MeOC_6H_4CH_2CO_2$) with $Na_2EDTA \cdot 2H_2O$ in water–methanol solutions led to substitution and hydrolysis to furnish the acyl amides $\{EtC(=O)\}_2NH$ (**12**) and $\{p\text{-}MeOC_6H_4CH_2C(=O)\}_2NH$ (**13**). Alternatively, **12** and **13** were obtained by hydrolysis of **10** and **11** in water at pH ca. 8.5. It was shown that the oxime complexes *trans*-$[NiCl_2(C_4H_8C=NOH)_4]$ (**14**) or *cis*-$[Ni(O,O\text{-}NO_3)_2(C_4H_8C=NOH)_2]$ (**15**) can be intermediates in the formation of amidines and imidoylamidines. The sequence of the Ni(II)/oxime mediated formation of (imidoylamidine)Ni complexes and liberation (or hydrolytic liberation) of the ligands opens up a novel, facile and environmentally benign route to imidoylamidines and acyl amides.

Introduction

The activation of organonitriles by metal centers toward nucleophilic or electrophilic additions or cycloaddition is a frontier area of studies targeted on the exploration of synthetic transformations of RCN species, and this subject has recently been reviewed by two of us[1] and previously by others.[2] Literature up to date clearly shows that in the vast majority of cases coordination of organonitriles to metal centers makes their reactions with nucleophilic reagents favorable giving versatile imino compounds with new C−N, C−O, C−C, C−P, and C−S bonds. Despite that some of the imino complexes are important by themselves, e.g., as antitumor agents,[3] it is rather likely that the most promising

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subdirection of the research on organonitriles is the synthesis of organic species involving metal compounds.

As far as the formation of C−N bonds via nucleophilic addition to metal-bound nitriles is concerned, the known types of reactions include the coupling between ligated nitriles and primary and secondary amines giving amidines, hydrazines leading to amidrazones, heterocycles resulting in their iminoacylation,[1] and addition of imines[1] and sulfimides[4] to yield 1,3-diazadienes. A rather small, albeit of practical importance, fraction of these results is relevant to metal-mediated or metal-catalyzed amidation[5,6] or hydrolytic amidation of nitriles.[7]

In particular, within the framework of our project on metal-mediated nitrile−oxime coupling,[8−10] an unusual transformation of sterically unhindered alkyl nitriles RCN which can be easily converted to the appropriate amidines (**I**, Figure 1) and carboxylic acids in the presence of Co(II)/ketoxime systems has recently been found.[11] This route opens up a good *stoichiometric* access to amidines which otherwise are conventionally obtained by the hazardous two-step Pinner synthesis.[1] Moreover, further development of the systems, comprising a metal salt and a ketoxime, have shown that

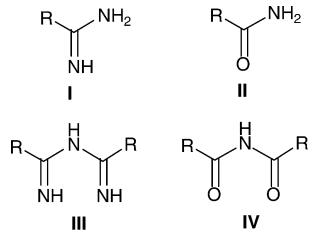

Figure 1.

when Zn(II) instead of Co(II) is employed, the transformation of RCN is metal-*catalyzed* and gives either carboxamides (**II**, Figure 1) or amidines (both types of compounds of superior industrial and/or pharmacological significance), depending on the presence or absence of water in the system.[12]

Our interest in further exploration of the metal/ketoxime systems for C−N bond formation has recently been sparked by the report of the reaction between acetonitrile and the dinuclear nickel(II) complex $[Ni_2(\mu\text{-}OH)_2(tpa)_2](ClO_4)_2$ [where *tpa* is the tetradentate tris(2-pyridylmethyl)amine] giving a novel *imidoylamidine* (**III**, Figure 1) compound [Ni{HNC(Me)NC(Me)NH}$_2$],[13] in which the ligand **III** (R = Me) is in a deprotonated form. The mechanism of this remarkable conversion has not yet been established, but the authors[13] suggested that MeCN, activated by the Ni(II) center, converts to an (amidine)Ni(II) intermediate followed by the known[14,15] metal-templated condensation of two amidines (and elimination of NH_3) to give the imidoylamidine complex.

Inspired by these observations, we attempted to apply a system of high simplicity, i.e., Ni(II)/ketoxime, to the conversion of organonitriles to imidoylamidines. The chemistry of the latter compounds is very little developed despite the well-established interest of amidines as synthons for further transformations[16] as well as in biology and medicine.[17]

We anticipated a dual benefit for the present work: (i) to get an entry into the almost unexplored field of coordination chemistry of imidoylamidines, and (ii), in organic chemistry, to find an easy and environmentally benign access to imidolylamidines and to acetyl amides (**IV**, Figure 1), the latter via hydrolysis of the former. In the course of these studies, we observed a novel Ni(II)/ketoxime-mediated transformation of RCN to accomplish new (imidoylamidine)-Ni(II) complexes from which the ligands can be liberated and, if necessary, converted to acetyl amides by hydrolysis.

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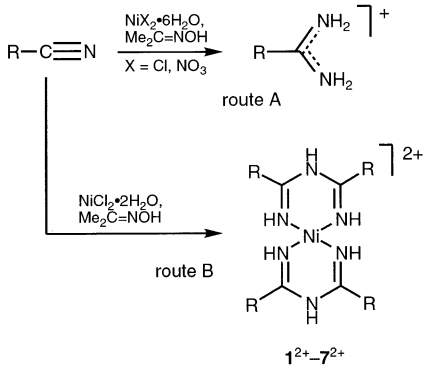
Scheme 1



Cation	R	Isolated	X-ray
$\mathbf{1}^{2+}$	Me	**1**•Cl_2	**1**•Cl_2
$\mathbf{2}^{2+}$	Et	**2**•Cl_2	[**2** − H]Cl•H_2O
$\mathbf{3}^{2+}$	*n*-Pr	**3**•Cl_2	[**3** − H]Cl•H_2O
$\mathbf{4}^{2+}$	*i*-Pr	**4**•Cl_2	**4**•Cl_2
$\mathbf{5}^{2+}$	*n*-Bu	**5**•Cl_2	**5**•Cl_2
$\mathbf{6}^{2+}$	CH_2Cl	**6**•Cl_2	[**6** − H]Cl•H_2O
$\mathbf{7}^{2+}$	R'	**7**•(Cl)(X)	**7**•$(X)_2$•MeOH

R' = *p*-$MeOC_6H_4CH_2$
X^- = *p*-$MeOC_6H_4CH_2CO_2^-$

In this work, all these results along with structural studies of the imidoylamidine nickel compounds and of possible oxime intermediate complexes are reported.

Results and Discussion

We have recently reported an unusual reaction between a nitrile and an oxime, mediated by a Co(II) center, providing a facile conversion of an alkyl nitrile, RCN, to the appropriate amidine, RC(═NH)NH_2, and carboxylic acid, RC(═O)OH.[11] This reaction has now been extended to a Ni(II)/oxime system, and it has been observed that treatment of alkyl nitriles with $Ni(NO_3)_2$•$6H_2O$ or $NiCl_2$•$6H_2O$, in the presence of 2-propanone oxime, followed by, in the latter case, addition of isopropylammonium nitrate for precipitation of the product, under the same experimental conditions (50 °C for 8 h) as for the Co(II)/oxime system, results in the formation of amidinium nitrates [RC(═NH_2)NH_2](NO_3) [R = Me, Et, *n*-Pr] (Scheme 1, route A) isolated in 60−80% yields. All these nitrates were identified by comparison of their melting points and IR and NMR spectra with those of genuine samples. The former product was additionally characterized by comparison of the space group and crystal lattice parameters with those previously found for [MeC(═NH_2)NH_2](NO_3).[11]

When the less hydrated $NiCl_2$•$2H_2O$ was employed, the Ni(II)/oxime/nitrile system opened a new type of reaction. Thus, the reaction between neat RCN (R = Me, Et, *n*-Pr, *i*-Pr, *n*-Bu, CH_2Cl, $CH_2C_6H_4OMe$-*p*) and $NiCl_2$•$2H_2O$/2-propanone oxime (other ketoximes, e.g., 2-butanone or cyclopentanone oximes, can also be used) proceeds under reflux conditions (R = Me, Et), at room temperature for R = CH_2Cl or at 100 °C (for the other nitriles) for 24 h to give the (imidoylamidine)Ni(II) complexes [Ni{N(H)═C(R)-NHC(R)═NH}$_2$]$^{2+}$ ($\mathbf{1}^{2+}$−$\mathbf{7}^{2+}$, Scheme 1, route B). The latter were isolated in good yields (65−91%) as the bis-chloride salts **1**•Cl_2−**6**•Cl_2 and the mixed salt **7**•(Cl)(*p*-$MeOC_6H_4CH_2$-CO_2). Remarkably, the above reactions do not proceed at all if the nickel(II) salt or Me_2C═NOH is taken alone; the process is efficient when the molar ratio $NiCl_2$•$2H_2O$:2-propanone oxime is 1:4. However, with less oxime, e.g., a ratio of 1:2, a significant retardation of the reaction rate and decrease of yield (to ca. 15%) are observed.

The (imidoylamidine)Ni(II) complexes were characterized (i) by satisfactory C, H, N elemental analyses and expected fragmentation/isotopic patterns in FAB^+-MS; (ii) by IR and ^1H and $^{13}C\{^1H\}$ NMR spectroscopies [in the IR spectra of all compounds there are characteristic stretches of ν(NH) in the range 3100−3300 cm^{-1}, strong δ(NH) peaks at ca. 1550 cm^{-1}, and also strong ν(C═N) vibrations at ca. 1600 cm^{-1}; in the NMR spectra, the chemical shifts for the peaks are close (within 0.01−0.15 ppm in the ^1H and 1−4 ppm in the $^{13}C\{^1H\}$ NMR spectra) to those observed for the corresponding amidinium nitrates]; and (iii) by X-ray crystallographic studies for six complexes indicated in Scheme 1 in their biscationic [**4**•Cl_2, **5**•Cl_2, **7**•(*p*-$MeOC_6H_4CH_2CO_2)_2$•MeOH] and deprotonated monocationic forms ([**2** − H]Cl, [**3** − H]-Cl, [**6** − H]Cl); the latter compounds formed upon slow crystallization of **2**•Cl_2, **3**•Cl_2, and **6**•Cl_2, correspondingly, from aqueous solutions (a water−acetone solution for **2**•Cl_2). A view of the cation $\mathbf{7}^{2+}$, as a representative of these groups of complexes, is given in Figure 2, and crystallographic data for all six complexes are summarized in Table 1. The study also revealed the formation of the *p*-$MeOC_6H_4CO_2^-$ anion (Figure 3) which obviously originates from the two-step hydrolysis of the appropriate nitrile (see Final Remarks).

Inspection of the X-ray data along with the available literature data[13,14] shows that the N−C bond order in the Ni−(H)*N*═*C* and C−N−C moieties does not depend on the degree of deprotonation. Indeed, the C═N bond is in the range 1.282(3)−1.294(3) Å for the bis-cationic **4**•Cl_2, **5**•Cl_2, and **7**•(*p*-$MeOC_6H_4CH_2CO_2)_2$•MeOH complexes, 1.277(4)−1.304(4) Å for the monocationic complexes [**2** − H]Cl,

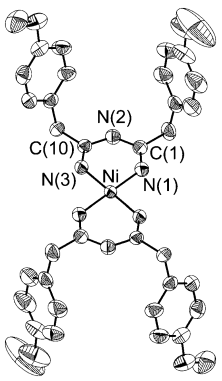


Figure 2. The complex $\mathbf{7}^{2+}$. Thermal ellipsoids represent a 70% probability. H atoms omitted. Only the crystallographically independent atoms are labeled. Selected bond lengths: Ni−N(1) 1.861(2), N(1)−C(1) 1.291(4), C(1)−N(2) 1.357(4), N(2)−C(10) 1.374(4), C(10)−N(3) 1.282-(3), N(3)−Ni 1.853(3) Å.

Table 1. Crystallographic Data

	[**2** − H]Cl	[**3** − H]Cl	**4**·Cl_2	**5**·Cl_2	[**6** − H]Cl	**7**·(*p*-$MeOC_6H_4CH_2CO_2)_2$·MeOH	**12**	**14**	**15**
CCDC no.	198739	198741	198742	198743	198744	198745	198740	198746	198747
sum formula	$C_{12}H_{25}ClN_6Ni$	$C_{16}H_{35}ClN_6Ni$	$C_{16}H_{34}Cl_2N_6Ni$	$C_{20}H_{42}Cl_2N_6Ni$	$C_8H_{13}Cl_5N_6NiO$	$C_{56}H_{66}N_6NiO_{12}$	$C_6H_{11}NO_2$	$C_{20}H_{36}Cl_2N_4NiO_4$	$C_{20}H_{36}N_6NiO_8$
M_r [g·mol^{-1}]	363.54	421.66	440.11	496.21	445.21	1073.88	129.16	526.15	547.25
crystal size [mm^3]	0.1 × 0.1 × 0.05	0.3 × 0.3 × 0.2	0.05 × 0.05 × 0.03	0.3 × 0.2 × 0.2	0.1 × 0.03 × 0.03	0.4 × 0.3 × 0.2	0.6 × 0.08 × 0.05	0.5 × 0.3 × 0.2	0.4 × 0.2 × 0.2
crystal system	monoclinic	orthorhombic	monoclinic	triclinic	monoclinic	monoclinic	orthorhombic	orthorhombic	monoclinic
space group	$P2_1/n$	$Pca2_1$	$P2_1/n$	$P\bar{1}$	$P2_1/n$	$P2_1/c$	$Pccn$	$Pcca$	$C2/c$
a [Å]	13.534(2)	26.5984(4)	6.2129(2)	12.5893(1)	10.0017(3)	12.4148(1)	15.998(2)	14.6795(7)	13.562(2)
b [Å]	9.233(3)	11.0714(2)	14.9895(5)	15.5296(2)	11.4728(4)	13.2229(2)	5.1479(6)	9.3712(5)	11.828(1)
c [Å]	14.556(3)	14.7694(2)	12.5335(4)	21.4581(2)	14.8062(5)	17.8389(2)	8.8210(8)	18.283(1)	10.483(2)
α [deg]	90	90	90	78.3836(4)	90	90	90	90	90
β [deg]	104.14(1)	90	102.830(1)	83.6505(4)	92.831(2)	108.2261(4)	90	90	111.51(1)
γ [deg]	90	90	90	77.0417(4)	90	90	90	90	90
V [Å^3]	1763.9(7)	4349.3(1)	1138.08(6)	3995.21(7)	1696.9(1)	2781.51(6)	726.5(2)	2515.0(2)	1564.5(2)
Z	4	8	2	6	4	2	4	4	4
ρ_{calcd} [g·cm^3]	1.369	1.288	1.284	1.237	1.743	1.282	1.181	1.390	1.162
μ [mm^{-1}]	1.259	1.031	1.098	0.946	1.935	0.414	0.088	1.016	0.665
θ_{max} [deg]	27.63	27.47	27.50	27.48	26.36	26.39	23.3	27.5	25.0
hkl range	$-17 \le h \le 17$ $-11 \le k \le 11$ $-18 \le l \le 18$	$-32 \le h \le 34$ $-11 \le k \le 14$ $-19 \le l \le 17$	$-17 \le h \le 17$ $-17 \le k \le 17$ $-17 \le k \le 17$	$-16 \le h \le 16$ $-20 \le k \le 18$ $-27 \le l \le 27$	$-12 \le h \le 12$ $-14 \le k \le 12$ $-18 \le l \le 18$	$-15 \le h \le 15$ $-15 \le k \le 16$ $-22 \le l \le 19$	$-17 \le h \le 15$ $-5 \le k \le 5$ $-9 \le l \le 9$	$-15 \le h \le 19$ $-12 \le k \le 10$ $-23 \le l \le 22$	$-16 \le h \le 16$ $-13 \le k \le 14$ $-12 \le l \le 12$
no. of reflns	13068	26672	10534	78741	14002	51145	1963	17075	6187
no. of indep reflns, R_{int}	4013, 5.98%	9128, 3.99%	2313, 5.93%	18186, 3.73%	3450, 9.63%	5634, 8.99%	517, 6.62%	2832, 4.93%	1370, 4.83%
no. of reflns with $I > 2\sigma$(I)	2396	8213	1794	15640	2500	4502	378	1980	1121
no. of params	190	451	115	784	190	340	42	141	105
R (obs reflns)	4.86%	3.59%	4.66%	4.22%	4.84%	7.81%	5.54%	4.49%	3.54%
R (all reflns)	9.92%	4.37%	6.26%	5.20%	8.06%	9.13%	8.17%	7.50%	5.07%
wR_2	14.0%	8.47%	11.9%	11.4%	9.97%	23.1%	15.8%	13.0%	8.22%
GOF	1.115	1.040	1.051	1.063	1.090	1.060	1.093	1.062	1.054
largest diff peaks	0.54/−0.37	0.39/−0.27	0.53/−0.31	1.78/−0.90	0.57/−0.48	0.87/−1.14	0.18/−0.18	0.59/−0.52	0.51/−0.30

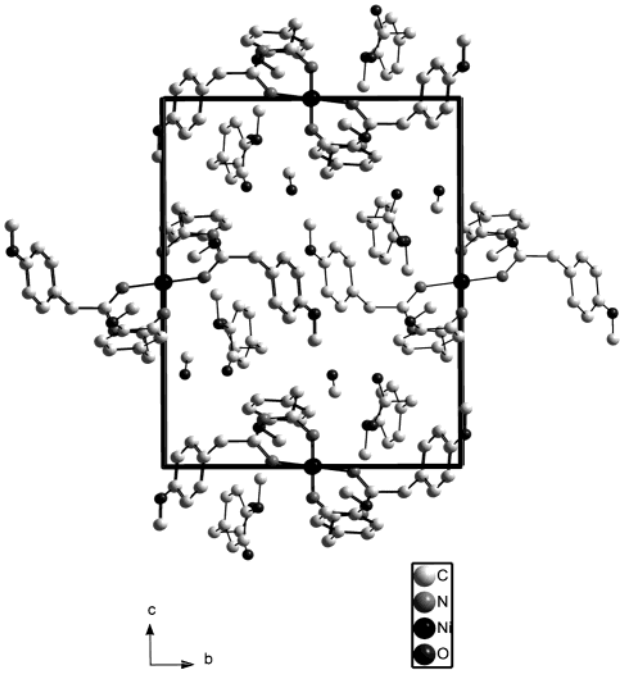


Figure 3. The unit cell of **7**·(*p*-$MeOC_6H_4CH_2CO_2)_2$·MeOH in a view along the crystallographic *a*-axis.

[**3** − H]Cl, and [**6** − H]Cl, 1.282(6)−1.285(6) Å for the previously characterized complex $[C_8H_{17.5}N_6Ni^{1.5+}]Cl_{1.5}$·$3H_2O$,[14] and 1.296(3) Å for the fully deprotonated [**2** − 2H].[13] Concurrently, the C−N bond in the C−N−C functionality lies between 1.357(4) and 1.374(4) Å for the biscationic complexes, 1.346(5) and 1.374(4) Å for the monocationic [**2** − H]Cl, [**3** − H]Cl, and [**6** − H]Cl, and 1.362(5) and 1.367(5) Å for $[C_8H_{17.5}N_6Ni^{1.5+}]Cl_{1.5}$·$3H_2O$,[14] and in the range 1.353(3)−1.360(3) Å for the neutral compound.[13] Moreover, the N═C and N−C bond distances perfectly agree with the typical double and single NC bonds and all these observations favor the lack of significant electron delocalization within the chelate ring.

Liberation of Imidoylamidines. Known methods for the preparation of imidoylamidines RC(═NH)NHCR[1](═NH) include a reaction between the first [i.e., imino ester RC(═NH)OR[2]] and the second [i.e., amidine $R^1C(═NH)NH_2$] products of the Pinner synthesis (the reaction proceeds at 25−35 °C for 2 days in the presence of NaOMe[18]), or, alternatively, imidoylamidines can be obtained by treating 1,2,4-dithiazolium salts with RNH_2, optionally in the presence of an oxidizing agent.[19] In our case, the liberation of the corresponding ligand (imidoylamidine) was exemplified for one alkyl-containing complex [**2**·Cl_2, R = Et] and one benzyl-containing complex [**7**·(Cl)(*p*-$MeOC_6H_4CH_2CO_2$), R = $CH_2C_6H_4OMe$], by (i) addition of HBF_4·Et_2O to the acetonitrile solution of the corresponding complex (Scheme 2; the liberated imidoylamidine is conditionally presented in the parent tautomeric form) or (ii) substitution for ethanediamine (en) with following precipitation of the well-known compound $[Ni(en)_3]Cl_2$[20] (Scheme 2), separation of the solid by filtration, and evaporation of the filtrate.

Hydrolytic Liberation of Acyl Amides. We have also studied the reaction between the (imidoylamidine)Ni(II) complexes and 1 equiv of the disodium EDTA salt in aqueous methanolic solution, illustrated also for one alkyl-containing complex [**2**·Cl_2, R = Et] and one benzyl-containing complex [**7**·(Cl)(*p*-$MeOC_6H_4CH_2CO_2$), R = $CH_2C_6H_4OMe$], followed by extraction of the organic material from the water−methanol phase with diethyl ether. In contrast to the liberation with HBF_4/MeCN, the reaction with Na_2EDTA furnishes the amides, i.e., $\{RC(═O)\}_2NH$ (**12**, **13**), in ca. 70% yield, which are derived from hydrolysis of the initially formed free imidoylamidines as proved by the hydrolysis of $\{RC(═NH)\}_2NH$ (R = Et, *p*-$CH_2C_6H_4OMe$) in water−methanol (1:1, v/v) media at pH ca. 8.5 (Scheme 2). The dipropionamide $\{EtC(═O)\}_2NH$ (**12**) was identified by comparison of its melting point and IR spectrum with those given in the literature,[21−23] and its crystal structure was determined by X-ray crystallography (Figure 4), while the other amide (**13**) was characterized by conventional methods (see Experimental Section).

The acetyl amides $\{RC(═O)\}_2NH$ exhibit a biological activity[24] and have previously been used as agents for molecular recognition (host−guest chemistry)[25] and synthons for further organic synthesis.[26] The conventional synthesis of these compounds involves acylation of the corresponding carboxamides, $RC(═O)NH_2$, with the acetyl chlorides RC(═O)Cl or interaction of the amides with the appropriate lithium alkyls followed by treatment with RC(═O)Cl.[21,26] The observed sequence of the Ni(II)/oxime-mediated reaction and EDTA/H_2O substitution/hydrolysis suggests an alternative and more environmentally friendly route to this class of organic compounds.

Trapping and Characterization of Ketoxime Plausible Intermediates. When the nickel salt $NiCl_2$·$2H_2O$ or $Ni(NO_3)_2$·$6H_2O$ was dissolved in acetonitrile in the presence of 4 equiv of $C_4H_8C═NOH$, subsequent evaporation of the solvent to dryness in a vacuum at 20−25 °C and careful washing with diethyl ether, as well as drying in a vacuum, led to the isolation of the stable blue-colored oxime nickel(II) complex *trans*-$[NiCl_2(C_4H_8C═NOH)_4]$ (**14**) or *cis*-$[Ni(O,O\text{-}NO_3)_2(C_4H_8C═NOH)_2]$ (**15**). These oxime complexes were prepared by independent syntheses via heating the appropriate nickel salts with 4 or 2 equiv, respectively, of the oxime in acetone (see Experimental Section); the latter complex is also formed when 10 equiv of the oxime is used. These complexes gave satisfactory C, H, and N elemental analyses and expected fragmentation/isotopic patterns in the

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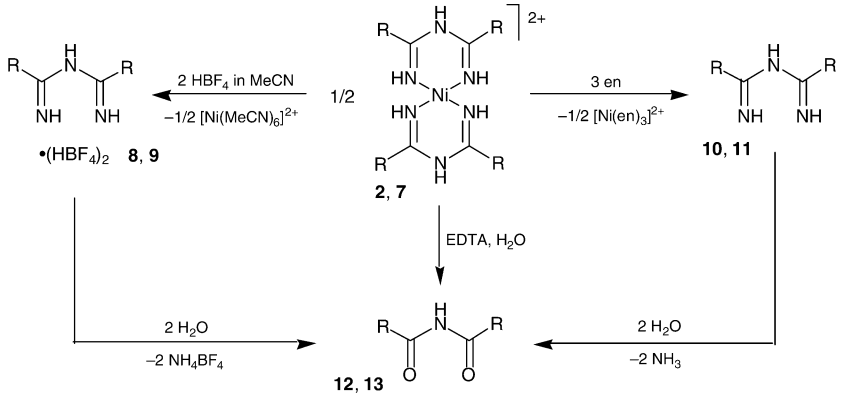
Scheme 2



FAB mass spectra; they were also characterized by IR spectroscopy as well as by X-ray diffraction studies (Figures 5 and 6). It is noteworthy to mention that the structures of **14** and **15** are rare examples of nickel(II) complexes with so-called "simple" oximes which merely have only one oxime group as the coordination site. The only relevant Ni(II) structure previously reported is the aldoxime complex $[NiCl_2(MeCH{=}NOH)_4]$.[27]

In the $NiCl_2{\cdot}2H_2O/C_4H_8C{=}NOH/ClCH_2CN$ system, the blue powder of $[NiCl_2(C_4H_8C{=}NOH)_4]$ (**14**) is formed at room temperature after ca. 10 min of stirring, and the complex can be separated by filtration and characterized as described in Experimental Section. However, if the reaction is continued without separation of $[NiCl_2(C_4H_8C{=}NOH)_4]$ (**14**), the blue precipitate is fully dissolved after ca. 30 min, the reaction mixture becomes brown, and a yellow precipitate of $[Ni\{\underline{N}(H){=}C(CH_2Cl)NHC(CH_2Cl){=}\underline{N}H\}_2]Cl_2$ (**6**·Cl_2) is obtained after ca. 10 h. It can be isolated in approximately 60% yield. The latter product can also be obtained by mixing 1 equiv of the nickel complex $[NiCl_2(C_4H_8C{=}NOH)_4]$ (**14**), 2 equiv of water, and 16 equiv of $ClCH_2CN$. This experiment gives evidence that the complex **14** can be at least one of the intermediates involved in the conversion depicted in Scheme 1, route B. However, with other studied nitriles the reaction does not proceed at room temperature. Heating the mixture at ca. 50 °C resulted in the formation of a broad spectrum of yet unidentified products.

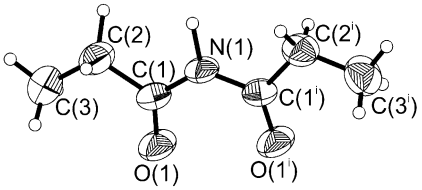


Figure 4. The molecule of dipropionamide **12** in the crystal structure. Thermal ellipsoids represent a 70% probability. Bond lengths (Å) and angles (deg): N(1)−C(1) 1.378(3), C(1)−O(1) 1.208(3), C(1)−C(2) 1.503(4), C(2)−C(3) 1.501(5); N(1)−C(1)−O(1) 123.0(3), N(1)−C(1)−C(2) 113.7(2), C(1)−N(1)−C(1^i) 128.6(3), O(1)−C(1)−C(2) 123.4(2), C(1)−C(2)−C(3) 113.9(3).

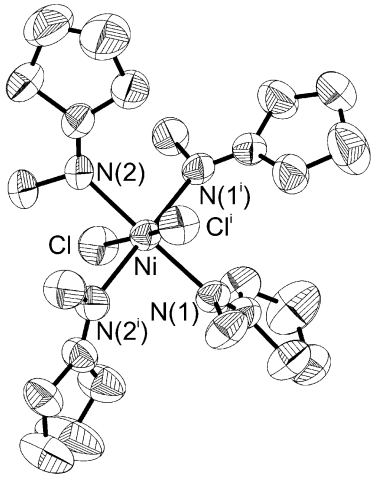


Figure 5. The complex **14**. Thermal ellipsoids represent a 70% probability. Bond lengths (Å) and angles (deg): Ni−N(1) 2.108(2), Ni−N(2) 2.123(2), Ni−Cl 2.4402(8), N(1)−O(1) 1.402(3), N(1)−C(7) 1.269(4), N(2)−O(2) 1.405(3), N(2)−C(12) 1.271(4); Ni−N(1)−O(1) 113.8(2), Ni−N(1)−C(7) 135.4(2), Ni−N(2)−O(2) 114.0(2), Ni−N(2)−C(12) 135.0(2).

We have also observed that the complex *cis*-$[Ni(O,O\text{-}NO_3)_2(C_4H_8C{=}NOH)_2]$ (**15**) promotes the conversion of the nitriles to amidinium salts (Scheme 1, route A). Thus, the amidinium nitrates were obtained by mixing 1 equiv of **15**, 6 equiv of water, and 16 equiv of RCN (R = Me, Et, *n*-Pr) and heating the mixture at 50 °C.

The oxime complexes **14** and **15** are so far the only isolable intermediates for the conversion, and our attempts to detect other species involved in the process have not yet been successful. Thus, in preparative experiments, treatment of **14** or **15** with an additional amount of the oxime (the complex:oxime molar ratio has been varied from 1:2 to 1:10) in acetone followed by removal of the solvent in vacuo and of the excess of the oxime by washing with diethyl ether led to recovery of the intact metal complexes. Paramagnetic properties of these complexes precluded NMR studies.

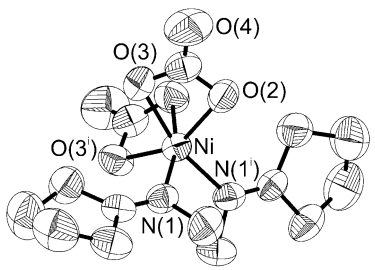
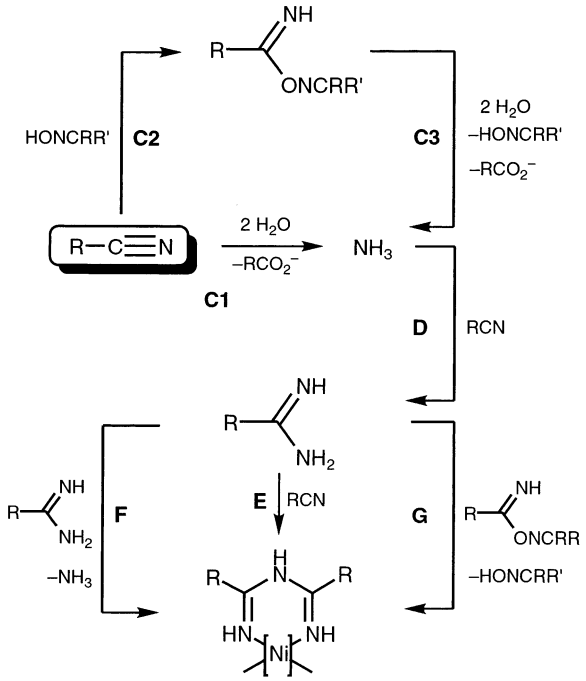


Figure 6. The complex **15**. Thermal ellipsoids represent a 70% probability. Bond lengths (Å) and angles (deg): Ni−N(1) 2.031(2), N(1)−O(1) 1.399(3), N(1)−C(1) 1.270(4); Ni−N(1)−O(1) 117.8(2), Ni−N(1)−C(1) 129.2(2).

Scheme 3



Hence, the lack of additional experimental data on intermediates involved in the studied system makes the interpretation of the mechanism somewhat ambiguous.

Final Remarks

Based on the relevant works—previously done by us and by the other groups—and as an extension of the scheme suggested earlier,[13] we propose here a number of metal-mediated and oxime-catalyzed steps that might lead to the formation of imidoylamidines: (i) The boxed nitrile (Scheme 3) is subject to the two-step hydrolysis. Thus, when $\mathbf{7}^{2+}$ is formed, the carboxylic anion *p*-$MeOC_6H_4CH_2CO_2^-$ (Figure 3) was unambiguously identified, thus confirming the occurrence of the suggested process. The latter might occur via route C1. However, although the conversion of a nitrile to ammonia and carboxylic acid has been detected at Pt(IV),[28] Nb(V),[29] Os(IV),[30] and Re_2(III)[31] metal centers, all reported examples of Ni(II)-mediated hydrolysis of RCN[32] include only the conversion of nitriles to carboxamides without further transformation to NH_3 and RCO_2H. Hence, one more plausible pathway should be taken into account, i.e., Ni(II)-mediated coupling of complexed RCN species with an oxime (step C2; such iminoacylated oximes were recently detected at Ni(II) centers[33] and previously by two of us at Pt(IV), Pt(II), Re(IV), and Rh(III) centers[1]) followed by their hydrolysis (step C3; the hydrolysis of this type was recently observed at a Pt(IV) center[34]). (ii) Ammonia, formed in step C, couples with the nitrile to give the amidine (step D). This step is also metal-mediated insofar as nonactivated nitriles do not react with amines without metal ions (ref 1a, section V). The formation of amidines has also been detected in this work when $NiCl_2 \cdot 6H_2O$ was employed instead of $NiCl_2 \cdot 2H_2O$ (Scheme 1). Moreover, the metal-mediated formation of amidines directly from nitriles, in nondried solvents, was observed at Co(II)[11] and Pt(II)[35] centers. (iii) Further conversion of amidines to imidoylamidines can proceed by Ni(II)-templated coupling with nitriles (step E; recently the nitrile−amidine coupling at Pt(IV) center has been observed[36]), by coupling with one more molecule of amidine (step F; the Ni(II)-templated coupling of amidines to achieve (imidoylamidine)Ni complex and NH_3 has been reported[14]), or by coupling with iminoacylated oxime species (step G). We believe that all steps in Scheme 3 are metal-mediated, while C3 and/or G are additionally oxime-catalyzed thus explaining the oxime involvement in the overall process. Studies on trapping of other intermediates and elucidation of the mechanism of this new conversion in more detail are on the way in our group.

It is anticipated that the method of synthesis developed in this work for the preparation of imidoylamidines will make them more accessible, expand their number, and encourage further research on their chemical and biological properties. We also believe that significant progress can be achieved by the application of imidoylamidines, as triaza analogues of acetylacetone, for chelation of metal ions exhibiting *soft* character and forming rather weak complexes with *hard O*-donor acetylacetone(ate). It is also noteworthy to mention that imidoylamidines are useful synthons for the preparation of triazines[37] and imidoylamidine-terminated polymers are widely used as precursors for triazine-containing polymers,[38] exhibiting a range of useful properties, e.g., as good heat resisting[39] or water- and oil-proofing ones.[40] Moreover, imidoylamidines are precursors for the facile syntheses of sulfur−[41] and phosphorus−nitrogen[42] heterocycles by their treatment with S or P chlorides.

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Experimental Section

Materials and Instruments. Nickel(II) hexaaquachloride (Merck), acetonitrile (Lab-Scan), propionitrile (Aldrich), butyronitrile (Aldrich), isobutyronitrile (Merck), valeronitrile (Aldrich), chloroacetonitrile (Merck), *p*-methoxybenzoacetonitrile (Lancaster), 2-propanone oxime (Lancaster), and cyclopentanone oxime (Aldrich) were obtained from commercial sources and used as received. Preparation of $NiCl_2 \cdot 2H_2O$: $NiCl_2 \cdot 6H_2O$ (2.38 g, 10 mmol) is finely grounded and partially dehydrated by refluxing in acetone (75 mL) for 3 h and then with a new portion of acetone (75 mL) for 1 h. The solid is then filtered off and dried under vacuum at room temperature. The yield is almost quantitative. In $NiCl_2 \cdot 2H_2O$, the water content was determined by EDTA titration.

C, H, and N elemental analyses were carried out by the Microanalytical Service of the Instituto Superior Técnico. Melting points were determined on a Kofler table. Positive-ion FAB mass spectra were obtained on a Trio 2000 instrument by bombarding 3-nitrobenzyl alcohol (NBA) matrices of the samples with 8 keV (ca. 1.18×10^{15} J) Xe atoms. Mass calibration for data system acquisition was achieved using CsI. Infrared spectra (4000−400 cm^{-1}) were recorded on a BIO-RAD FTS 3000MX instrument in KBr pellets. ^1H and $^{13}C\{^1H\}$ NMR spectra were measured on a Varian UNITY 300 spectrometer at ambient temperature.

X-ray Structure Determinations. Diffraction data for all crystals were collected using a Bruker-Nonius KappaCCD diffractometer (Mo Kα, $\lambda = 0.71073$ Å). Structural models were obtained using direct methods.[43] H atoms were refined on calculated positions using a riding model. All structure models were refined on F^2 using anisotropic displacement parameters for all non-H atoms.[44] The crystallographic data and the results of the structure determinations are summarized in Table 1.

Synthetic Work and Characterization. Conversion of RCN to $RC(=NH_2)NH_2^+NO_3^-$ (R = Me, Et, *n*-Pr) Mediated by the Ni(II)/2-Propanone Oxime System. The amidinium nitrates were obtained in accord with the previously described method,[11] by using $Ni(NO_3)_2 \cdot 6H_2O$ instead of the cobalt(II) salt. Yields are 60−80%, based on Ni.

Formation of the (Imidoylamidine)Ni(II) Complexes. General procedure: $NiCl_2 \cdot 2H_2O$ (166 mg, 1.00 mmol) is stirred in the corresponding nitrile (5 mL) for 5 min, whereupon 2-propanone oxime (4.00 mmol) is added and the reaction mixture is heated in an oil bath at 100 °C (refluxing for acetonitrile and propionitrile; in the case of $ClCH_2CN$ the reaction is performed at room temperature) for 1 day. In all the cases, the reaction mixture homogenizes for 10 min after the addition of the oxime, giving a greenish-blue solution. The color of the reaction mixture changes with time from greenish-blue to brown (ca. 1 h), and a yellow powder begins to form after ca. 3 h, which is then (after 24 h) separated by filtration, washed with three 5-mL portions of acetone, and dried in a vacuum at room temperature.

[Ni{N(H)=C(Me)NHC(Me)=NH}$_2$]Cl$_2$ (1·Cl$_2$). Yield is 65%, based on Ni. Yellow powder is insoluble in acetone and chloroform, slightly soluble in methanol and DMSO, and soluble in water. Anal. Calcd for $C_8H_{18}N_6Cl_2Ni$: C, 29.31; H, 5.53; N, 25.63. Found: C, 29.30; H, 5.50; N, 25.69. FAB$^+$-MS, *m*/*z*: 255 $[M - 2Cl - 2H]^+$. The compound does not have a characteristic melting point (mp), and upon heating it decomposes at >300 °C. IR spectrum, selected bands, cm^{-1}: 3165 s ν(NH), 2958 s ν_{as}(CH), 2918 s ν_s(CH), 1665 vs ν(C=N), 1542 s ρ(NH). ^1H NMR in D_2O, δ: 2.02 (s, Me), NH groups were not observed. $^{13}C\{^1H\}$ NMR in D_2O, δ: 21.9 (CH_3), 162.4 (C=N).

[Ni{N(H)=C(Et)NHC(Et)=NH}$_2$]Cl$_2$ (2·Cl$_2$). Yield is 83%, based on Ni. Yellow powder is insoluble in acetone and chloroform and soluble in water, methanol, and DMSO. Anal. Calcd for $C_{12}H_{26}N_6Cl_2Ni$: C, 37.54; H, 6.83; N, 21.89. Found: C, 37.59; H, 6.16; N, 21.91. FAB$^+$-MS, *m*/*z*: 659 [2M − Cl − 2H], 311 [M − 2Cl − 2H]$^+$. Mp = 260 °C (sublimation) and 264 °C (dec). IR spectrum, selected bands, cm^{-1}: 3298 and 3156 s ν(NH), 2978 s ν_{as}(CH), 2920 s ν_s(CH), 1655 vs ν(C=N), 1529 s ρ(NH). ^1H NMR in D_2O, δ: 1.01 (t, *J* 7.7 Hz, 3H, Me), 2.29 (q, *J* 7.7 Hz, 2H, CH_2), NH groups were not observed. $^{13}C\{^1H\}$ NMR in D_2O, δ: 11.2 (CH_3), 29.6 (CH_2), 167.3 (C=N). Crystallization of **2**·Cl_2 from a water−acetone mixture (1:1, v/v) at ca. 25 °C results in dehydrochlorination and release of the monocationic complex [**2** − H]Cl as the solid. The X-ray structure of the latter was determined by X-ray crystallography.

[Ni{N(H)=C(*n*-Pr)NHC(*n*-Pr)=NH}$_2$]Cl$_2$ (3·Cl$_2$). Yield is 85%, based on Ni. Yellow powder is insoluble in acetone and chloroform and soluble in water, methanol, and DMSO. Anal. Calcd for $C_{16}H_{32}N_6Cl_2Ni$: C, 43.86; H, 7.36; N, 19.18. Found: C, 43.66; H, 7.34; N, 19.23. FAB$^+$-MS, *m*/*z*: 402 $[M - Cl - 2H]^+$, 367 $[M - 2Cl - 2H]^+$. Mp = 249 (sublimation) °C and 257 °C (dec). IR spectrum, selected bands, cm^{-1}: 3153 s ν(NH), 2963 s ν_{as}(CH), 2911 s ν_s(CH), 1659 vs ν(C=N), 1527 s ρ(NH). ^1H NMR in D_2O, δ: 0.91 (t, *J* 7.3 Hz, 3H, Me), 1.62 (sextet, *J* 7.5 Hz, 2H, CH_2), 2.43 (t, *J* 7.6 Hz, 2H, CH_2), NH groups were not observed. $^{13}C\{^1H\}$ NMR in D_2O, δ: 12.9 (CH_3), 20.8 (CH_2), 37.8 (CH_2), 166.0 (C=N). Slow evaporation of water solution of **3**·Cl_2 at ca. 25 °C results in dehydrochlorination and release of the monocationic complex [**3** − H]Cl as the solid. The X-ray structure of the latter was determined by X-ray crystallography.

[Ni{N(H)=C(*i*-Pr)NHC(*i*-Pr)=NH}$_2$]Cl$_2$ (4·Cl$_2$). Yield is 63%, based on Ni. Yellow powder is insoluble in acetone and chloroform but slightly soluble in water, methanol, and DMSO. Anal. Calcd for $C_{16}H_{34}N_6Cl_2Ni$: C, 43.67; H, 7.79; N, 19.10. Found: C, 43.44; H, 7.67; N, 18.75. FAB$^+$-MS, *m*/*z*: 404 $[M - Cl]^+$, 367 $[M - 2Cl - 2H]^+$. Mp = 267 °C (dec). IR spectrum, selected bands, cm^{-1}: 3159 s ν(NH), 2965 s ν_{as}(CH), 2925 s ν_s(CH), 1655 vs ν_{as}(C=N), 1523 s ρ(NH). ^1H NMR in D_2O, δ: 1.02 (d, *J* 7.2 Hz, 6H, 2Me), 2.60 (septet, $J_{apparent}$ 7.2 Hz, 1H, CH), NH groups were not observed. $^{13}C\{^1H\}$ NMR in D_2O, δ: 19.3 ($2CH_3$), 35.5 (CH), 170.8 (C=N). Crystals for the X-ray study were obtained by slow evaporation of methanol solution of the complex at ca. 25 °C.

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[Ni{N(H)=C(*n*-Bu)NHC(*n*-Bu)=NH}$_2$]Cl$_2$ (5·Cl$_2$). Yield is 91%, based on Ni. Yellow powder is insoluble in acetone and chloroform, slightly soluble in water, and soluble in methanol and DMSO. Anal. Calcd for $C_{20}H_{42}N_6Cl_2Ni$: C, 48.41; H, 8.53; N, 16.94. Found: C, 48.81; H, 8.65; N, 16.42. FAB$^+$-MS, *m*/*z*: 423 [M − 2Cl − 2H]$^+$. Mp = 246 °C (dec). IR spectrum, selected bands, cm^{-1}: 3150 s ν(NH), 2958 s ν_{as}(CH), 2870 s ν_s(CH), 1658 vs ν(C=N), 1525 s ρ(NH). ^{1}H NMR in D_2O, δ: 0.72 (t, *J* 7.3 Hz, 3H, Me), 1.21 (sextet, $J_{apparent}$ 7.3 Hz, 2H, CH_2), 1.41 (quintet, $J_{apparent}$ 7.6 Hz, 2H, CH_2), 2.29 (t, J 7.6 Hz, 2H, CH_2), NH groups were not observed. ^{13}C{^{1}H} NMR in D_2O, δ: 13.5 (CH_3), 21.83 (CH_2), 29.3 (CH_2), 35.9 (CH_2), 166.2 (C=N). Crystals for the X-ray study were obtained by slow evaporation of methanol solution of the complex at ca. 25 °C.

[Ni{N(H)=C(CH$_2$Cl)NHC(CH$_2$Cl)=NH}$_2$]Cl$_2$ (6·Cl$_2$). Yield is 65%, based on Ni. Yellow powder is insoluble in acetone and chloroform but soluble in water, methanol, and DMSO. Anal. Calcd for $C_8H_{14}N_6Cl_6Ni$: C, 20.64; H, 3.03; N, 18.05. Found: C, 20.66; H, 3.07; N, 18.02. FAB$^+$-MS, *m*/*z*: 393 [M − 2Cl − 2H]$^+$. The compound has no specific mp, and it is slowly sublimated at ca. 200 °C and decomposes above 300 °C. IR spectrum, selected bands, cm^{-1}: 3094 s ν(NH), 2968 s ν_{as}(CH), 2851 s ν_s(CH), 1664 vs ν(C=N), 1538 s ρ(NH). ^{1}H NMR in D_2O, δ: 3.96 (s, 2H, CH_2), NH groups were not observed. ^{13}C{^{1}H} NMR in D_2O, δ: 41.9 (CH_2), solubility is insufficient to observe C=N groups even at high acquisition time. Slow evaporation of water solution of **6**·Cl$_2$ at ca. 25 °C results in dehydrochlorination and release of the monocationic complex [**6** − H]Cl as the solid. The X-ray structure of the latter was determined by X-ray crystallography.

[Ni{N(H)=C(CH$_2$C$_6$H$_4$OMe-*p*)NHC(CH$_2$C$_6$H$_4$OMe-*p*)=NH}$_2$](Cl)(*p*-MeOC$_6$H$_4$CH$_2$CO$_2$) [7·(Cl)(*p*-MeOC$_6$H$_4$CH$_2$CO$_2$)]. Yield is 87%, based on Ni. Yellow powder is insoluble in chloroform, acetone, and water, slightly soluble in methanol and dichloromethane, and well soluble in DMSO. Anal. Calcd for $C_{45}H_{49}ClN_6NiO_7$: C, 61.41; H, 5.61; N, 9.55. Found: C, 61.32; H, 5.65; N, 9.69. FAB$^+$-MS, *m*/*z*: 679 [M$_{cation}$ − 2H]$^+$. Mp = 257 °C. IR spectrum, selected bands, cm^{-1}: 3387 m-w and 3121 m-w ν(NH), 2958 m-w ν_{as}(CH), 2837 m-w ν_s(CH), 1672 s ν(C=O), 1612 s ν(C=N). ^{1}H NMR in DMSO-d_6, δ: 3.50 (s, 2H, CH_2), 3.72 (s, 3H, OMe), 6.84 (d, *J* 8.5 Hz, 2H, CH), 7.22 (d, *J* 8.5 Hz, 2H, CH), ca. 8.90 (s, br, NH), ca. 9.10 (s, br, NH). ^{13}C{^{1}H} NMR in DMSO-d_6, δ: 37.0 (CH_2), 55.0 (OCH_3), 113.8 (CH), 129.6 (CH), 164.0 (C=N). Signals from *p*-MeOC$_6$H$_4$CH$_2$CO$_2^-$ counterion: ^{1}H NMR in DMSO-d_6, δ, 3.60 (s, 0.5H, CH_2), 3.74 (s, 0.75H, OMe), 6.93 (d, *J* 8.4 Hz, 0.5H, CH), 7.33 (d, J 8.4 Hz, 0.5H, CH); ^{13}C{^{1}H} NMR in DMSO-d_6, δ, 37.0 (CH_2), 55.1 (OCH_3), 114.2 (CH), 130.0 (CH), signal for −C(=O)O$^-$ group was not observed. Slow evaporation of methanol solution of **7**·(Cl)(*p*-MeOC$_6$H$_4$CH$_2$CO$_2$) at ca. 25 °C results in the release of the solvate **7**·(*p*-MeOC$_6$H$_4$-CH$_2$CO$_2$)$_2$·MeOH. The X-ray structure of the latter was determined by X-ray crystallography.

Liberation and Hydrolytic Liberation of the Ligands. 1. Liberation of the Imidoylamidines via Protonation. HBF$_4$·Et$_2$O (4 mmol; 50% solution in Et$_2$O) is added dropwise and with vigorous stirring to a solution of the corresponding complex (1 mmol) dissolved in a mixture of dry acetonitrile and methanol (4 mL, 3:1, v/v), whereupon the reaction mixture is refluxed with stirring for 1 h, the solvent is evaporated under vacuum to dryness, and the product is recrystallized from methanol at 50 °C.

[N(H)=C(Et)NHC(Et)=NH]·2HBF$_4$ (8). Yield is 37%, based on Ni. Colorless crystalline material is soluble in acetone, chloroform, water, methanol, dichloromethane, and DMSO. Anal. Calcd for $C_6H_{15}N_3B_2F_8$: C, 23.80; H, 4.99; N, 13.88. Found: C, 23.99; H, 5.16; N, 13.91. FAB$^+$-MS, *m*/*z*: 129 [M − 2BF$_4$]$^+$. Mp = 126 °C (dec). IR spectrum, selected bands, cm^{-1}: 3290 s, br ν(NH), 2958 s ν_{as}(CH), 2910 s ν_s(CH), 1633 vs ν(C=N), 1090 s, br δ(BF$_4$). ^{1}H NMR in $CDCl_3$, δ: 1.05 (t, *J* 7.3 Hz, 3H, Me), 2.32 (q, *J* 7.3 Hz, 2H, CH_2), 8.34 (s, br, NH), 8.90 (s, br, N=H). ^{13}C{^{1}H} NMR in $CDCl_3$, δ: 10.5 (CH_3), 24.2 (CH_2), 170.0 (C=N).

[N(H)=C(CH$_2$C$_6$H$_4$OMe-*p*)NHC(CH$_2$C$_6$H$_4$OMe-*p*)=NH]·2HBF$_4$ (9). Yield is 57%, based on Ni. Colorless crystalline material is soluble in acetone, chloroform, water, methanol, dichloromethane, and DMSO. Anal. Calcd for $C_{18}H_{23}N_3B_2F_8O_2$: C, 44.39; H, 4.76; N, 8.63. Found: C, 44.09; H, 5.00; N, 8.82. FAB$^+$-MS, *m*/*z*: 312 [M − 2HBF$_4$]$^+$. Mp = 165 °C. IR spectrum, selected bands, cm^{-1}: 3275 s, br ν(NH), 2969 m-w ν_{as}(CH), 2840 m-w ν_s(CH), 1614 s ν(C=N), 1515 s ρ(NH), 1080 vs, br δ(BF$_4$). ^{1}H NMR in DMSO-d_6, δ: 3.55 (s, 2H, CH_2), 3.74 (s, 3H, OMe), 7.17 (d, *J* 8.4 Hz, 2H, CH), 7.35 (d, *J* 8.4 Hz, 2H, CH), NH groups were not observed. ^{13}C{^{1}H} NMR in DMSO-d_6, δ: 34.1 (CH_2), 55.1 (OCH_3), 114.1 (CH), 130.5 (CH), 168.2 (C=N).

2. Liberation of Imidoylamidines via Substitution. Ethanediamine (3 mmol) is added to the corresponding (imidoylamidine)-Ni(II) complex (1 mmol) dissolved in a methanol:chloroform (4 mL, 3:1 v/v) solution, and the reaction mixture is refluxed for 1 h, whereupon diethyl ether (4 mL) is added and a pink powder of [Ni(en)$_3$]Cl$_2$ complex[20] is precipitated, which is separated by filtration, and the filtrate is dried under vacuum at room temperature.

N(H)=C(Et)NHC(Et)=NH (10). Yield is 43%, based on Ni. Colorless, hygroscopic, crystalline material is unstable toward the hydrolysis and soluble in acetone, chloroform, water, methanol, dichloromethane, and DMSO. Anal. Calcd for $C_6H_{13}N_3$: C, 52.91; H, 10.36; N, 30.85. Found: C, 52.95; H, 10.50; N, 30.75. FAB$^+$-MS, *m*/*z*: 129 [M + 2H]$^+$. Mp = 86 °C. IR spectrum, selected bands, cm^{-1}: 3160 s br ν(N−H), 2953 m-w ν_{as}(CH), 2890 m-w ν_s(CH), 1643 s ν_{as}(C=N), 1524 s ρ(NH). ^{1}H NMR in $CDCl_3$, δ: 1.01 (t, *J* 7.2 Hz, 3H, Me), 2.36 (q, *J* 7.2 Hz, 2H, CH_2), NH groups were not observed. ^{13}C{^{1}H} NMR in $CDCl_3$, δ: 10.4 (CH_3), 31.7 (CH_2), 169.3 (C=N).

N(H)=C(CH$_2$C$_6$H$_4$OMe-*p*)NHC(CH$_2$C$_6$H$_4$OMe-*p*)=NH (11). Yield is 57%, based on Ni. Colorless crystalline material is soluble in acetone, chloroform, water, methanol, dichloromethane, and DMSO. Anal. Calcd for $C_{18}H_{21}N_3O_2 \cdot {}^1/_2H_2O$: C, 67.48; H, 6.92; N, 13.12. Found: C, 67.25; H, 7.05; N, 13.08. FAB$^+$-MS, *m*/*z*: 307 [M − 4H]$^+$. Mp = 113 °C (with partial sublimation at ca. 105 °C). IR spectrum, selected bands, cm^{-1}: 3423 ν(OH), 3136 m-w ν(NH), 2933 m-w ν_{as}(CH), 2853 m-w ν_s(CH), 1610 s ν_{as}(C=N), 1514 s ρ(NH). ^{1}H NMR in DMSO-d_6, δ: 3.36 (s, 2H, CH_2), 3.67 (s, 3H, OMe), 6.81 (d, *J* 8.1 Hz, 2H, CH), 7.16 (d, *J* 8.1 Hz, 2H, CH), NH groups were not observed. ^{13}C{^{1}H} NMR in DMSO-d_6, δ: 34.4 (CH_2), 55.5 (OCH_3), 114.2 (CH), 130.4 (CH), 158.4 (C=N).

3. Hydrolytic Liberation. (i) Na$_2$EDTA·2H$_2$O (2 mmol) is added to a water−methanol (1:1, v/v) solution (5 mL) of the corresponding complex (1.00 mmol), whereupon the reaction mixture is refluxed with stirring for 1 h and cooled to room temperature, the organic product is extracted with diethyl ether, the solvent is evaporated under vacuum at 20−25 °C, and the product is purified by dissolution in 5 mL of acetone at 50 °C and evaporation of the solvent at room temperature to ca. 0.5 mL. (ii) Water (5 mL) is added to the corresponding imidoylamidinium tetrafluoroborate (1.00 mmol), and the reaction mixture is refluxed for 1 h. In the case of R = CH$_2$C$_6$H$_4$OMe-*p*, the product precipitates, while for R = Et, the solvent should be removed under vacuum at 20 °C and the residue is purified as indicated above.

{**EtC(═O)**}$_2$**NH (12).** Mp = 156 °C from acetone [mp lit.[21] 155 °C]. This compound has been characterized by X-ray diffraction study (see above).

{***p*-MeOC$_6$H$_4$CH$_2$C(═O)**}$_2$**NH (13).** Yield is 57%, based on Ni. Colorless crystalline material is soluble in acetone, chloroform, water, methanol, dichloromethane, and DMSO. Anal. Calcd for $C_9H_{10}NO_3$: C, 59.99; H, 5.59; N, 7.77. Found: C, 59.95; H, 6.05; N, 7.65. Mp = 96 °C. IR spectrum, selected bands, cm^{-1}: 3419 vs ν(NH), 2954 m-w ν_{as}(CH), 2836 m-w ν_s(CH), 1671 vs (C═O), 1509 ρ(NH), 1250 s δ(CH$_3$). ^{1}H NMR in $CDCl_3$, δ: 3.49 (s, 2H, CH_2), 3.78 (s, 3H, OMe), 6.86 (d, *J* 8.1 Hz, 2H, CH), 7.16 (d, *J* 8.1 Hz, 2H, CH), NH was not observed. ^{13}C{^{1}H} NMR in $CDCl_3$, δ: 41.3 (CH_2), 56.3 (OCH_3), 114.4 (CH_2) 130.5 (CH_2), solubility is insufficient to observe the C═N groups.

Preparation of (Ketoxime)Ni(II) Complexes. The ketoxime C_4H_8C═NOH (4 mmol) is added to $NiCl_2 \cdot 2H_2O$ or $Ni(NO_3)_2 \cdot 6H_2O$ (1 mmol), whereupon acetone or acetonitrile (10 mL) is added. The reaction mixture is refluxed for 1 h on stirring (or stirred at room temperature for 10 min if nitrile is used as solvent). The solvent is removed under vacuum to dryness at room temperature, and the precipitate is washed with three 5-mL portions of diethyl ether. Yields are 90−97%, based on Ni. These complexes can also be isolated when any of the nitriles is used as the solvent.

***trans*-[NiCl$_2$(C$_4$H$_8$C═NOH)$_4$] (14).** Anal. Calcd for $C_{20}H_{36}N_4Cl_2O_4Ni$: C, 45.66; H, 6.90; N, 10.65. Found: C, 45.84; H, 6.83; N, 10.43. FAB$^+$-MS, *m*/*z*: 425 [M − oxime − 2H]$^+$, 356 [M − oxime − 2Cl]$^+$, 329 [M − 2oxime + H]$^+$. This complex has no specific mp and gradually decomposes on heating above 100 °C. IR spectrum, selected bands, cm^{-1}: 3278 s ν(OH), 2961 s ν_{as}(CH), 2871 m-w ν_s(CH), 1668 m-w ν(C═N).

***cis*-[Ni(*O*,*O*-NO$_3$)$_2$(C$_4$H$_8$C═NOH)$_2$] (15).** Anal. Calcd for $C_{10}H_{18}N_4O_8Ni$: C, 31.56; H, 4.77; N, 14.74. Found: C, 31.21; H, 5.01; N, 14.54. FAB$^+$-MS, *m*/*z*: 319 [M − NO_3]$^+$, 255 [M − 2NO_3 − 2H]$^+$. This complex has no specific mp and gradually decomposes on heating above 100 °C. IR spectrum, selected bands, cm^{-1}: 3420 s br ν(OH), 2980 m-w ν_{as}(CH), 2888 m-w ν_s(CH), 1632 s ν(C═N) + ν_{as}(NO_3), 1383 vs, br ν_s(NO_3) + δ(CH), 825 s δ (NO_3).

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Supporting Information Available: Crystallographic data including positional parameters, thermal parameters, and bond lengths and angles (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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