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Ni^{II}-Mediated Coupling between Iminoisoindolinones and Nitriles Leading to Unsymmetrical 1,3,5-Triazapentadienato Complexes

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Treatment of nickel acetate $Ni(OAc)_2 \cdot 4H_2O$ with 2 equiv of various 3-iminoisoindolin-1-ones in a suspension of RCN in the presence of triethanolamine leads to the formation of the nickel 1,3,5-triazapentadienato complexes $[Ni\{NH{=}C(R)N{=}C(C_6R^1R^2R^3R^4CO)N\}_2]$ (**1**–**17**) isolated in good 50–83% yields. The reaction proceeds under relatively mild conditions (from 5 to 7 h at 25–115 °C, depending on the boiling point of the nitrile) and has a general character insofar as it was successfully conducted with various nitriles RCN bearing donor (R = Me, Et, Pr^n, Pr^i, Bu^n), weak donor (R = CH_2Ph, $CH_2C_6H_4OMe$-*p*), acceptor (R = CH_2Cl), and strong acceptor (R = CCl_3) groups R of different steric hindrance and also with the nonsubstituted iminoisoindolinone (3-iminoisoindolin-1-one) or the iminoisoindolinones bearing donor methyl (3-imino-5-methylisoindolin-1-one) or acceptor fluoro (4,5,6,7-tetrafluoro-3-iminoisoindolin-1-one) groups in the benzene ring.

Introduction

Activation of organonitriles toward nucleophilic addition upon coordination to a metal center is currently an area of studies targeted on the exploration of synthetic transformations of RCN species at industrial or laboratory scale, and this subject has repeatedly been surveyed[1–6] (including reviews written by some of us[2–5]). In the majority of cases, coordination of organonitriles to a metal center increases significantly the electrophilicity of the RCN species, allowing the coupling even with very weak nucleophiles[2] to give versatile [M]−N(H)=CRR′ (R = alkyl, aryl; R′ = OH, OR″, ON=CR″$_2$, ONR″$_2$, N=CPh$_2$, and others) imino derivatives.

Following our ongoing project on reactions of metal-activated nitriles, we recently discovered approaches to a series of important coordination and organic compounds derived from organonitriles and generated via metal-mediated and/or "HON"-nucleophile-promoted processes. Thus, we observed, an unusual transformation of alkyl nitriles RCN to the appropriate symmetric (1,3,5-triazapentadiene)Ni^{II} complexes (route I, Scheme 1) in the Ni^{II}/ketoxime systems.[7] This route opens up a good access to 1,3,5-triazapentadienes which otherwise are conventionally obtained by the hazardous two-step Pinner synthesis.[2] When phthalonitrile (Pn) is used as an RCN source, the formation of nickel phthalocyanines (Pcs) instead of (1,3,5-triazapentadienes)Ni^{II} has been achieved in the "Ni^{II}/ketoxime" or "Ni^{II}/diethyl hydroxylamine" systems (route II, Scheme 1).[8–10] These oxime- or hydroxylamine-promoted reactions represent an advanced synthetic route to phthalocyanines species, which operate at low temperatures and do not require expensive reagents and/

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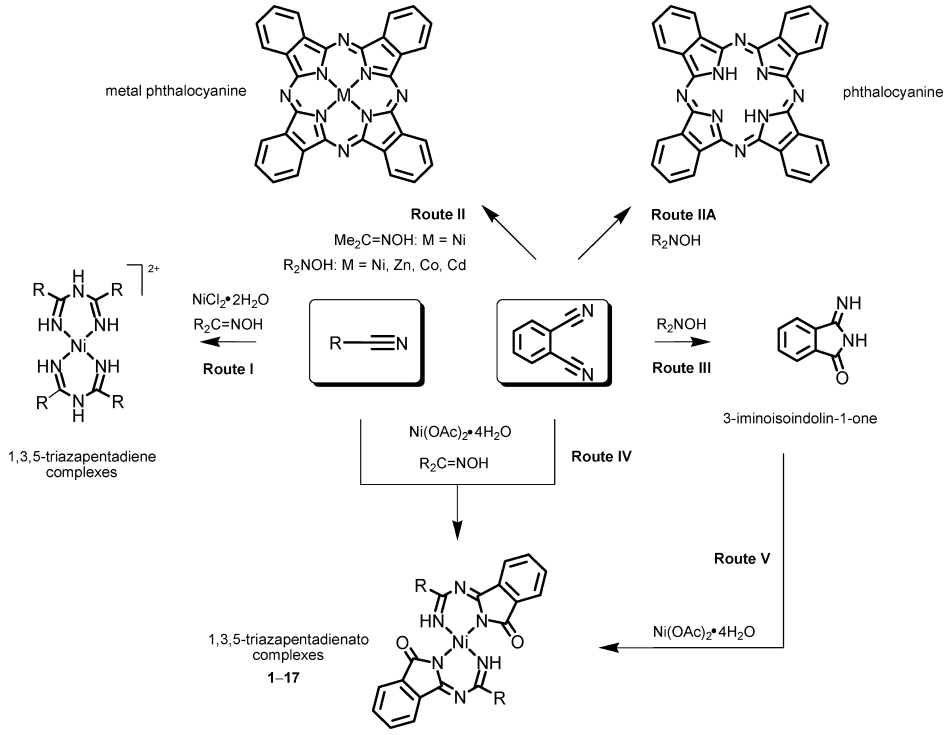
Scheme 1



or unconventional techniques (e.g., microwave irradiation) for their preparation.[8–10] Noteworthy, the hydroxylamine-assisted reaction shows higher promoting ability and versatility than those in the case of the oxime, and it can be applied for the preparation of various metal-bound phthalocyanines, viz. Ni, Zn, Co, and Cd (route II, Scheme 1).[10]

In a recent kinetic study,[11] we estimated that in the addition of HON species (such as diethyl hydroxylamines or oximes) to metal-activated nitriles the former are ca. 10^4 times better nucleophiles than the latter.[11] Taking into account the known higher reducing abilities of hydroxylamines vs oximes,[12] we studied the promoting ability of the hydroxylamine species in the conversion of Pns to Pcs and observed that Et_2NOH can so greatly enhance the cyclotetramerization of Pns in alcohols that this reaction could even proceed without a metal source (route IIA, Scheme 1). Curiously, the latter metal-free transformation of Pn promoted by Et_2NOH shows a dramatic solvent dependence. Thus, in alcohols the reaction furnishes free Pcs (route IIA, Scheme 1), while if chloroform is used instead of an alcohol, it proceeds in another direction, yielding 3-iminoisoindolin-1-ones (route III, Scheme 1).[10,13]

The latter method is one of the most advantageous for the preparation of these heterocyclic species useful as precursors for the manufacture of pigments (e.g., phthalocyanines), heat-sensitive colorants, some components for thermal-recording sheets, charge-controlling agents for electrophotographic toners, stabilizers for plastics, pharmaceuticals, and cosmetics, and also for the synthesis of other heterocycles.[14,15]

In all the above-mentioned examples, *only one* aliphatic or aromatic organonitrile was used as the starting material. However, treatment of a *mixture* of both alkylnitrile and nonsubstituted phthalonitrile (route IV, Scheme 1), in the presence of $Ni(OAc)_2 \cdot 4H_2O$, provides an easy single-pot entry to a series of new unsymmetrical (1,3,5-triazapentadienato)Ni^{II} compounds.[16] Inspecting the structure of $[Ni\{NH{=}C(R)N{=}C(C_6H_4CO\mathit{N})\}_2]$, we assumed that the unsymmetrical (1,3,5-triazapentadienato)Ni^{II} species are generated upon a previously unreported nucleophilic attack of

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Scheme 2

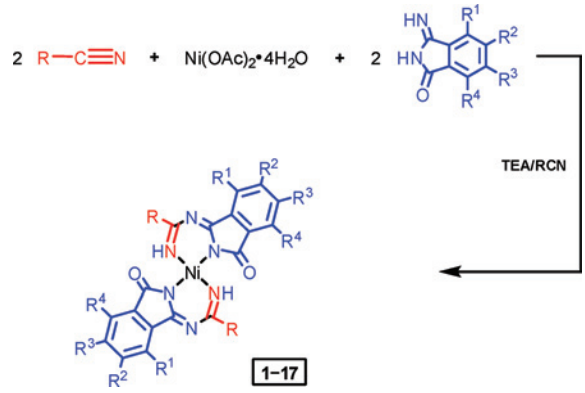

Table 1. Compounds Numbering and Yields

	R	no.	yield, %	R	no.	yield, %
R^1–R^4 = H	Me	**1**	50	Bu^n	**5**	60
	Et	**2**	60	CH_2Cl	**6**	67
	Pr^n	**3**	57	CCl_3	**7**	77
	Pr^i	**4**	55	CH_2Ph	**8**	58
				$CH_2C_6H_4OMe$-*p*	**9**	83
R^1, R^3, R^4 = H	Me	**10**	55	Pr^i	**13**	45
R^2 = Me	Et	**11**	51	CCl_3	**14**	73
	Pr^n	**12**	52	CH_2Ph	**15**	57
R^1–R^4 = F	Et	**16**	50	CCl_3	**17**	71

the 3-iminoisoindolin-1-one (formed *in situ* in accord with our observations[10,13]) on the nitrile at a nickel center.

Consequently, the main goals of the current work are (i) to study the nucleophilic properties of 3-iminoisoindolin-1-ones toward metal-bound organonitriles and to shed light on the mechanism of the one-pot formation of (1,3,5-triazapentadienato)Ni^{II} and (ii) to establish a new synthetic route to (1,3,5-triazapentadienato)Ni^{II} complexes starting from various nonsubstituted and substituted 3-iminoisoindolin-1-ones. All our results are reported in this article.

Results and Discussion

Ni^{II}-Mediated Coupling between Iminoisoindolinones and Nitriles. Treatment of nickel acetate $Ni(OAc)_2 \cdot 4H_2O$ with 2 equiv of the iminoisoindolinones (Scheme 2) in a suspension of RCN in the presence of triethanolamine (TEA) leads to the formation of 1,3,5-triazapentadienato complexes **1**–**17** (Scheme 2, Table 1) isolated in good (with two exceptions, i.e., **10** and **13**) 50–83% yields. The reaction has a general character, and it was successfully conducted with (i) various nitriles bearing donor (R = Me, Et, Pr^n, Pr^i, Bu^n), weak donor (R = CH_2Ph, $CH_2C_6H_4OMe$-*p*), acceptor (R = CH_2Cl), and strong acceptor (R = CCl_3) groups R of different steric hindrance and (ii) the nonsubstituted iminoisoindolinone (3-iminoisoindolin-1-one) or the iminoisoindolinones bearing donor methyl (3-imino-5-methylisoindolin-1-one) or acceptor fluoro (4,5,6,7-tetrafluoro-3-iminoisoindolin-1-one) groups in the benzene ring. Temperature range (25−115 °C) and the reflux/heating time (5−7 h) for the reaction depend on the boiling point of the nitrile, the degree of RCN activation, and the solubility of the starting iminoisoindolinones.

The addition of TEA is crucial for conducting the coupling and the best results were obtained at a molar ratio $Ni(OAc)_2 \cdot 4H_2O$:TEA equal to 2:1. The increase of TEA amount to 1:(1−2) and subsequent increase of pH value results in lowering the yield of the 1,3,5-triazapentadienato complexes and their substantial contamination with byproducts. We believe that the promoting role of TEA is dual. On one hand, the amine affects the acidity of the reaction mixture and the buffering prevents protonation of the iminoisoindolinones and also allows the isolation of the neutral (1,3,5-triazapentadienato-)Ni^{II} complexes in one distinct protolytic form. On the other hand, TEA promotes the dissolution of the solid nickel acetate by complexation to the nickel(II) center,[17] thus allowing the performance of the reaction in the homogeneous liquid phase. In accord with these assumptions, application in the synthesis of other sterically demanded amines such as triethylamine and trioctylamine, which cannot form Ni^{II} chelates, brings about formation of a broad mixture of products, where the target 1,3,5-triazapentadienato complexes are strongly contaminated with yet unidentified products. The nature of the anion of the nickel salt NiX_2 is also important, and usage of a weak acid salt, i.e. $Ni(OAc)_2 \cdot 4H_2O$, was proved to be significant for the conductance of the coupling, while the synthesis fails when the anion of NiX_2 is a derivative of a strong acid, e.g., X = Cl, NO_3.

It is important to mention that (i) the iminoisoindolinones under the reaction conditions do not react with RCN species in the absence of the promoting metal center, and this gives an indication that the observed coupling is Ni^{II}-mediated and the promoting effect of the metal is conceivably due to the activation of ligated RCN toward nucleophilic attack and also to the stabilization of the 1,3,5-triazapentadiene formed by chelation and (ii) the obtained data shed light on the mechanism of the previously reported single-pot synthesis of unsymmetrical (1,3,5-triazapentadienato)Ni^{II} complexes (route III, Scheme 3). Thus, phthalonitrile in the presence of a HON-nucleophile (oxime or hydroxylamine) is subject to transformation to 3-iminoisoindolin-1-one species via a known procedure (route I, Scheme 3).[10,13] The nitrile, which is used as both solvent and reactant in the one pot synthesis[16] and also in this work, upon coordination to a metal center leads to the formation of a metal-organonitrile complex, M−N≡CR. The 3-iminoisoindolin-1-one attack on the complexed nitrile furnishes 1,3,5-triazapentadienato complexes (route II, Scheme 3).

Characterization of (1,3,5-Triazapentadienato)Ni^{II} Complexes. The formulation of complexes **1**–**17** was supported by satisfactory C, H, and N microanalyses. The FAB^+/ESI^+ mass spectra of **1**–**17** display peaks from $[M]^+$ or $[M + H]^+$ ions. The complexes were also characterized by IR and 1D ^1H, $^{13}C\{^1H\}$, and 2D ^1H,^1H-COSY, ^1H,^{13}C-HMQC, ^1H,^{13}C-HSQC, and ^1H,^{13}C-HMBC NMR spectroscopies; **16**

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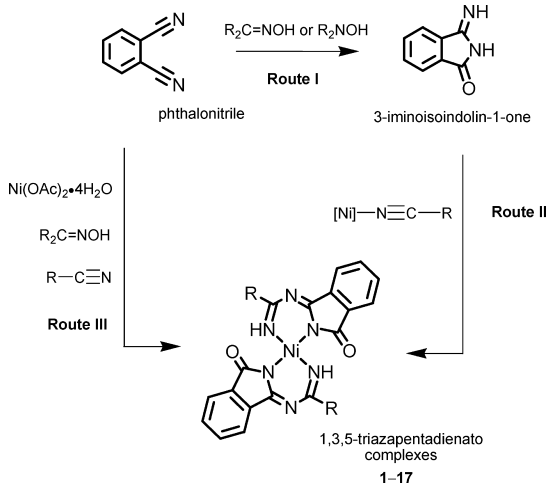
Scheme 3



and **17** were additionally characterized by ^{19}F NMR spectroscopy and **16** by X-ray diffraction. Moreover, compounds **1**–**4** were previously synthesized in the single-pot synthesis,[16] and the authenticity of those samples with those obtained in the current study was confirmed by elemental analyses, IR, ^{1}H, and ^{13}C{^{1}H} NMR spectroscopies.

The IR spectra of **1**–**17** compounds display strong ν(C═O), ν(C═N), and δ(N−H) bands in the ranges of 1721–1689, 1631−1605, and 1563–1544 cm^{-1}, respectively, and ν(N−H) stretching vibrations in the range between 3186 and 3003 cm^{-1}. These frequency intervals agree well with the appropriate values for the ν(C═N) (1665−1612 cm^{-1}) and δ(N−H) (1542−1523 cm^{-1}) bands and of the N−H stretching vibrations (3165–3094 cm^{-1}) for the previously prepared symmetric (1,3,5-triazapentadiene/ato)Ni^{II} complexes.[16] In the IR spectrum of **9**, the weak ν(C≡N) vibrations due to the solvation N≡C$CH_2C_6H_4$OMe-*p* molecule were also observed.

The ^{1}H NMR spectra of all (1,3,5-triazapentadienato)Ni^{II} complexes display one broad singlet from the N*H* proton resonating in the range between 11 and 10 ppm. The position of these signals at such a low field gives indirect evidence that the N*H* proton is involved in hydrogen bonding in solution probably with the neighboring oxygen carbonyl atom of the 3-iminoisoindolin-1-one fragment of the 1,3,5-triazapentadienato ligands; this H-bonding was also observed for complex **16** in the solid state (see later). ^{1}H NMR spectra of **10**–**15** show the presence of two isomers (with the methyl group in 5- and 6-position) for each compound obtained upon nucleophilic addition of an isomeric mixture of 3-imino-5-methylisoindolin-1-one/3-imino-6-methylisoindolin-1-one. The spectra of **9** and **10** indicate the presence of the solvated N≡C$CH_2C_6H_4$OMe-*p* and CH_3CO_2H molecules. Compounds **16** and **17**, which do not have protons in the aromatic ring of the 3-iminoisoindolin-1-one fragment, were additionally characterized by ^{19}F NMR spectroscopy, and a typical multiplet due to J_{F-F} was observed in both spectra. The ^{13}C{^{1}H} spectra of **1**–**17** show no evidence for the C≡N group (which typically resonates in the range of 120–130 ppm) but indicate the presence of the signals from the newly

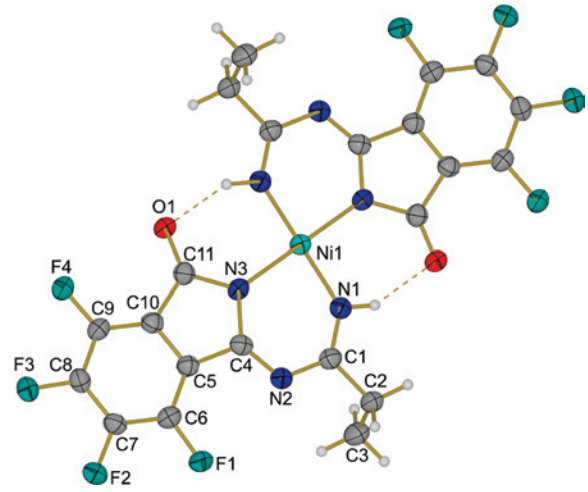


Figure 1. Thermal ellipsoid view of complex **16** with atomic numbering scheme. Thermal ellipsoids are drawn with 50% probability.

formed imine C═N moiety; these peaks appear in the range of 165–175 ppm, which is typical for the C═N groups.

The accurate assignment of the ^{1}H and ^{13}C signals for **1**–**17** was performed using 2D (^{1}H,^{1}H-COSY, ^{1}H,^{13}C-HMQC, ^{1}H,^{13}C-HSQC, and ^{1}H,^{13}C-HMBC) NMR correlation experiments. ^{1}H,^{13}C-HMQC and ^{1}H,^{13}C-HSQC approaches were found to be particularly useful for studies of compounds containing groups with very close ^{13}C chemical shifts, e.g. for compound **11** (see Figure S1, Supporting Information). The ^{1}H,^{13}C-HMBC experiment allows to discriminate the quaternary C═N signal of the imine fragment from the C═O resonance of the 3-iminoisoindolin-1-one moiety, due to the observed $^{2}J_{H-C}$ and $^{3}J_{H-C}$ couplings, e.g., in case of the imine HN═C group between the imine carbon and the protons of the nitrile residue (performed for **1**–**7**, **9**–**13**, and **15**–**17**).

The structure of **16** has been determined by X-ray diffraction (Figure 1). The complex exhibits the square-planar geometry with two uninegatively charged 1,3,5-triazapentadienato species. The ligands have distinct single and double CN bonds and almost no electron delocalization within the Ni(1)N(1)C(1)N(2)C(4)N(3) ring. The bond lengths N(1)−C(1) and N(2)−C(4) [1.296(4) and 1.295(4) Å, respectively] have values typical for the corresponding N═C bonds in Pt^{II},[18] Pd^{II},[19] and (1,3,5-triazapentadiene/ato)Ni^{II} complexes[16] and, within 3σ, for the N═C bond in compounds bearing the C_{Ar}−C═N−C moiety[20] [mean value 1.279(8) Å]. The bond length N(2)−C(1) [1.374(4) Å] has a value typical for the corresponding N−C bonds in (1,3,5-triazapentadiene/ato)M (M = Pt^{II}, Pd^{II}, Ni^{II}) complexes.[16–20] The bond distance N(3)−C(4) is longer than the N−C single bonds of the previously reported Pt^{II} unsymmetrical and Pd^{II}, Ni^{II} symmetrical 1,3,5-triazapentadiene complexes. The bond distance O(1)−C(11) [1.217(3) Å] within 3σ agrees with the Csp^{2}═O

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double bond in amides having the $NH_2-C(-Csp^3)=O$ [mean value 1.234(12) Å[20]] functionality. Intramolecular hydrogen bonding is observed between the NH group and the O carbonyl atom; the distance H(1)•••O(1)#1 is 1.872(18) Å. Atoms of the metallacycle lie in one plane with the maximum deviation of −0.041(2) Å for N(3) in the Ni(1)N(1)C(1)N(2)C(4)N(3) plane, and the rms of the deviations for this ring is 0.041(3) Å.

Final Remarks

The study establishes a novel type of high yielding metal-mediated coupling, i.e., between iminoisoindolinones and nitriles, which proceeds at a Ni^{II} center and does not require any of "NOH" promoters. The observed reaction shed light on the mechanism of the single-pot synthesis of unsymmetrical (1,3,5-triazapentadienato)Ni^{II} complexes[16] and suggests that the latter process consists of two principal steps, i.e., oxime-promoted generation of a iminoisoindolinone from Pn followed by the coupling of the iminoisoindolinone and alkylnitrile at a Ni^{II} center.

This work adds more on the synthetic routes to *unsymmetrical* 1,3,5-triazapentadiene/ato complexes, which are rare and the known cases involve species obtained previously by us at Pt^{II} and Pt^{IV} centers (via the nitrile−amidine coupling[18]) and at a Ni^{II} center (via the oxime-mediated single-pot reaction of nitriles and phthalonitriles[16]). Further studies directed toward widening the family of unsymmetrical 1,3,5-triazapentadiene complexes to other metal centers are currently under way in our group with particular emphasis on compounds, which cannot be achieved in the oxime-mediated single-pot synthesis[16] (e.g., of Cu^{II}, Pd^{II}, and Pt^{II}).

Experimental Section

Materials and Instrumentation. Solvents, $Ni(OAc)_2 \cdot 4H_2O$, and all organonitriles were obtained from commercial sources and used as received. 3-Iminoisoindolin-1-one and its substituted derivatives were prepared in accord with a previously reported procedure.[10,13] C, H, and N elemental analyses were carried out by the Microanalytical Service of the Instituto Superior Técnico. For TLC, Merck UV 254 SiO_2 plates have been used. FAB^+ and FAB^- mass spectra were obtained on a Trio 2000 instrument by bombarding 3-nitrobenzyl alcohol (NBA) matrices of the samples with 8 keV (ca. 1.28×10^{15} J) Xe atoms. Mass calibration for data system acquisition was achieved using CsI. ESI^+ mass spectra were obtained on VARIAN 500-MS LC ion trap mass spectrometer. Infrared spectra (4000–400 cm^{-1}) were recorded on a BIO-RAD FTS 3000MX instrument in KBr pellets. 1D NMR experiments, i.e., 1D ^1H, $^{13}C\{^1H\}$, ^{19}F, and 2D $^1H,^1H$-COSY, $^1H,^{13}C$-HMQC, $^1H,^{13}C$-HSQC, and $^1H,^{13}C$-HMBC spectra were recorded on Bruker Avance II 300 and 400 MHz (UltraShield Magnet) spectrometers at ambient temperature.

X-ray Structure Determinations. The crystals of **16** and $[Ni\{NH{=}C(CCl_3)NC(CCl_3){=}NH\}_2]$ were immersed in cryo-oil, mounted in a Nylon loop, and measured at a temperature of 120 K. The X-ray diffraction data were collected by means of a Nonius KappaCCD diffractometer using Mo Kα radiation ($\lambda = 0.710\,73$ Å). The Denzo-Scalepack[21] or EvalCCD[22] program packages were used for cell refinements and data reductions. The structure was solved by direct methods using the SIR2004[23] or SHELXS-97[24] with the WinGX[25] graphical user interface. An empirical absorption correction (SORTAV[26] or SADABS[27]) was applied to the data. Structural refinements were carried out using SHELXL-97.[28] In $[Ni\{NH{=}C(CCl_3)NC(CCl_3){=}NH\}_2]$, the oxygen and the methyl carbon atoms in the solvent of crystallization (acetone) were disordered over two sites with equal occupancies. In **16**, the NH hydrogen atom was located from the difference Fourier map but refined with fixed N−H = 0.880 Å. In **16**, the NH hydrogen atoms were located from the difference Fourier map but constrained to ride on their parent atom, with $U_{iso} = 1.5$. Other hydrogens were positioned geometrically and constrained to ride on their parent atoms, with C−H = 0.98–0.99 Å and $U_{iso} = 1.2$–$1.5U_{eq}$ (parent atom). The crystallographic details are summarized in Table 2 and selected bond lengths and angles in Table 3.

Table 2. Crystal Data

	16	$[Ni\{NH{=}C(CCl_3)NC(CCl_3){=}NH\}_2]$
empirical formula	$C_{22}H_{12}F_8N_6NiO_2$	$C_{14}H_{16}Cl_{12}N_6NiO_2$
fw	603.09	784.44
temp (K)	120(2)	120(2)
λ (Å)	0.71073	0.71073
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$C2/m$
a (Å)	5.6247(5) Å	12.8243(6)
b (Å)	8.8801(11)	9.4600(6)
c (Å)	11.1999(11)	13.3469(7)
α (deg)	100.583(5)	90
β (deg)	102.770(6)	115.994(3)
γ (deg)	100.797(6)	90
V (Å^3)	520.92(10)	1455.42(14)
Z	1	2
ρ_{calc} (Mg/m^3)	1.922	1.790
μ (Mo Kα) (mm^{-1})	1.041	1.795
no. reflns.	9081	11635
unique reflns	2377	1781
R_{int}	0.0655	0.0432
R1[a] ($I \geq 2\sigma$)	0.0452	0.0271
wR2[b] ($I \geq 2\sigma$)	0.0893	0.0569

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

Synthetic Work. Reaction of $Ni(OAc)_2 \cdot 4H_2O$, 3-Iminoisoindolin-1-one [or 5-Methyl-3-iminoisoindolin-1-one, or 4,5,6,7-Tetrafluoro-3-iminoisoindolin-1-one] (2 equiv), and RCN. Nickel acetate $Ni(OAc)_2 \cdot 4H_2O$ (249 mg, 1 mmol) was added to a flask with neat RCN (5 mL for R = Me, Et, Pr^n, Pr^i; 2 mL for R = Bu^n, CH_2Cl, CCl_3, CH_2Ph, $CH_2C_6H_4OMe$-*p*), equipped with a magnetic stirrer, and the emerald-green suspension was refluxed (R = Me, Et, Pr^n, Pr^i, CH_2Cl, CCl_3) or heated at 100 °C (R = Bu^n, CH_2Ph, $CH_2C_6H_4OMe$-*p*) for 15 min. Triethanolamine (75 mg, 0.5 mmol) was added, and the suspension was refluxed (R = Me, Et, Pr^n, Pr^i, CH_2Cl, CCl_3) or heated for an additional 20 min at 100 °C

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Table 3. Selected Bond Lengths (Å) and Angles (deg)

	16	[Ni{*N*H=C(CCl$_3$)NC(CCl$_3$)=*N*H}$_2$]
Ni1−N1	1.846(2)	1.854(2)
Ni1−N3	1.942(2)	1.863(2)
N3−C3		1.299(3)
N3−C4	1.387(3)	
C3−N2		1.333(3)
C4−N2	1.295(4)	
N2−C1	1.374(4)	1.330(3)
C1−N1	1.296(4)	1.299(3)
N1−Pt1−N3	88.29(10)	89.43(9)
C1−N2−C3		118.3(2)
C1−N2−C4	118.9(2)	
N1−C1−N2	124.5(3)	128.1(2)
N3−C3−N2		128.1(2)
N3−C4−N2	130.9(3)	

(R = Bu^n, CH_2Ph, $CH_2C_6H_4OMe$-*p*) to give a bright yellowish-green solution. Then, 3-iminoisoindolin-1-one (5-methyl-3-iminoisoindolin-1-one/6-methyl-3-iminoisoindolin-1-one or 4,5,6,7-tetrafluoro-3-iminoisoindolin-1-one can also be used) (2 mmol) was added to the solution, and the reaction mixture was refluxed for 7 h (R = Me, Et) or 5 h (R = Pr^n, Pr^i, CH_2Cl) or left at 20–25 °C for 2 h with a following slow heating up to 50 °C and heating for 5 h at 50 °C (R = CCl_3) or heated for 5 h at 100 °C (R = Bu^n, CH_2Ph, $CH_2C_6H_4OMe$-*p*). During heating the color of the solution turned from bright yellowish green to dark brownish orange, followed by the release of a bright orange precipitate. The latter was filtered off, washed with five 5 mL portions of acetone and two 5 mL portions of Et_2O, and dried in air at 20–25 °C. Yields ranges from 35 to 83% (Scheme 2) depending on solubilities of the final complexes and corresponding difficulties in their isolation.

Compounds **1**–**4** were previously synthesized in the single-pot synthesis;[16] the authenticity of the samples was confirmed by elemental analyses, IR, ^{1}H, and ^{13}C{^{1}H} NMR spectroscopies.

[Ni{*N*H=C(Bu^n)N=C(C$_6$H$_4$CO*N*)$_2$] (5). Anal. Calcd for $C_{26}H_{28}N_6NiO_2$: C, 60.61; H, 5.48; N, 16.31. Found: C, 60.79; H, 5.28; N, 15.83%. FAB$^+$-MS, *m*/*z*: 515 [M]$^+$. IR (KBr, selected bands, cm^{-1}): 3181 (m-w), 3128 (m-w), ν (N−H); 3086 (m-w), ν (C−H from Ar); 2958 (m-w), 2927 (m-w), 2859 (m-w), ν(C−H from Bu); 1690 (m-s), ν(C=O); 1622 (s), ν(C=N); 1553 (s), δ(N−H); 723 (s), δ(C−H from Ar). ^{1}H NMR ($CDCl_3$, δ): 10.49 (s, br, 2H, NH), 7.82 (br, 2H), 7.65 (d, 6 Hz, 2H), 7.52 (q, 6 Hz, 4H) (Ar's), 2.54 (t, 7.2 Hz, 4H), 1.69 (q, 7.2 Hz, 4H), 1.39 (sec, 7.2 Hz, 4H) (C*H*$_2$ from Bu), 0.95 (t, 7.2 Hz, 6H, C*H*$_3$ from Bu). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 184.5 (C=O), 172.0, 166.4 (C=N), 138.6, 134.3, 132.8, 131.6, 122.3, 121.6 (carbons in Ar), 40.3 (α-*C*H$_2$), 28.4 (β-*C*H$_2$), 22.2 (γ-*C*H$_2$), 13.8 (*C*H$_3$) (Bu).

[Ni{*N*H=C(CH$_2$Cl)N=C(C$_6$H$_4$CO*N*)$_2$] (6). Anal. Calcd for $C_{20}H_{14}N_6Cl_2NiO_2$: C, 48.05; H, 2.82; N, 16.81. Found: C, 47.48; H, 2.71; N, 16.41%. FAB$^+$-MS, *m*/*z*: 499 [M − H]$^+$. IR (KBr, selected bands, cm^{-1}): 3151 (w), 3090 (m-w), ν(N−H); 3043 (m-w), ν(C−H from Ar); 2975 (w), 2928 (w), ν(C−H from CH_2); 1705 (s), ν(C=O); 1627 (s), ν(C=N); 1556 (s), δ(N−H); 721 (vs), δ(C−H from Ar). ^{1}H NMR ($CDCl_3$, δ): 7.83–7.45 (m, 10H, Ar's), 4.30 (s, 4H, CH_2Cl). The compound is poorly soluble in the most common deuterated solvents, and this precluded ^{13}C{^{1}H} NMR measurements.

[Ni{*N*H=C(CCl$_3$)N=C(C$_6$H$_4$CO*N*)$_2$] (7). Anal. Calcd for $C_{20}H_{10}N_6Cl_6NiO_2$: C, 37.67; H, 1.58; N, 13.18. Found: C, 37.49; H, 1.66; N, 12.90%. FAB$^+$-MS, *m*/*z*: 637 [M]$^+$. IR (KBr, selected bands, cm^{-1}): 3139 (w), 3048 (w), 3003 (w), ν(N−H and/or C−H from Ar); 1708 (m-s), ν(C=O); 1605 (m-s), ν(C=N); 1549 (m-s), δ(N−H); 723 (m-s), δ(C−H from Ar). ^{1}H NMR ($CDCl_3$, δ): 11.09 (s, br, 2H, NH), 7.92 (d, 1H), 7.90 (d, 1H), 7.73–7.70 (m, 2H), 7.62–7.57 (m, 4H) (Ar's). The compound is poorly soluble in the most common deuterated solvents, and this precluded ^{13}C{^{1}H} NMR measurements.

[Ni{*N*H=C(CH$_2$Ph)N=C(C$_6$H$_4$CO*N*)$_2$]·$^1/_2$H$_2$O (8). Anal. Calcd for $C_{32}H_{25}N_6NiO_{2.5}$: C, 64.89; H, 4.25; N, 14.19. Found: C, 64.91; H, 4.10; N, 14.34%. FAB$^+$-MS, *m*/*z*: 583 [Ni{*N*H=C(CH$_2$Ph)N=C(C$_6$H$_4$CO*N*)$_2$]$^+$. IR (KBr, selected bands, cm^{-1}): 3179 (m-w), 3123 (m-w), ν(N−H); 3060 (m-w), ν(C−H from Ar); 2919 (w), ν(C−H from CH_2); 1693 (s), ν(C=O); 1608 (s), ν(C=N); 1544 (s), δ(N−H); 725 (vs), 698 (s), δ(C−H from Ar). ^{1}H NMR ($CDCl_3$, δ): 10.44 (s, br, 2H, NH), 7.89–7.86 (m), 7.79–7.75 (m), 7.61–7.58 (m), 7.53–7.49 (m) (18H, Ar's), 3.81 (s, 4H, C*H*$_2$Ph). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): (carbons in Ar), 45.00 (*C*H$_2$Ph).

[Ni{*N*H=C(CH$_2$C$_6$H$_4$OMe-*p*)N=C(C$_6$H$_4$CO*N*)$_2$]·N≡CCH$_2$-C$_6$H$_4$OMe-*p*·$^1/_2$H$_2$O (9). Anal. Calcd for $C_{43}H_{38}N_7NiO_{5.5}$: C, 64.60; H, 4.79; N, 12.26. Found: C, 64.33; H, 4.62; N, 12.24%. FAB$^+$-MS, *m*/*z*: 661 [Ni{*N*H=C(CH$_2$C$_6$H$_4$OMe-*p*)N=C(C$_6$H$_4$CO*N*)}$_2$ + H$_2$O]$^+$. IR (KBr, selected bands, cm^{-1}): 3178 (w), 3123 (w), ν(N−H); 3065 (w), ν(C−H from Ar); 2909 (w), 2834 (w), ν(C−H from CH_2 and/or CH_3); 2249 (w), ν(C≡N) from the solvated nitrile; 1690 (m-s), ν(C=O); 1616 (m-s), ν(C=N); 1548 (m), δ(N−H); 720 (vs), δ(C−H from Ar). ^{1}H NMR ($CDCl_3$, δ): 10.34 (s, br, 2H, NH), 7.89–7.75 (m), 6.89–7.27 (m) (16H, Ar's), 3.82 (s, 4H, C*H*$_2$Ph), 3.69 (s, 6H, OMe). The compound is poorly soluble in the most common deuterated solvents, and this precluded ^{13}C{^{1}H} NMR measurements.

[Ni{*N*H=C(Me)N=C(C$_6$H$_3$(Me)CO*N*)$_2$]·2MeCO$_2$H (10). Despite the addition of TEA, the complex releases from the reaction mixture as the bis-acetate, and it is anticipated that the acetic acid derives from a metal-mediated hydrolysis of MeCN. Complex **10** was isolated from the reaction mixture in 35% yield, while evaporation of the filtrate to dryness, followed by washing of the latter with cold acetone (5 mL, 10 °C), allows the isolation of additional amount of **10** (ca. 20%), which was treated in an identical way. In the presence of higher quantities of TEA (up to 2 mmol) the reactions becomes not selective and **10** is isolated in lower yields along with other yet unidentified products. Total yield is 55%. Anal. Calcd for $C_{26}H_{28}N_6NiO_6$: C, 53.91; H, 4.87; N, 14.51. Found: C, 54.14; H, 4.77; N, 14.57%. FAB$^+$-MS, *m*/*z*: 459 [Ni{*N*H=C(Me)N=C(C$_6$H$_3$(Me)CO*N*)$_2$]$^+$. IR (KBr, selected bands, cm^{-1}): 3174 (m-w), 3138 (m-w), ν(N−H); 2922 (m-w), 2860 (m-w), ν(C−H from Me and/or C*H*$_3$CO$_2$H); 1701 (vs), ν(C=O); 1631 (s), ν(C=N); 1554 (s), δ(N−H); 741 (s), δ(C−H from Ar). ^{1}H NMR ($CDCl_3$, δ): 10.67 (s, br, 2H, NH), 7.66 (d, 7.5 Hz), 7.60 (s), 7.51 (d, 7.5 Hz), 7.43 (s), 7.32 (d, 7.5 Hz), 7.30 (d, 7.5 Hz) (6H, Ar's), 2.45 (s), 2.43 (s) (6H, *Me*), 2.32 (s), 2.31 (s) (6H, HN=CMe), 1.26 (s, 6H, C*H*$_3$CO$_2$H). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 185.1, 185.0 (C=O), 168.6, 168.5, 166.7 (C=N), 143.9, 142.5, 138.8, 135.9, 134.7, 133.5, 132.3, 131.8, 122.9, 122.4, 122.0, 121.3 (carbons in Ar), 29.7 (*C*H$_3$CO$_2$H), 27.1 (HN=C*C*H$_3$), 21.8, 21.7 (*C*H$_3$).

[Ni{*N*H=C(Et)N=C(C$_6$H$_3$(Me)CO*N*)$_2$] (11). Anal. Calcd for $C_{24}H_{24}N_6NiO_2$: C, 59.17; H, 4.96; N, 17.25. Found: C, 58.62; H, 4.68; N, 17.23%. FAB$^+$-MS, *m*/*z*: 487 [M]$^+$. IR (KBr, selected bands, cm^{-1}): 3174 (m), 3127 (m), ν(N−H); 3068 (m-w), ν(C−H from Ar); 2975 (m-w), 2922 (m-w), ν(C−H from CH_2 and/or CH_3); 1695 (s), ν(C=O); 1615 (s), ν(C=N); 1554 (s), δ(N−H); 741 (s), δ(C−H from Ar). ^{1}H NMR ($CDCl_3$, δ): 10.45 (s, br, 2H, NH), 7.67 (d, 7.5 Hz, 2H), 7.60 (s, 2H), 7.51 (d, 7.5 Hz, 2H), 7.44 (s, 2H), 7.30 (d + s, 4H) (Ar's), 2.57 (q, 7.5 Hz, 4H, C*H*$_2$ from Et), 2.44 (s, 3H), 2.42 (s, 3H) (Me), 1.27 (t, 7.5 Hz, 3H), 1.26 (t, 7.5 Hz, 3H) (C*H*$_3$ from Et). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 184.6, 184.5 (C=O), 172.9, 172.8, 166.5, 166.4

(C═N), 143.8, 142.4, 139.0, 136.1, 134.7, 133.4, 132.2, 131.8, 122.9, 122.2, 122.0, 121.4 (carbons in Ar), 33.7 (CH_2), 21.8, 21.7 (CH_3), 10.8, 10.7 (CH_3 from Et).

[Ni{*N*H═C(Pr^n)N═C(C$_6$H$_3$(Me)CO*N*)}$_2$] (12). Anal. Calcd for $C_{26}H_{28}N_6NiO_2$: C, 60.61; H, 5.48; N, 16.31. Found: C, 60.41; H, 5.25; N, 16.30%. FAB$^+$-MS, *m*/*z*: 515 $[M]^+$. IR (KBr, selected bands, cm^{-1}): 3177 (m-w), 3128 (m-w), ν(N−H); 2959 (m-w), 2928 (m-w), 2871 (m-w), ν(C−H from CH_2 and/or CH_3); 1693 (s), ν(C═O); 1616 (s), ν(C═N); 1548 (s), δ(N−H); 746 (m-s), δ(C−H from Ar). ^{1}H NMR ($CDCl_3$, δ): 10.34 (s, br, 2H, NH), 7.49 (d, 8 Hz), 7.43 (s), 7.34 (d, 8 Hz), 7.27 (s), 7.15–7.09 (m) (6H, Ar's), 2.33 (t, 7.3 Hz, 4H, N≡C*H*$_2$ from Pr^n), 2.27 (s), 2.25 (s) (6H, Me), 1.58 (sec, 7.3 Hz, 4H, N≡CH$_2$C*H*$_2$ from Pr^n), 0.82 (t, 7.3 Hz, 6H) (C*H*$_3$ from Pr^n). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 184.8, 184.7 (C═O), 171.8, 171.7, 166.5, 166.4 (C═N), 143.8, 142.4, 139.0, 136.1, 134.8, 133.4, 132.2, 131.8, 122.9, 122.2, 122.0, 121.4 (carbons in Ar), 42.6 (N≡C*C*H$_2$ from Pr^n), 21.8, 21.7 (*C*H$_3$), 19.8 (N≡CH$_2$*C*H$_2$ from Pr^n), 13.6 (*C*H$_3$ from Pr^n).

[Ni{*N*H═C(Pr^i)N═C(C$_6$H$_3$(Me)CO*N*)}$_2$] (13). Anal. Calcd for $C_{26}H_{28}N_6NiO_2$: C, 60.61; H, 5.48; N, 16.31. Found: C, 60.08; H, 5.24; N, 16.31%. FAB$^+$-MS, *m*/*z*: 515 $[M]^+$. IR (KBr, selected bands, cm^{-1}): 3176 (m-w), 3128 (m-w), ν(N−H); 2969 (m-w), 2922 (m-w), 2867 (m-w), ν(C−H from CH and/or CH_3); 1694 (s), ν(C═O); 1615 (s), ν(C═N); 1553 (s), δ(N−H); 762 (vs), 723 (s), δ(C−H from Ar). ^{1}H NMR ($CDCl_3$, δ): 10.31 (s, br, 2H, NH), 7.69 (d, br), 7.63 (s), 7.53 (d, 7.5 Hz), 7.46 (s), 7.31 (t, 7.5 Hz) (6H, Ar's), 2.76 (sep, 6.9 Hz) (2H, C*H*Me$_2$), 2.46 (s), 2.43 (s) (6H, Me), 1.25 (d, 6.9 Hz), 1.23 (d, 6.9 Hz) (12H, CH*Me*$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 184.5 (C═O), 176.4, 166.7 (C═N), 143.9, 142.5, 139.3, 136.4, 134.9, 133.5, 132.4, 132.0, 123.0, 122.4, 122.2, 121.6 (carbons in Ar), 39.2 (N≡C*C*H from Pr^i), 22.0, 21.9 (*C*H$_3$), 20.3 (N≡CCH(C*H*$_3$)$_2$ from Pr^i).

[Ni{*N*H═C(CCl$_3$)N═C(C$_6$H$_3$(Me)CO*N*)}$_2$] (14). Anal. Calcd for $C_{22}H_{14}N_6Cl_6NiO_2$: C, 39.69; H, 2.12; N, 12.62. Found: C, 39.32; H, 1.91; N, 12.38%. ESI$^+$-MS, *m*/*z*: 667 $[M + H]^+$. IR (KBr, selected bands, cm^{-1}): 3139 (m-w), 3059 (m-w), 3006 (m-w), ν(N−H and/or C−H from Ar); 2941 (m-w), 2831 (m-w), ν(C−H from Me); 1705 (s), ν(C═O); 1611 (s), ν(C═N); 1558 (m), δ(N−H); 743 (m-s), δ(C−H from Ar). ^{1}H NMR ($CDCl_3$, δ): 11.05 (s, br, 2H, NH), 7.77 (d, 7.6 Hz), 7.69 (s), 7.61 (d, 7.6 Hz), 7.58 (d, 7.6 Hz), 7.53 (s), 7.51 (s), 7.37 (t, 8.5 Hz) (6H, Ar's), 2.49 (s), 2.45 (s) (6H, Me). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 182.3 (C═O), 171.2, 167.6 (C═N), 143.1, 142.9, 136.7, 135.0, 131.0, 130.1, 128.6, 123.5 (carbons in Ar), 56.8 (CCl_3), 22.9, 21.8 (Me). The filtrate after performing the synthesis was a subject of slow evaporation in air at 20–25 °C to give crystals of the symmetrical byproduct, i.e. [Ni{*N*H═C(CCl$_3$)NC(CCl$_3$)═*N*H}$_2$], which is formed upon the known nucleophile-mediated coupling.[7] The latter compound has been characterized by X-ray crystallography and also by IR and ^{1}H and ^{13}C{^{1}H} NMR spectroscopies (see Supporting Information).

[Ni{*N*H═C(CH$_2$Ph)N═C(C$_6$H$_3$(Me)CO*N*)}$_2$] (15). Anal. Calcd for $C_{34}H_{28}N_6NiO_2$: C, 66.80; H, 4.62; N, 13.75. Found: C, 66.04; H, 4.46; N, 13.70%. FAB$^+$-MS, *m*/*z*: 613 $[M + 2H]^+$. IR (KBr, selected bands, cm^{-1}): 3172 (m-w), 3123 (m-w), ν(N−H); 3060 (m-w), 3028 (m-w), ν(C−H from Ar); 2921 (w), ν(C−H from CH_2 and/or Me); 1689 (s), ν(C═O); 1612 (s), ν(C═N); 1553 (s), δ(N−H); 725 (s), 698 (m), δ(C−H from Ar). ^{1}H NMR ($CDCl_3$, δ): 10.43 (s, br, 2H, NH), 7.64 (d, 7.5 Hz), 7.57 (s), 7.47 (d, 7.5 Hz), 7.39–7.28 (m) (16H, Ar's), 3.81 (s, 4H, C*H*$_2$Ph), 2.46 (s), 2.43 (s) (6H, Me). ^{13}C{^{1}H} NMR ($CDCl_3$, δ): 184.0 (C═O), 170.3, 167.4 (C═N), 144.1, 142.8, 135.7, 135.1, 131.4, 129.4, 128.7, 127.1, 122.3 (carbons in Ar), 46.6 (*C*H$_2$Ph), 21.8, 21.6 (Me).

[Ni{*N*H═C(Et)N═C(C$_6$F$_4$CO*N*)}$_2$] (16). Anal. Calcd for $C_{22}H_{12}N_6F_8NiO_2$: C, 43.82; H, 2.01; N, 13.94. Found: C, 43.75; H, 2.17; N, 13.66%. ESI$^+$-MS, *m*/*z*: 611 $[M + Li + 2H]^+$. IR (KBr, selected bands, cm^{-1}): 3192 (m-w), 3143 (m-w), ν(N−H); 2981 (m-w), 2932 (m-w), ν(C−H from CH_2 and/or CH_3); 1710 (s), ν(C═O); 1618 (s), ν(C═N); 1559 (s), δ(N−H). ^{1}H NMR ($CDCl_3$, δ): 10.16 (s, br, 2H, NH), 2.58 (q, 7.5 Hz, 4H, C*H*$_2$), 0.89 (t, 7.5 Hz, 6H, C*H*$_3$) (*Et*). The compound is poorly soluble in the most common deuterated solvents, and this precluded ^{13}C{^{1}H} NMR measurements. ^{19}F NMR ($CDCl_3$, δ): −137.1 (t, J_{F-F} = 21 Hz), −139.9 (t, J_{F-F} = 20.2 Hz), −145.3 (t, J_{F-F} = 14.5 Hz), −147.2 (t, J_{F-F} = 21.8 Hz).

[Ni{*N*H═C(CCl$_3$)N═C(C$_6$F$_4$CO*N*)}$_2$]·1^1/$_2$H$_2$O (17). Anal. Calcd for $C_{20}H_5N_6Cl_6F_8NiO_3$: C, 29.70; H, 0.62; N, 10.39. Found: C, 29.97; H, 0.76; N, 9.78%. ESI$^+$-MS, *m*/*z*: 777 [Ni{*N*H═C(CCl$_3$)N═C(C$_6$F$_4$CO*N*)}$_2$ − F + H$_2$O]$^+$. IR (KBr, selected bands, cm^{-1}): 1721 (s), ν(C═O); 1608 (s), ν(C═N); 1563 (s), δ(N−H). ^{1}H NMR ($CDCl_3$, δ): 11.12 (s, br, 2H, NH). The compound is poorly soluble in the most common deuterated solvents, and this precluded ^{13}C{^{1}H} NMR measurements. ^{19}F NMR ($CDCl_3$, δ): −137.5 (t, J_{F-F} = 20.2 Hz), −140.1 (t, J_{F-F} = 20.2 Hz), −144.3 (t, J_{F-F} = 14.1 Hz), −148.2 (t, J_{F-F} = 22.0 Hz).

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Supporting Information Available: High-field region of the ^{1}H,^{13}C-HSQC spectrum of complex **11** (Figure S1), molecular structure of [Ni{*N*H═C(CCl$_3$)NC(CCl$_3$)═*N*H}$_2$] (Figure S2), and its IR and NMR data; crystallographic data in CIF format for complexes **16** and [Ni{*N*H═C(CCl$_3$)NC(CCl$_3$)═*N*H}$_2$]. This material is available free of charge via the Internet at http://pubs.acs.org.

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