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Intramolecular Nitrile C−H Bond Activation in Nickel NHC Complexes: A Route to New Nickelacycles

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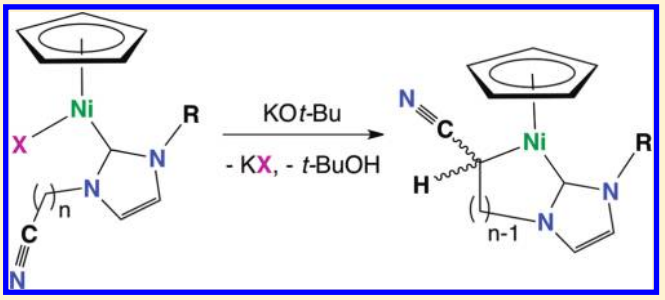
Supporting Information

ABSTRACT: Cyclopentadienyl N-heterocyclic carbene (NHC) nickel complexes of general formula [Ni(NHC)XCp] (NHC = 1-(propylnitrile)-3-methylimidazol-2-ylidene, 1-(2,4,6-trimethylphenyl)-3-(butylnitrile)imidazol-2-ylidene, 1-(2,4,6-trimethylphenyl)-3-(pentylnitrile)imidazol-2-ylidene, 1-(2,4,6-trimethylphenyl)-3-(hexylnitrile)imidazol-2-ylidene; X = Cl, Br, I; Cp = η^5-C_5H_5), which bear an alkylnitrile side chain attached to one of the nitrogen atoms of the NHC ring, were prepared by the direct reaction of nickelocene with the corresponding imidazolium salts (NHC·HX). The new complexes [Ni{Me-NHC-$(CH_2)_2$CN}ICp] (**1a**), [Ni{Mes-NHC-$(CH_2)_3$CN}ClCp] (**1b**), [Ni{Mes-NHC-$(CH_2)_4$CN}ICp] (**1c**), and [Ni{Mes-NHC-$(CH_2)_5$CN}BrCp] (**1d**) were obtained in good yields and were fully characterized by standard spectroscopic techniques and elemental analyses and, in the cases of **1a**,**b**, by single-crystal X-ray crystallography. Structural studies established their two-legged piano-stool geometry. The cationic derivatives [Ni{Mes-NHC-$(CH_2)_n$CN}(NCMe)Cp]$^+$ (**2b**−**d**; n = 3−5) were prepared from the reaction of their neutral homologues **1b**−**d** with KPF_6 in acetonitrile at room temperature. Upon treatment of the neutral complexes **1** or of the cationic compounds **2** with KO-*t*-Bu, a C−H bond α to the nitrile group in each molecule underwent a base-promoted C−H activation and the new nickelacyclic complexes [Ni{Me-NHC-CH_2CH(CN)}Cp] (**3a**) and [Ni{Mes-NHC-$(CH_2)_n$CH(CN)}Cp] (**3b**−**d**; n = 2−4) were obtained. All of these metallacycles contain Ni−C σ-bonds, and their synthesis generated a new asymmetric carbon center. The cyclic complexes **3** were fully characterized by ^{1}H and ^{13}C NMR spectroscopy, IR spectroscopy, and elemental analyses. The structures of complexes **3b** and **3d**, which contain six- and eight-membered metallacyclic rings, respectively, were determined by single-crystal X-ray diffraction studies. DFT studies, carried out to probe the mechanism of these cyclonickelation reactions, indicated that the mechanism of formation of these nickelacycles was similar to that observed for the formation of cyanomethyl ligands from coordinated acetonitrile. Nevertheless, the base deprotonation of an α-C−H ligand in a side arm, while thermodynamically comparable to that of a simultaneously coordinated acetonitrile ligand, is kinetically favored, and this leads to the formation of nickelacycles rather than cyanomethyl complexes in the case of the base-assisted activation of the cationic complexes **2**.



INTRODUCTION

Since the first isolation of a stable imidazol-2-ylidene as a free ligand,[1] N-heterocyclic carbenes (NHCs) have become an important class of ligands in organometallic chemistry.[2] The easy preparation and handling of their precursors and their high modularity, as well as their strong σ-donor properties,[3] which allow them to form strong NHC−metal bonds that prevent ligand dissociation,[4] have made them popular as supporting ligands in transition-metal catalysis.[2,5]

Nickel NHC systems offer significant potential advantages, including a lower cost and a reduced tendency to deposit metallic nanoparticles,[6] as compared to many noble metal NHC systems, but they have been less studied than palladium, ruthenium, or even rhodium NHC systems. Nevertheless, nickel NHC catalysts have now found applications in a vast number of organic transformations, including notably C−C cross-coupling reactions,[7−10] the amination of arylamines,[11] and [2 + 2 + 2] cycloadditions.[12] Moreover, nickel NHC complexes are capable of activating small molecules such as O_2[13] and CO_2,[14] as well as the fairly unreactive C−S and C−C bonds in sulfoxides[15] and organonitriles,[16] respectively.

We recently described the base-promoted C−H activation of a labile acetonitrile ligand on a nickel NHC center. This reaction results in the acetonitrile ligand formally losing a proton and doing a sharp flip to give a nickel cyanomethyl complex

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(Scheme 1).[17] Examples of C−H activation remain rare in nickel chemistry,[18,19] and it was of interest to attempt an intramolecular version of this reaction. Herein, we describe the synthesis of a series of cyclopentadienyl nickel NHC complexes [Ni(NHC)-XCp] (X = Cl, Br, I; Cp = η^5-C_5H_5) that bear an alkylnitrile side chain attached to one of the nitrogen atoms of the NHC ring and the subsequent activation of a C−H bond α to the nitrile group to give novel nickelacycles. Part of this work has been reported in a preliminary communication.[17]

RESULTS AND DISCUSSION

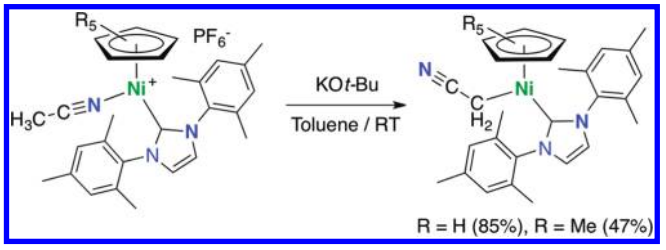
We recently described the synthesis of the labile acetonitrile cationic complexes $[Ni(Ar_2NHC)(CH_3CN)Cp]^+$, where Ar_2NHC = 1,3-diarylimidazol-2-ylidene. These species catalyze the Suzuki coupling of arylboronic acids with aryl halides without additional reductants and without the addition of triarylphosphine ligands.[7a] However, the lifetime of the catalytic species present in these reactions is not long, and this led us to explore the synthesis of hemilabile ligands that could conceivably coordinate to the metal when necessary, so as to stabilize any reactive intermediates. Imidazolium salts containing a nitrile functionality on a side chain were chosen to be presursors to hemilabile NHC ligands. Our recent report of the C−H activation of nickel-coordinated acetonitrile[17] led us to investigate the reactivity of the ligated NHC ligands with nitrile side chains toward this kind of reaction.

(a). Synthesis of the Imidazolium Salts. The complexes [Ni(NHC)XCp] we describe here were all prepared by reaction of the corresponding imidazolium salt with nickelocene. The synthesis of some of the imidazolium salts, namely 1-(2,4,6-trimethylphenyl)-3-(butylnitrile)imidazolium chloride (**b**)[17,20] and 1-(2,4,6-trimethylphenyl)-3-(hexylnitrile)imidazolium bromide (**d**),[21] has been reported in the literature. However, we synthesized salt **b** with an anion different from what was reported,[20] and experimental details of the synthesis of **b** were not given in the literature.[21] Furthermore, we could not obtain 1-(propylnitrile)-3-methylimidazolium iodide (**a**) by the method cited in the literature,[22] and 1-(2,4,6-trimethylphenyl)-3-(pentylnitrile)-imidazolium iodide (**c**) has not yet been described. Hence for these reasons, except for the synthesis of **b**,[17] full details of these syntheses are given in the Experimental Section. The iodide salt **a** was readily prepared by addition of iodomethane to 1-(propylnitrile)-1*H*-imidazole, as outlined in Scheme 2a. The mesityl-substituted imidazolium salts were prepared by reaction of 1-(2,4,6-trimethylphenyl)-1*H*-imidazole with the appropriate haloalkylnitrile in 1,2-dimethoxyethane at reflux. In the case of **c**, addition of potassium iodide allowed us to reduce the long reaction time usually required when reacting arylimidazoles with unreactive chloroalkyls (Scheme 2b).[17,23] All the organic salts were isolated as white or off-white hygroscopic solids in high yields.

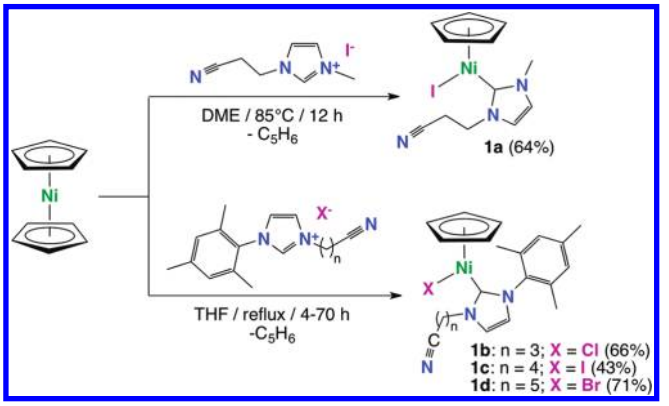
(b). Synthesis of the Neutral Complexes [Ni{R-NHC-$(CH_2)_n$CN}XCp]. The complexes [Ni{Me-NHC-$(CH_2)_2$CN}-ICp] (**1a**) and [Ni{Mes-NHC-$(CH_2)_n$CN}XCp] (**1b**, n = 3, X = Cl;[17] **1c**, n = 4, X = I; **1d**, n = 5, X = Br) bear a dangling alkylnitrile side arm on their NHC ligands and were obtained in respectable yield (43−71%) from the reaction of nickelocene and the imidazolium salts **a**−**d** by using the standard synthetic methods that were established for other Ni(NHC)Cp complexes with symmetrically substituted alkyl-[24] and aryl-NHC[25] ligands (Scheme 3). All complexes are dark red to violet air-stable compounds, which were fully characterized by ^{1}H and ^{13}C{^{1}H} NMR and IR spectroscopy and by CHN microanalysis.

The spectroscopic features of these complexes are typical of neutral [Ni(NHC)XCp] species previously characterized by us[24,25c] and others.[25a,b] The carbene carbon is observed in the 164−167 ppm range in the ^{13}C NMR spectrum, while the Cp carbon atoms appear at ca. 91−92 ppm, as is the case for the

Scheme 1. Base-Promoted C−H Activation of Coordinated CH_3CN[17]



Scheme 3. Preparation of the Neutral Ni-NHC Complexes 1a−d



Scheme 2. Preparation of the Imidazolium Salts a−d

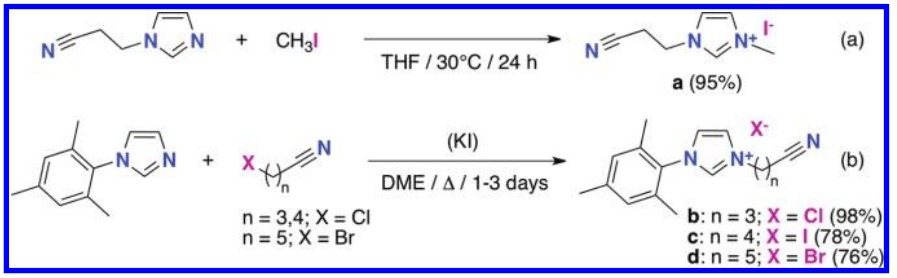


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Table 1. Selected Bond Lengths (Å) and Angles (deg) for Complexes 1a,b with Esd's in Parentheses

	1a (molecule A)	**1a** (molecule B)	**1b**
Ni−C1	1.884(6)	1.866(7)	1.882(3)
Ni−X[a]	2.5083(10)	2.4979(10)	2.2140(8)
C≡N3	1.145(12)	1.145(11)	1.098(5)
Ni−Cp_{cent}	1.775	1.748[b]	1.773
Ni−C_{Cp}: *av*, min, max	*2.126*, 2.102(8), 2.166(8)	*2.125*, 2.043(17), 2.170(17)[b]	*2.141*, 2.058(3), 2.175(3)
C_{Cp}−C_{Cp}: *av*, min, max	*1.375*, 1.335(16), 1.448(17)	*1.42*, 1.54(3), 1.27(3)[b]	*1.412*, 1.387(5), 1.439(5)
C1−Ni−X	93.4(2)	92.9 (2)	98.41(9)
C1−Ni−Cp_{cent}	134.1	135.8[b]	132.2
X−Ni−Cp_{cent}	132.2	131.2[b]	129.3

[a] **1a**, X = I; **1b**, X = Cl. [b] The Cp ring in molecule B is rotationally disordered over two equally populated sites, and the positional esd's are relatively large. The centroid is based on all 10 Cp carbon atoms.

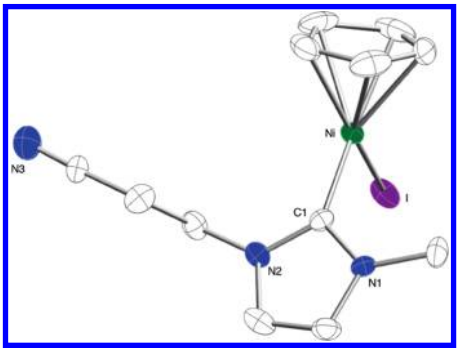


Figure 1. Molecular structure of **1a** showing all non-H atoms. Ellipsoids are shown at the 50% probability level, and key atoms are labeled. Only the molecule with the ordered Cp ligand (molecule A) is shown.

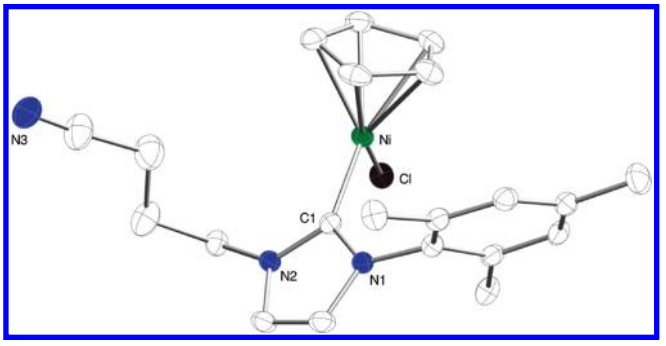


Figure 2. Molecular structure of **1b** showing all non-H atoms. Ellipsoids are shown at the 50% probability level, and key atoms are labeled.

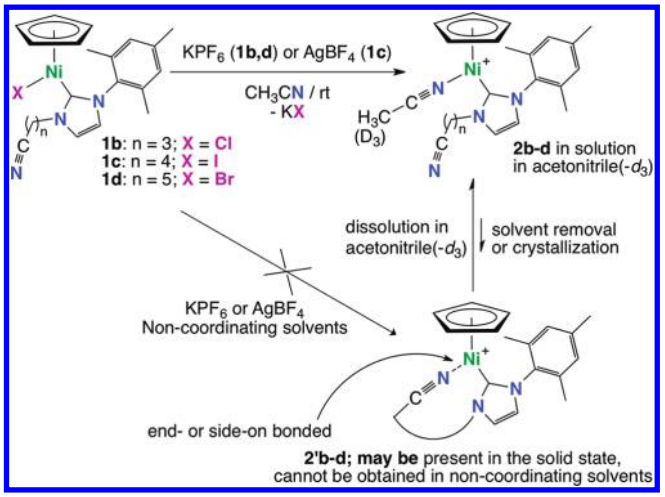
neutral symmetrically substituted complexes.[24,25] In the ^{1}H NMR spectrum of **1a**, the Cp protons resonate as a singlet in the same range as observed for the Cp protons of the only other known alkyl-substituted complex [NiCp(Me_2NHC)I] (Me_2NHC = 1,3-dimethylimidazol-2-ylidene),[24] at 5.3 ppm. The Cp protons of **1b**−**d** appear between 4.7 and 4.9 ppm and are slightly downfield of the signals seen between 4.5 and 4.6 ppm for [NiCp(Ar_2NHC)X] complexes that bear symmetrically substituted aryl-NHC ligands.[25] Complexes **1a,c**, which bear bulky iodide ligands, exhibit diastereotopic NCH_2 protons at ambient temperature and temperature-dependent ^{1}H NMR spectra that result from the restricted rotation about the mesityl−nitrogen, alkyl−nitrogen, and nickel−NHC bonds. Complex **1d**, which bears a bromide ligand, also shows broad signals at ambient temperature. Similar behavior has been observed previously in sterically congested [Ni(Ar_2NHC)Cl(η^5-C_5Me_5)] complexes and does not merit further comment.[24] Finally, ν(C≡N) stretches observed in the 2251−2239 cm^{-1} range in the IR spectra are at essentially the same frequencies as seen for the free imidazolium salts.

(c). Structural Studies of [Ni{Me-NHC-(CH_2)$_2$CN}ICp] (1a) and [Ni{Mes-NHC-(CH_2)$_3$CN}ClCp] (1b). The structures of **1a,b**, each containing an asymmetric NHC ligand with a functionalized side arm, were established by X-ray diffraction studies. Crystals suitable for X-ray structure determination were grown from dichloromethane/diethyl ether (**1a**) and toluene (**1b**) solutions. Crystallographic data and data collection and refinement parameters are grouped together in Table S1 (see the Supporting Information). Key bond lengths and bond angles for both molecules are collected in Table 1. Note that complex **1a** crystallizes in a noncentrosymmetric space group with two independent molecules (A and B) in the unit cell. These are almost related by a pseudo inversion center, but one of the two independent molecules exhibits some rotational disorder of the Cp ligand. Figure 1 shows the ordered molecule (molecule A) of **1a**; Figure 2 depicts the structure of complex **1b**.

Complexes **1a,b** have structures that are closely related to each other and to those established by us[7a,24] and others[25a,b] for similar [Ni(NHC)XCp$^+$] (X = Cl, I; Cp$^+$ = Cp, Cp*) complexes. In each case, a two-legged piano-stool geometry is adopted, with the nickel atoms at the center of a pseudo-trigonal-planar coordination geometry. The sum of the angles subtended at the nickel atom by the Cp ligand centroid, the halogen atom, and the carbene carbon atom of the NHC ligand is indeed almost exactly 360°. However, there are significant departures from the idealized 120° angles of a trigonal structure in both molecules (Table 1). The carbenoid carbon C(1) and the iodide atom I of **1a** subtend an angle of 93.4(2)° (molecule A) and of 92.9(2)° (molecule B) at the nickel atom. The carbenoid carbon C(1) and the chloride atom Cl of **1b** make a slightly larger angle of 98.4(9)° at the nickel atom. These values are in the range of those observed for the closely related symmetrically substituted iodo and chloro complexes [Ni(Me_2NHC)ICp][24] and [Ni(Mes_2NHC)ClCp] (Mes_2NHC = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene),[25a] for which values of 93.63(13) and 98.4(2)° have been determined, respectively.

The nickel−carbene carbon bond lengths are not significantly different from each other (Ni−C(1) = 1.884(6) Å (**1a**, molecule

Scheme 4. Preparation and Possible Structures of the Cationic Ni-NHC Complexes 2b−d and 2′ b−d



A), 1.866 (7) Å (**1a**, molecule B), 1.882(3) Å (**1b**)). These values are comparable to those reported for [Ni(Me$_2$NHC)ICp] (1.880(4) Å)[24] but are somewhat shorter than what is seen for [Ni(Mes$_2$NHC)ClCp] (1.917(9) Å).[25a] In contrast, the Ni−Cl distance of 2.2140(8) Å in **1b** is slightly longer than that reported for [Ni(Mes$_2$NHC)ClCp], where a value of 2.185(2) Å was observed.[25a] The Ni−I distances in molecules A and B of **1a** (2.5083(10) and 2.4979(10) Å) are in the same range as what was observed in [Ni(Me$_2$NHC)ICp] (2.5006(6) Å).[24]

In both structures, the Cp ring exhibits structural distortions, as there are significant variations in both the C−C and Ni−C distances (see Table 1). In addition, in the (nondisordered) molecule A of **1a**, the C−C−C angles in this ligand range from 104.1 to 111.2°; the internal angles of the Cp ligand in complex **1b** are much more regular (107.9 ± 0.8°). Similar distortions have been previously observed and studied in other Cp or Cp*Ni systems.[26]

The two independent molecules A and B of **1a** both exhibit short contacts between their respective nitrile nitrogen atoms and selected hydrogen atoms of a neighboring molecule: these include an N···H−C$_{Me}$ interaction of 2.617 Å and an N···H−C$_{CH_2CN}$ interaction of 2.515 Å. The other observed short N···H contacts of 2.406, 2.640, and 2.709 Å are with Cp hydrogen atoms. Similar interactions of a comparable magnitude are seen in **1b**, with a N···H−C$_{CH_2CN}$ distance of 2.611 Å and a N···H−C$_{Cp}$ distance of 2.676 Å.

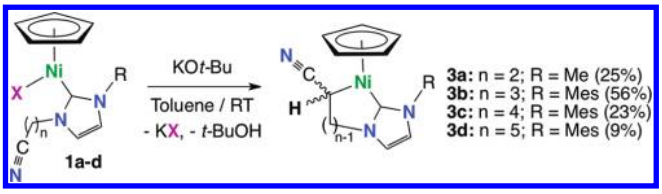
(d). Synthesis of the Cationic Complexes. Complexes **1b−d**, like their symmetric counterparts [Ni(Mes$_2$NHC)ClCp$^+$] without functionalized arms on the NHC ligands,[7a] react almost instantaneously with KPF_6 (**1b,d**) or $AgBF_4$ (**1c**) in acetonitrile at room temperature to give the corresponding halide-free cationic compounds **2b−d/2′b−d**, which were isolated as yellow solids (Scheme 4). We have reported that the bis-mesityl nickel NHC chloro complexes afford the cationic species [Ni(Mes$_2$NHC)(NCMe)Cp$^+$]$^+$, which contain an N-bound acetonitrile ligand.[7a] It was hoped that the nitrile-functionalized NHC ligands in complexes **1** would displace acetonitrile and act as hemilabile ligands with the nitrile group in the side chain coordinating to the nickel atom, either in a linear or in a π-fashion to afford new cyclic species. However, as discussed below, despite our efforts, we have been unable to clearly establish side arm coordination. Instead, it is acetonitrile and not the side arm nitrile group that appears to bind preferentially to the nickel center.

Complexes **2b−d/2′b−d** were characterized by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy in CD_3CN solution and by IR spectroscopy in the solid state. The ^{1}H and ^{13}C{^{1}H} NMR spectra of the cationic species are all well resolved in CD_3CN at ambient temperature and show the presence of one η^5-Cp group and the functionalized NHC ligand. However, no CH_3CN signals are observed. This is in contrast with NMR data observed for the cationic species [Ni(Ar$_2$NHC)(NCMe)Cp$^+$]$^+$, in which there is exchange of coordinated CH_3CN with CD_3CN, and where a signal for free CH_3CN is always seen.[7a] The possible existence of cyclic species in which there is coordination of the nitrile side arm to the nickel center cannot be excluded, especially in the solid state, but we have been unable to isolate such species or to have definitive evidence for their existence. Attempts to characterize **2b−d/2′b−d** in noncoordinating deuterated solvents such as $CDCl_3$ and CD_2Cl_2 resulted in their ready decomposition. Similarly, when complexes **1b−d** were reacted with KPF_6 or $AgBF_4$ in the absence of acetonitrile, no stable species could be characterized. IR spectra of solid samples of complexes **2b/2′b** and **2c/2′c** even suggest a lack of side arm coordination, as *weak* ν(C≡N) stretches for the alkylnitrile side arm at 2249 (**2b/2′b**) and 2248 cm^{-1} (**2c/2′c**) are seen at frequencies that are almost identical with the free imidazolium salt values. In addition, weak ν(C≡N) stretches, whose values are consistent with those reported for the acetonitrile ligands of the cationic symmetric species [Ni(Ar$_2$NHC)(NCMe)Cp$^+$]$^+$[7a] and for other Ni(II) N-bound acetonitrile complexes,[27] are observed for both complexes at 2294 (**2b/2′b**) and 2291 cm^{-1} (**2c/2′c**).[28] Nevertheless, no ν(C≡N) stretches were detected in the IR spectra of various solid samples of complexes **2d/2′d**, and despite repeated attempts, good microanalytical data could not be obtained for any of these complexes.

In summary, it seems reasonable that the N-bound acetonitrile complexes [Ni{Mes-NHC-(CH$_2$)$_n$CN}(NCMe)Cp]$^+$ (**2b−d**) are the predominant, if not the only species, present in acetonitrile solution. However, an equilibrium mixture of N-bound acetonitrile complexes **2b−d** and of end- or side-bonded nitrile cyclic species [Ni{Mes-NHC-(CH$_2$)$_n$CN}Cp]$^+$ (**2′b−d**) in the solid state cannot be excluded, in view of the poor elemental analysis obtained for these solids and of the absence of CH_3CN signals in the ^{1}H NMR spectra in CD_3CN.

(e). Base-Assisted C−H Activation of Complexes 1 and 2 To Afford Nickelacycles 3. Upon treatment of complexes **1a−d** with a suspension of potassium *tert*-butoxide in toluene, one of the methylene hydrogen atoms of the methylene group α to the nitrile functionality is abstracted, in what is effectively a base-assisted intramolecular C−H activation reaction.[17,29] The carbon atom α to the nitrile group forms a new σ-bond to the nickel atom to give the nickelacyclic complexes [Ni{Me-NHC−CH$_2$-CH(CN)}Cp] (**3a**) and [Ni{Mes-NHC-(CH$_2$)$_n$CH(CN)}Cp] (**3b**, n = 2;[17] **3c**, n = 3; **3d**, n = 4), which contain five- to eight-membered rings (Scheme 5). The new species were isolated as air-stable dark green to brown crystals in moderate to low yields, depending on the ring size. They were characterized by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy, by IR spectroscopy, and by elemental analysis.[30] The structures of **3b,d** were established by single crystal X-ray diffraction studies. It is noteworthy that complex **3b** could also be obtained in 47% isolated yield by activation of the cationic complex **2b/2′b** under similar reaction conditions. No acetonitrile activation was observed.

Scheme 5. Formation of Nickelacycles 3a−d by Base-Assisted Intramolecular C−H Activation of Neutral Complexes 1a−d



This reaction mirrors that observed for acetonitrile itself, in which the cationic complexes $[Ni\{Mes_2NHC\}(NCCH_3)Cp^+]^+$ are activated by potassium *tert*-butoxide to afford the cyanomethyl complexes $[Ni\{Mes_2NHC\}(CH_2CN)Cp^+]$ (Scheme 1).[17] In this reaction, the labile acetonitrile ligands have undergone a base-assisted C−H activation. However, in the reactions we now report, the activation reaction that leads to the metallacycles is intramolecular.

The new metallacyclic complexes have C_1 symmetry. The ^1H and $^{13}C\{^1H\}$ NMR spectra of the methyl-substituted complex **3a** at room temperature are straightforward and do not deserve any particular comment. All the signals are sharp and are easily assigned. The ^1H NMR spectra of the mesityl-substituted nickelacycles **3b−d** are, however, more complex, as (i) the two protons of each methylene group in the new ring are not isochronous with each other and (ii) the two *m*-hydrogens and the two *o*-methyl groups of the mesityl rings are observed, respectively, either as two singlets (**3b,d**) or as a broad signal (**3c**). In addition, the ^1H spectra of the large-ring complexes **3c,d** show broad peaks for the metallacyclic methylene protons. Whereas the nonequivalence of the *o*- and *m*-mesityl ring groups most probably results from the restricted rotation about the mesityl−nitrogen bond, similar to what has been observed for the sterically congested $[Ni(Ar_2NHC)ClCp^*]$ complexes,[24] the broad signals observed for the methylene protons of **3c,d** are likely due to the stereochemically nonrigid and floppy nature of the metallacyclic rings present in both complexes. In contrast, the complexes with smaller ring sizes (**3a,b**) exhibit sharp ^1H NMR spectra.

The carbene carbon atoms of the cyclic complexes **3a−d** appear in the 171−177 ppm range in their ^{13}C NMR spectrum in $CDCl_3$. These signals are downfield of the signals seen for their corresponding carbon atoms in the 164−167 ppm range (in $CDCl_3$) for their neutral acyclic precursors **1a−d** and at 159−158 ppm (in CD_3CN) for their cationic precursors **2b−d/2′b−d**. This may indicate increased π-back-donation from the more electron-rich nickel atoms in the cyclic complexes **3a−d** as compared to their acyclic precursors **1** and **2**.[31] The *C*HCN carbon atoms attached to the nickel atom in **3a−d** exhibit large negative chemical shifts between −11.6 and −25.2 ppm, as seen for the CH_2CN methylene carbon atoms in the cyanomethyl complexes $[Ni\{Mes_2NHC\}(CH_2CN)Cp^+]$.[17]

In the IR spectra of the nickelacyclic species, strong $\nu(C{\equiv}N)$ stretches are now observed at 2179 (**3a**), 2181 (**3b**), and 2176 cm^{-1} (**3c**): i.e., at frequencies similar to those observed for the cyanomethyl complexes.[17] This shift to lower frequencies from ca. 2245 cm^{-1} in the acyclic precursors **1** and **2** indicates a decrease in the C≡N bond order, which is most likely due to electron donation from the metal center.

(f). Structural Studies of [Ni{Mes-NHC-$(CH_2)_2$CH(CN)}Cp] (3b)[17] and [Ni{Mes-NHC-$(CH_2)_4$CH(CN)}Cp] (3d). The structures of metallacycles **3b,d** were established by X-ray diffraction studies (the structure of **3b** was reported in the Supporting Information of the preliminary communication but has not been discussed).[17] Crystals of **3d** suitable for an X-ray structure determination were grown from a thf solution at room temperature. Crystallographic data and data collection and refinement parameters are grouped with those of complexes **1a** and **1b** in Table S1 (see Supporting Information). Geometrical parameters for both metallacycles are given in Table 2. The molecular structures of **3b,d** are shown in Figures 3 and 4 respectively.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complexes 3b[17] and 3d with Esd's in Parentheses

	3b[17]	3d
Ni−C1	1.8560(19)	1.866(4)
Ni−C2	1.9718(19)	1.987(6)
C1−N1	1.372(3)	1.362(5)
C1−N2	1.351(2)	1.360(5)
C2−C3	1.438(3)	1.446(7)
C3≡N3	1.143(3)	1.127(6)
$Ni-Cp_{cent}$	1.768	1.765
$Ni-C_{Cp}$: *av*,	*2.133*, 2.096(2),	*2.123*, 2.079(6),
min, max	2.160(2)	2.156(5)
$C_{Cp}-C_{Cp}$: *av*,	*1.405*, 1.380(16),	*1.386*, 1.315(8),
min, max	1.433(4)	1.452(10)
C1−Ni−C2	93.95(8)	90.1(3)
$C1-Ni-Cp_{cent}$	135.9	137.2
$C2-Ni-Cp_{cent}$	130.0	132.5
NHC/mesityl angle[a]	76.9	91.0
Σ(angles at Ni)	359.9	359.8

[a] Defined as the best least-squares plane between the five atoms of the NHC imidazolylidene ligand and the six aromatic carbon atoms of the mesityl group.

Complex **3b** adopts a two-legged piano-stool geometry with the nickel atom attached to a η^5-C_5H_5 group and to two carbon atoms, which form part of a new six-membered NiC_3NC ring. The ring results from the hydrogen abstraction from the methylene group α to the nitrile group, and it adopts a twisted-boat conformation; the aft and stern positions are occupied by the nickel atom and by the carbon atom that is attached to the NHC nitrogen atom. Complex **3d** has a similar structure but contains a puckered eight-membered ring. In both structures, the bite angles of the metallacycle α-carbon atoms subtended at the nickel atom are close to 90° (94 and 90° for **3b,d**, respectively). This is in line with values observed with the C−Ni−X angles observed in acyclic [Ni(NHC)XCp] complexes, where X is a halogen[24,25a,25b] such as in **1a,b** (vide supra and Table 1) or an N-bound acetonitrile ligand.[7a,17]

The nickel−carbene carbon bond lengths are not significantly different from each other (Ni−C(1) = 1.8560(19) Å (**3b**), 1.866(4) Å (**3d**)) and are comparable to those observed for **1a,b** (Table 1). The Ni−C2 distances in the metallacycles **3b,d** (1.9718(19) and 1.987(6) Å) are in the same range as that observed for the Ni−CH_2CN bond in $[Ni\{Mes_2NHC\}(CH_2CN)Cp]$.[17]

Both complexes display asymmetry in their $Ni-C_{Cp}$ and $C_{Cp}-C_{Cp}$ distances, but the distortions are somewhat more pronounced in complex **3d**.[26] Both complexes also exhibit short CN···H intermolecular contacts, and in each case, the nitrile

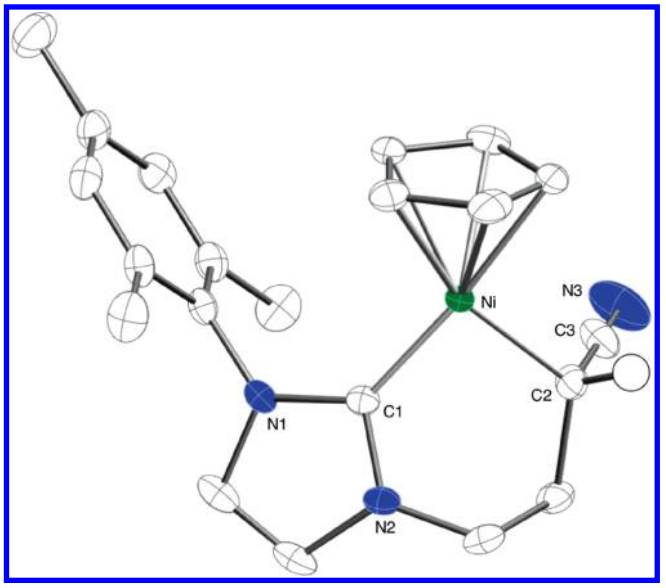


Figure 3. Molecular structure of **3b**.[17] The only hydrogen atom shown is that of the C*H*CN group (as a white isotropic sphere). Ellipsoids are shown at the 50% probability level, and key atoms are labeled.

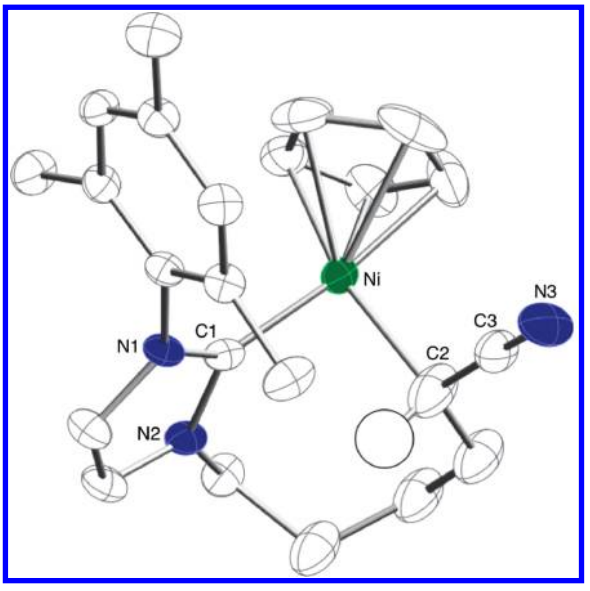


Figure 4. Molecular structure of **3d**. The only hydrogen atom shown is that of the C*H*CN group (as a white isotropic sphere). Ellipsoids are shown at the 50% probability level, and key atoms are labeled.

nitrogen atom interacts with two hydrogen atoms; distances of 2.531 Å for an NHC ligand hydrogen atom and of 2.691 Å for a mesityl hydrogen atom are observed in **3b**, while values of 2.667 and 2.588 Å, respectively, are seen for an NHC hydrogen atom and for a methylene hydrogen atom that is α to the NHC nitrogen atom in **3d**.

It is noteworthy that the annelation reaction leads to the generation of a new stereocenter, at the α-carbon, attached to the nickel atom, but nevertheless polarimetric studies indicate that a racemic mixture was obtained.

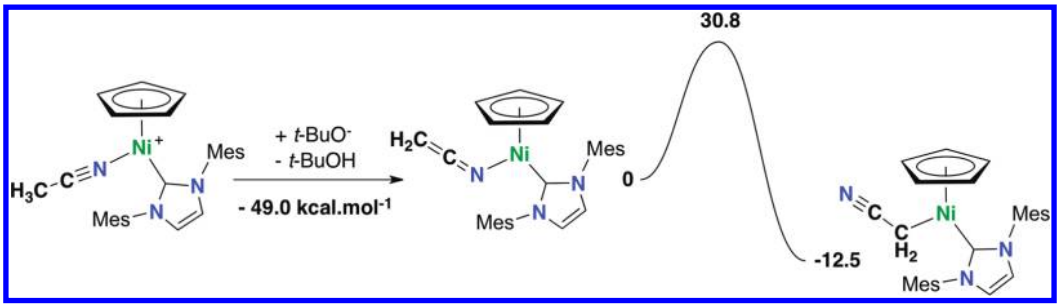
(g). Density Functional Theory (DFT) Studies. *C−H Activation of [Ni{Mes$_2$NHC}(NCCH$_3$)Cp]$^+$. Nickel N-Bound Acetonitrile Activation.* DFT calculations on the base-assisted activation of [Ni(Mes$_2$NHC)(NCCH$_3$)Cp]$^+$ have already been reported but are summarized here, since the results are pertinent to this study and more complete studies have probed the energy profile of the second step.[17] These calculations suggest that the reaction takes place via a one-step acid−base mechanism to give the deprotonated acetonitrile ligand H$_2$C═C═N, which is N-bound to the nickel atom (ΔE = −49.9 kcal mol^{-1}). This species then rearranges in a one-step process (with an activation energy of 30.8 kcal mol^{-1}) to give the final cyanomethyl complex, with a net energy gain of 12.5 kcal mol^{-1} (Scheme 6).[32]

*C−H Activation of the Complex [Ni{Mes-NHC-(CH$_2$)$_3$CN}-(NCCH$_3$)Cp]$^+$ (**2b**). Acetonitrile versus Side-Arm Nitrile C−H Activation.* The activation of the cationic N-bound acetonitrile complex [Ni{Mes-NHC-(CH$_2$)$_3$CN}(NCCH$_3$)Cp]$^+$ (**2b**) was also probed by DFT in order to compare activation of the coordinated acetonitrile ligand to that of the alkylnitrile side arm. The results show that the direct deprotonation of the side arm is energetically favorable (ΔE = −34.2 kcal.mol^{-1}) but is a "dead end", as no pathway from this neutral deprotonated species (Scheme 7) to the cyclic product **3b** could be unveiled by the calculations.

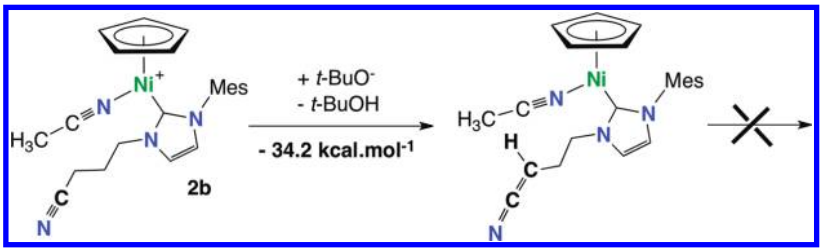
A more likely pathway is deprotonation of the coordinated acetonitrile to give the neutral H$_2$C═C═N−Ni species shown in Scheme 8 (ΔE = −51.6 kcal mol^{-1}). This species than could rearrange to give the neutral cyanomethyl complex [Ni{Mes-NHC-(CH$_2$)$_3$CN}(CH$_2$CN)Cp] (ΔE = −10.6 kcal mol^{-1}), in which the acetonitrile and not the side-arm nitrile C−H bond has been activated. The energy barrier calculated for this reaction (30.8 kcal mol^{-1}) is identical with that obtained for the bis-mesityl NHC complex [Ni{Mes$_2$NHC}(NCCH$_3$)Cp]$^+$ (Scheme 6).[17] Nevertheless, starting from compound **2b**/**2′b**, the complex resulting from acetontrile activation has never been observed. In other words, in what is essentially a competition experiment between acetonitrile and side-arm nitrile C−H activation, it is the latter that overwhelmingly predominates to give complex **3b**.

The calculations suggest that the most likely (lowest energy) pathway from **2b** to **3b** results from initial acetonitrile ligand dissociation to create a vacant coordination site at the nickel. This first step is rather facile, with an energy barrier of 24.3 kcal mol^{-1}. The side-arm nitrile ligand would then bind to the nickel atom first in a linear and then in a π-fashion to give successively the complexes **2′b-i** and **2′b-ii** (Scheme 9). This rearrangement of the coordination mode of the nitrile in the side arm has a negligible energy barrier (2.1 kcal mol^{-1}). Deprotonation of an α-C−H from the π-bound nitrile ligand would now be highly favored, to give the neutral π-bound cyclic species **4**. Finally, this species could rearrange to give the observed final product **3b** with a new Ni−C bond. This final rearrangement has a barrier 11.3 kcal mol^{-1} lower than that calculated for the slippage from N- to C-coordination of an independent CH$_2$CN ligand (Schemes 6 and 8). In the case of the cyclic system, the geometry constraint imposed by the metallacycle ring forces the intermediate **4** to be in a conformation that is closer to the final product, and thus, the reaction is easier to achieve here than in the case of an isolated CH$_2$CN ligand, where such a constraint is absent. Energetically, the final products that result from acetonitrile and side-arm C−H activation are comparable. Nevertheless, the metallacyclic product is obtained for kinetic reasons, as the final rearrangement step has a significantly lower energy barrier. In addition, these results tend to corroborate our earlier assumption based on the spectroscopic characterization of compound **2b**/**2′b** that the

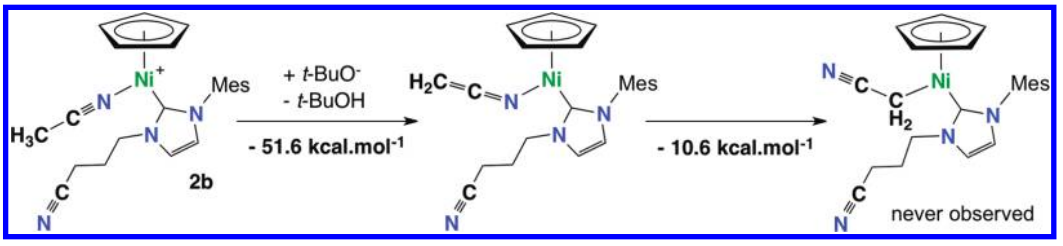
Scheme 6. Energetics of the Base-Assisted Activation of $[Ni(Mes_2NHC)(NCCH_3)Cp]^+$ To Give the Observed Cyanomethyl Complex[17]



Scheme 7. Deprotonation of the Nitrile Side Arm, Leading to a "Dead End"



Scheme 8. Energetics for the Deprotonation of an Acetonitrile C−H Bond in Complex 2b



N-bound acetonitrile complex $[Ni\{Mes\text{-}NHC\text{-}(CH_2)_3CN\}(NCMe)Cp]^+$ (**2b**) may be in equilibrium with the cyclic species $[Ni\{Mes\text{-}NHC\text{-}(CH_2)_3CN\}Cp]^+$ with an N- or π-bound side-arm nitrile ligand (**2′b-i** and **2′b-ii** in Scheme 9).

CONCLUSION

A series of half-sandwich nickel complexes, which contain NHC ligands that bear $-(CH_2)_nCN$ ($n = 2-5$) functionalities as side arms, have been prepared in moderate to high yield. These species can be isolated both as neutral halo complexes and as cationic compounds. The latter species probably exist as equilibrium mixtures between N-bound acetonitrile complexes $[Ni\{Mes\text{-}NHC\text{-}(CH_2)_nCN\}(NCMe)Cp]^+$ and end or side-on bonded alkylnitrile cyclic species $[Ni\{Mes\text{-}NHC\text{-}(CH_2)_3\text{-}CN\}Cp]^+$. The base-promoted C−H activation reaction that was previously observed for coordinated acetonitrile and that gave the corresponding cyanomethyl compounds[17] can be extended to these complexes. Treatment of the neutral or the cationic complexes with potassium *tert*-butoxide results in nickelacyclic complexes with five-, six-, seven-, or eight-membered rings in which a new asymmetric carbon center has been created (as a racemic mixture). The mechanism of this reaction has been probed by DFT studies. The calculations indicate that the reaction mechanism is a similar deprotonation reaction, but in contrast to the acetonitrile reaction, π-coordinated species are likely intermediates that facilitate the final rearrangement step.

EXPERIMENTAL SECTION

General Consideration. All reactions were carried out using standard Schlenk techniques under an atmosphere of dry argon. Solvents were distilled from appropriate drying agents under argon prior to use. Solution NMR spectra were recorded on FT-Bruker Ultra Shield 300 and FT Bruker-Spectrospin 400 spectrometers operating at 300.13 or 400.14 MHz for ^1H and at 75.47 or 100.61 MHz for $^{13}C\{^1H\}$. DEPT ^{13}C spectra were recorded for all compounds to help in the ^{13}C signal assignments. The chemical shifts are referenced to the residual deuterated solvent peaks. Chemical shifts (δ) and coupling constants (J) are expressed in ppm and Hz, respectively. IR spectra of solid samples of compounds **c**, **d**, **1a**, and **3a,c** were recorded on a FT-IR Nicolet 380 spectrometer equipped with a germanium SMART Omni-Sampler ATR or a diamond SMART iTR ATR. IR spectra of solid samples of compounds **1c,d** and **2b−d** were recorded on a FT-IR Nicolet 380 spectrometer with KBr pellets. Vibrational frequencies are expressed in cm^{-1}. Elemental analyses were performed by the Service d'Analyses, de Mesures Physiques et de

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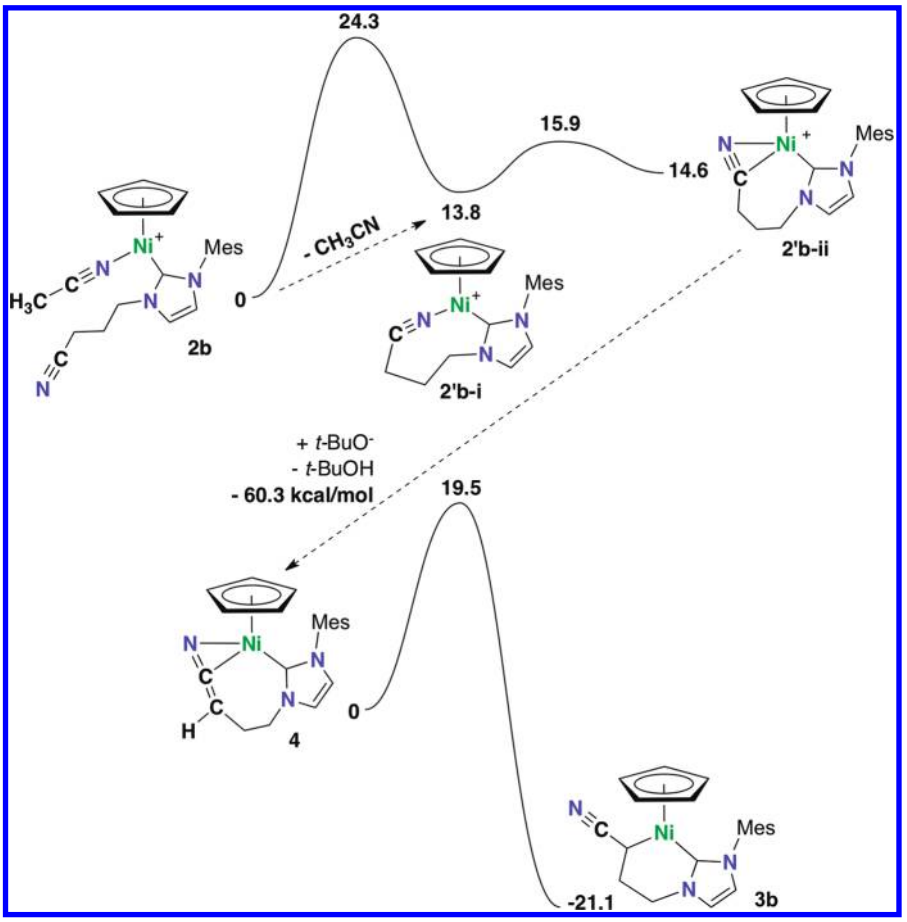
Scheme 9. Energetics for the Conversion of Complex 2b into Metallacycle 3b



Spectroscopie Optique, UMR CNRS 7177, Institut de Chimie, Université de Strasbourg. Commercial compounds were used as received. 1-(Propylnitrile)-1*H*-imidazole,[33] 1-(2,4,6-trimethylphenyl)-1*H*-imidazole,[34] 1-(2,4,6-trimethylphenyl)-3-(butylnitrile)imidazolium chloride (**b**),[17] [Ni{Mes-NHC-$(CH_2)_3$CN}ClCp] (**1b**),[17] and [Ni{Mes-NHC-$(CH_2)_2$CHCN}-Cp] (**3b**) (from **1b**),[17] were prepared according to published methods. 1-(Propylnitrile)-3-methylimidazolium iodide (**a**) could not be obtained via published methods[22] and was thus prepared by a modified procedure.

Synthesis of 1-(Propylnitrile)-3-methylimidazolium Iodide (a). A solution of 1-(propylnitrile)-1*H*-imidazole (1.11 g, 9.2 mmol) and iodomethane (0.62 mL, 10.0 mmol) in DME (20 mL) was stirred at 60 °C for 20 h. The resulting biphasic mixture was cooled to room temperature, and excess iodomethane and solvent were removed by syringe. The solid residue was washed with toluene (4 × 10 mL) and dried under vacuum for 2 h to afford **a** as a white solid (2.36 g, 9.0 mmol, 98%). ^{1}H NMR (D_2O, 298 K, 300.13 MHz): δ 8.91 (s, 1H, NC*H*N); 7.61 (t, 1H, NC*H*, ^3J = 1.5); 7.52 (t, 1H, NC*H*, ^3J = 1.5); 4.58 (t, 2H, NCH_2, ^3J = 6.3); 3.93 (s, 3H, Me); 3.17 (t, 2H, CH_2CN, ^3J = 6.3).

Synthesis of 1-(2,4,6-Trimethylphenyl)-3-(pentylnitrile)-imidazolium Iodide (c). A suspension of 1-(2,4,6-trimethylphenyl)-1*H*-imidazole (1.449 g, 7.78 mmol), 5-chloropentanenitrile (2.0 mL, 17.8 mmol), and KI (1.970 g, 11.9 mmol) in DME (20 mL) was vigorously stirred at 80 °C for 22 h. The brown reaction mixture was cooled to room temperature and the solvent removed under vacuum. The brown residue was extracted with acetonitrile (15 mL) and the extract filtered through Celite. This was rinsed with acetonitrile (20 mL) until the washings were colorless. Evaporation of the solvent followed by addition of DME (3 mL) to the resulting brown oil allowed crystallization of a white solid after 5 h at −18 °C. The solid was filtered, washed with DME (2 × 2 mL), and dried in vacuo to give **c** as a white solid (2.402 g, 6.08 mmol, 78%). Anal. Calcd for $C_{17}H_{22}N_3I$: C, 51.65; H, 5.61; N, 10.63. Found: C, 51.23; H, 5.32; N, 10.64. ^{1}H NMR ($CDCl_3$, 298 K, 300.13 MHz): δ 9.94 (s, 1H, NC*H*N); 8.11 (t, 1H, NC*H*, ^3J = 1.7); 7.20 (t, 1H, NC*H*, ^3J = 1.7); 6.99 (s, 2H, *m*-H); 4.79 (t, 2H, NCH_2, ^3J = 7.5); 2.55 (t, 2H, CH_2CN, ^3J = 7.1); 2.32 (s, 3H, *p*-Me); 2.23 (m, 2H, CH_2); 2.06 (s, 6H, *o*-Me); 1.83 (m, 2H, CH_2). ^{13}C{^{1}H} NMR ($CDCl_3$, 298 K, 75.47 MHz): δ 141.6 (*p*-C_{Ar} or *ipso*-C_{Ar}); 137.1 (NCHN); 134.2 (*o*-C_{Ar}); 130.6 (*ipso*-C_{Ar} or *p*-C_{Ar}); 130.0 (*m*-C_{Ar}); 123.8 and 123.5 (CH═CH); 119.5 (CN); 49.3 (NCH_2); 29.7 (CH_2); 22.1 (CH_2); 21.2 (*p*-Me); 17.9 (*o*-Me); 17.1 (CH_2). IR (ATR-Ge): ν(C_{sp^2}—H) 3104 (w), 3053 (m); ν(C_{sp^3}—H) 2967 (m), 2941 (m); ν(CN) 2247 (w).

Synthesis of 1-(2,4,6-Trimethylphenyl)-3-(hexylnitrile)-imidazolium Bromide (d). A solution of 1-(2,4,6-trimethylphenyl)-1*H*-imidazole (1.126 g, 6.05 mmol) and 6-bromohexanenitrile (95%; 1.2 mL, 8.60 mmol) in DME (20 mL) was refluxed for 22 h, affording a yellow suspension that was cooled to room temperature and filtered. The resulting solid was washed with DME (2 × 1 mL) and dried in vacuo to give **d** as white crystals (1.673 g, 4.62 mmol, 76%). Anal. Calcd for $C_{18}H_{24}N_3Br$: C, 59.67; H, 6.68; N, 11.60. Found: C, 59.40; H, 6.77; N, 11.66. ^{1}H NMR ($CDCl_3$, 298 K, 300.13 MHz): δ 10.25 (s, 1H, NC*H*N); 8.10 (t, 1H, NC*H*, ^3J = 1.5); 7.17 (t, 1H, NC*H*, ^3J = 1.5); 6.95 (s, 2H, *m*-H); 4.72 (t, 2H, NCH_2, ^3J = 7.2); 2.38 (t, 2H, CH_2CN, ^3J = 6.9); 2.29 (s, 3H, *p*-Me); 2.10 (m, 2H, CH_2); 2.02 (s, 6H, *o*-Me); 1.73 (m, 2H, CH_2); 1.54 (m, 2H, CH_2). ^{13}C{^{1}H} NMR ($CDCl_3$, 298 K, 75.47 MHz): δ 141.3 (*p*-C_{Ar} or *ipso*-C_{Ar}); 137.8 (NCHN); 134.2 (*o*-

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C_{Ar}); 130.7 (*ipso*-C_{Ar} or *p*-C_{Ar}); 129.9 (*m*-C_{Ar}); 123.5 and 123.3 (*C*H=*C*H); 119.7 (CN); 49.7 (NCH_2); 29.7 (CH_2); 25.0 (CH_2); 24.6 (CH_2); 21.1 (*p*-Me); 17.7 (*o*-Me); 17.1 (CH_2). IR [ATR-Ge]: $\nu(C_{sp2}-H)$ 3131 (w), 3056 (m); $\nu(C_{sp3}-H)$ 2939 (m), 2869 (w); ν(CN) 2243 (w).

Synthesis of [Ni{Me-NHC-(CH$_2$)$_2$CN}ICp] (1a). Nickelocene (152 mg, 0.805 mmol) and 1-(propylnitrile)-3-methylimidazolium iodide (**a**; 212 mg, 0.806 mmol) were heated in DME (10 mL) at 85 °C for 12 h. The solvent was then removed in vacuo, the residue was extracted with CH_2Cl_2 (10 mL), and the extract was filtered through Celite. This was rinsed with toluene until the washings were colorless, and CH_2Cl_2 was evaporated. Chromatography on silica (12 × 3 cm) using an ethyl acetate/pentane/NEt_3 (80/15/5) mixture as eluent followed by crystallization from CH_2Cl_2/pentane (1/3) at −28 °C then gave **1a** as dark red needles (200 mg, 0.518 mmol, 64%). Anal. Calcd for $C_{12}H_{14}N_3NiI$: C, 37.35; H, 3.66; N, 10.89. Found: C, 37.18; H, 4.04; N, 10.81. ^{1}H NMR ($CDCl_3$, 298 K, 300.13 MHz): δ 7.15 (s, 1H, NC*H*); 7.01 (s, 1H, NC*H*); 5.36 (s, 5H, C_5H_5); 5.15 (m, 1H, NCH_2); 4.71 (m, 1H, NCH_2); 4.19 (s, 3H, Me); 3.25 (m, 2H, CH_2CN). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 298 K, 75.47 MHz): δ 167.3 (NCN); 124.6 and 122.6 (NCH); 117.5 (CN); 92.0 (C_5H_5); 47.9 (NCH_2); 39.8 (CH_3); 19.6 (CH_2CN). IR (ATR-C): $\nu(C_{sp2}-H)$ 3155 (m), 3119 (m), 3101 (m); $\nu(C_{sp3}-H)$ 2980 (w), 2945 (m), 2921 (m); ν(CN) 2251 (m).

Synthesis of [Ni{Mes-NHC-(CH$_2$)$_4$CN}ICp] (1c). Nickelocene (830 mg, 4.39 mmol) and 1-(2,4,6-trimethylphenyl)-3-(pentylnitrile)-imidazolium iodide (**c**; 1.333 g, 3.37 mmol) were refluxed for 70 h in thf (20 mL). The solution slowly turned from dark green to purple-red. The solvent was then removed in vacuo, the residue was extracted with hot toluene (10 mL), and the extract was filtered through Celite. This was rinsed with toluene until the washings were colorless. The resulting purple-red solution was then concentrated under vacuum to 2−3 mL and allowed to stand at −28 °C for a couple of hours to afford **1c** as a violet powder (750 mg, 1.45 mmol, 43%) that was washed with pentane (3 × 2 mL) and dried under vacuum. Anal. Calcd for $C_{22}H_{26}N_3NiI$: C, 51.00; H, 5.06; N, 8.11. Found: C, 51.09; H, 5.30; N, 7.96. ^{1}H NMR ($CDCl_3$, 243 K, 400.14 MHz): δ 7.20 (s, 1H, NC*H*); 7.16 (s, 1H, *m*-H); 7.01 (s, 1H, *m*-H); 6.91 (s, 1H, NC*H*); 5.25 (m, 1H, NCH_2); 4.86 (s, 5H, C_5H_5); 4.68 (m, 1H, NCH_2); 2.57 (m, 2H, CH_2CN); 2.46 (s, 3H, *o*-Me); 2.42 (s, 3H, *p*-Me); 2.19 (m, 2H, CH_2); 1.86 (m, 2H, CH_2); 1.75 (s, 3H, *o*-Me). ^{1}H NMR ($CDCl_3$, 298 K, 400.14 MHz): δ 7.17 (d, 1H, NC*H*, ^3J = 1.6); 7.07 (b, 2H, *m*-H); 6.88 (d, 1H, *m*-H, ^3J = 1.6); 5.19 (vb, 1H, NCH_2); 4.88 (s, 5H, C_5H_5); 4.79 (vb, 1H, NCH_2); 2.52 (b, 2H, CH_2CN); 2.42 (vb, 3H, *o*-Me); 2.42 (s, 3H, *p*-Me); 2.23 (b, 2H, CH_2); 1.85 (m, 2H, CH_2); 1.77 (s, 3H, *o*-Me). ^{1}H NMR ($CDCl_3$, 333 K, 400.14 MHz): δ 7.18 (s, 1H, NC*H*); 7.07 (s, 2H, *m*-H); 6.88 (s, 1H, *m*-H); 5.00 (b, 2H, NCH_2); 4.90 (s, 5H, C_5H_5); 2.52 (m, 2H, CH_2CN); 2.42 (s, 3H, *p*-Me); 2.26 (m, 2H, CH_2); 2.13 (vb, 6H, *o*-Me); 1.89 (m, 2H, CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 298 K, 75.47 MHz): δ 167.6 (NCN); 139.4 and 136.8 (*ipso*-/*p*-C_{Ar}); 129.4 (b, *m*-C_{Ar}); 124.9 and 122.4 (NCH); 119.5 (CN); 92.0 (C_5H_5); 52.8 (NCH_2); 29.8 (CH_2); 22.9 (CH_2); 21.3 (*p*-Me); 17.4 (CH_2CN). IR (KBr): $\nu(C_{sp2}-H)$ 3169 (m), 3149 (m), 3116 (m), 3091 (m); $\nu(C_{sp3}-H)$ 2942 (s), 2927 (s), 2868 (m); ν(CN) 2247 (m).

Synthesis of [Ni{Mes-NHC-(CH$_2$)$_5$CN}BrCp] (1d). Nickelocene (152 mg, 0.805 mmol) and 1-(2,4,6-trimethylphenyl)-3-(hexylnitrile)imidazolium bromide (**d**; 280 mg, 0.773 mmol) were refluxed for 20 h in thf (10 mL). The solution color progressively turned from dark green to purple-red. The solvent was then removed in vacuo, the residue was extracted with hot toluene (10 mL), and the extract was filtered through Celite. This was rinsed with toluene until the washings were colorless. The resulting purple-red solution was then concentrated to dryness and recrystallized from an acetone/pentane mixture to afford **1d** as a violet powder (264 mg, 0.545 mmol, 71%) that was washed with pentane (3 × 2 mL) and dried under vacuum. Anal. Calcd for $C_{23}H_{28}N_3NiBr$: C, 56.95; H, 5.82; N, 8.66. Found: C, 56.31; H, 5.82; N, 8.52. ^{1}H NMR ($CDCl_3$, 298 K, 300.13 MHz): δ 7.16 (d, 1H, NC*H*, ^3J = 1.7); 7.07 (bs, 2H, *m*-H); 6.86 (d, 1H, *m*-H, ^3J = 1.7); 5.02 (b, 2H, NCH_2); 4.78 (s, 5H, C_5H_5); 2.45 (t, 2H, CH_2CN, ^3J = 6.6); 2.42 (s, 3H, *p*-Me); 2.24−1,99 (vb, 8H, CH_2 and *o*-Me); 1.83 (m, 2H, CH_2); 1.68 (m, 2H, CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 298 K, 75.47 MHz): δ 164.1 (NCN); 139.2 and 136.8 (*ipso*-/*p*-C_{Ar}); 135.9 (b, *o*-C_{Ar}); 129.2 (*m*-C_{Ar}); 124.1 and 122.4 (*C*H=*C*H); 119.6 (CN); 91.8 (C_5H_5); 52.2 (NCH_2); 30.2 (CH_2); 25.9 (CH_2); 25.1 (CH_2); 21.3 (*p*-Me); 18.7 (b, *o*-Me); 17.3 (CH_2CN). IR (KBr): $\nu(C_{sp2}-H)$ 3150 (m), 3117 (m), 3091 (m); $\nu(C_{sp3}-H)$ 2946 (s), 2927 (s), 2916 (w), 2863 (m); ν(CN) 2239 (m).

Synthesis of [Ni{Mes-NHC-(CH$_2$)$_3$CN}(NCMe)Cp]$^+$PF$_6^-$ (2b)/[Ni{Mes-NHC-(CH$_2$)$_3$CN}Cp]$^+$PF$_6^-$ (2′b). KPF_6 (211 mg, 1.15 mmol) was added to a solution of **1b** (468 mg, 1.13 mmol) in acetonitrile (10 mL). The color changed instantaneously from violet to dark yellow. After 45 min, the reaction medium was filtered through Celite and concentrated to dryness. Crystallization from an acetonitrile/toluene mixture then afforded **2b**/**2′b** as a yellow solid that was washed with diethyl ether (3 × 2 mL) and dried under vacuum (458 mg, 0.813 mmol, 72%). ^{1}H NMR (CD_3CN, 298 K, 300.13 MHz): δ 7.52 (d, 1H, NC*H*, ^3J = 2.0); 7.22 (d, 1H, NC*H*, ^3J = 2.0); 7.16 (s, 2H, *m*-H); 5.01 (s, 5H, C_5H_5); 4.78 (t, 2H, NCH_2, ^3J = 7.4); 2.61 (t, 2H, CH_2CN, ^3J = 6.9); 2.41 (s, 3H, *p*-Me); 2.38 (m, 2H, CH_2); 1.99 (s, 6H, *o*-Me). $^{13}C\{^1H\}$ NMR (CD_3CN, 298 K, 75.47 MHz): δ 159.1 (NCN); 140.7 and 137.1 (*ipso*-/*p*-C_{Ar}); 136.5 (*o*-C_{Ar}); 130.2 (*m*-C_{Ar}); 126.8 and 125.0 (NCH); 120.5 (CH_2CN); 93.9 (C_5H_5); 51.3 (NCH_2); 27.3 (CH_2); 21.2 (*p*-Me); 18.1 (*o*-Me); 15.3 (CH_2CN). IR (KBr): $\nu(C_{sp2}-H)$ 3176 (m), 3147 (m); $\nu(C_{sp3}-H)$ 2957 (m), 2925 (m), 2862 (w); ν(CN) 2294 (w), 2249 (w); ν(P−F) 840 (s).

Synthesis of [Ni{Mes-NHC-(CH$_2$)$_4$CN}(NCMe)Cp]$^+$BF$_4^-$ (2c)/[Ni{Mes-NHC-(CH$_2$)$_4$CN}Cp]$^+$BF$_4^-$ (2′c). $AgBF_4$ (31.3 mg, 0.161 mmol) was added to a solution of **1c** (83.5 mg, 0.161 mmol) in acetonitrile (10 mL). The color changed instantaneously from violet to dark yellow. After 1 h, the reaction medium was filtered through Celite and concentrated to dryness. The resulting yellow solid was washed with diethyl ether (3 × 2 mL), and dried under vacuum to afford **2c**/**2′c** (55 mg, 0.106 mmol, 66%). ^{1}H NMR (CD_3CN, 298 K, 300.13 MHz): δ 7.51 (d, 1H, NC*H*, ^3J = 2.1); 7.20 (d, 1H, NC*H*, ^3J = 2.1); 7.16 (s, 2H, *m*-H); 5.00 (s, 5H, C_5H_5); 4.70 (t, 2H, NCH_2, ^3J = 7.4); 2.56 (t, 2H, CH_2CN, ^3J = 7.1); 2.41 (s, 3H, *p*-Me); 2.14 (m, 2H, NCH_2CH_2); 1.98 (s, 6H, *o*-Me); 1.78 (m, 2H CH_2CH_2CN). $^{13}C\{^1H\}$ NMR (CD_3CN, 298 K, 75.47 MHz): δ 158.3 (NCN); 140.7 and 137.1 (*ipso*-/*p*-C_{Ar}); 136.5 (*o*-C_{Ar}): 130.1 (*m*-C_{Ar}); 126.7 and 125.0 (NCH); 121.1 (CH_2CN); 93.8 (C_5H_5); 51.9 (NCH_2); 30.7 (CH_2); 23.5 (CH_2); 21.2 (*p*-Me); 18.1 (*o*-Me); 17.5 (CH_2CN). IR (KBr): $\nu(C_{sp2}-H)$ 3167 (m), 3132 (m), 3101 (m); $\nu(C_{sp3}-H)$ 2926 (m), 2871 (m); ν(CN) 2291 (w), 2248 (w); ν(B−F) 1063 (s).

Synthesis of [Ni{Mes-NHC-(CH$_2$)$_5$CN}(NCMe)Cp]$^+$PF$_6^-$ (2d)/[Ni{Mes-NHC-(CH$_2$)$_5$CN}Cp]$^+$PF$_6^-$ (2′d). KPF_6 (211 mg, 1.15 mmol) was added to a solution of **1d** (468 mg, 1.13 mmol) in acetonitrile (10 mL). The color changed instantaneously from violet to dark yellow. After 45 min, the reaction medium was filtered through Celite and concentrated to dryness. Crystallization from an acetonitrile/toluene mixture then afforded **2d**/**2′d** as a yellow solid, which was washed with diethyl ether (3 × 2 mL), and dried under vacuum (458 mg, 0.813 mmol, 72%). ^{1}H NMR (CD_3CN, 298 K, 300.13 MHz): δ 7.50 (d, 1H, NC*H*, ^3J = 2.0); 7.20 (d, 1H, *m*-H, ^3J = 2.0); 7.16 (s, 2H, *m*-H); 4.99 (s, 5H, C_5H_5); 4.68 (t, 2H, NCH_2, ^3J = 7.4); 2.47 (t, 2H, CH_2CN, ^3J = 7.1); 2.41 (s, 3H, *p*-Me); 2.03 (m, 2H, CH_2); 1.98 (s, 6H, *o*-Me); 1.76 (m, 2H, CH_2); 1.57 (m, 2H, CH_2). $^{13}C\{^1H\}$ NMR (CD_3CN, 298 K, 75.47 MHz): δ 158.0 (NCN); 140.6 and 137.1 (*ipso*-/*p*-C_{Ar}); 136.5 (*o*-C_{Ar}); 130.1 (*m*-C_{Ar}); 126.6 and 124.9 (NCH); 121.2 (CH_2CN); 93.8 (C_5H_5); 52.4 (NCH_2); 30.8 (CH_2); 26.4 (CH_2); 25.7 (CH_2); 21.2 (*p*-Me); 18.1 (*o*-Me); 17.5 (CH_2CN). IR (KBr): $\nu(C_{sp2}-H)$ 3165 (w), 3134 (w); $\nu(C_{sp3}-H)$ 2935 (m), 2865 (w); ν(P−F) 832 (s).

Synthesis of [Ni{Me-NHC-CH_2CH(CN)}Cp] (3a). To a suspension of KO*t*Bu (56 mg, 0.499 mmol) in toluene (2.5 mL) at room temperature was added **1a** (193 mg, 0.500 mmol) with vigorous stirring over a period of 20 min. The mixture was stirred for 40 min and filtered over alumina, which was rinsed with thf (80 mL). The solvent was then evaporated under vacuum, and crystallization from a thf/pentane solution (1/4) at room temperature afforded **3a** as green crystals (32 mg, 0.124 mmol, 25%). Anal. Calcd for $C_{12}H_{13}N_3Ni$: C, 55.88; H, 5.08; N, 16.29. Found: C, 55.69; H, 5.07; N, 16.58. ^{1}H NMR ($CDCl_3$, 298 K, 400.13 MHz): δ 6.77 and 6.63 (2s, 2 × 1H, NC*H*); 5.35 (s, 5H, C_5H_5); 3.74 (m, 2H, NCH_2); 3.43 (s, 3H, CH_3); 2.70 (dd, 1H, C*H*CN, ^3J = 6.0). ^{13}C{^{1}H} NMR ($CDCl_3$, 300 K, 75.47 MHz): δ 173.5 (*N*CN); 131.3 (*C*N); 122.6 and 117.2 (NCH); 90.2 (C_5H_5); 53.9 (NCH_2); 37.7 (CH_3); −11.6 (*C*HCN). IR (ATR-C): ν(C_{sp^2}—H) 3156 (w), 3130 (w) 3093 (w); ν(C_{sp^3}—H) 2932 (m), 2875 (w); ν(CN) 2179 (m).

Synthesis of [Ni{Mes-NHC-$(CH_2)_2$CH(CN)}Cp] (3b) from [Ni{Mes-NHC-$(CH_2)_3$CN}(NCMe)Cp]$^+PF_6^-$ (2b). The procedure was similar to that used when starting from **1b**.[17] **2b** (191 mg, 0.339 mmol) and KO-*t*-Bu (38 mg, 0.339 mmol) in toluene (7 mL) at room temperature afforded **3b** (60 mg, 0.160 mmol, 47%).

Synthesis of [Ni{Mes-NHC-$(CH_2)_3$CH(CN)}Cp] (3c). To a suspension of KO*t*Bu (50 mg, 0.446 mmol) in toluene (9 mL) at room temperature was added **1c** (233 mg, 0.450 mmol) with vigorous stirring over a period of 30 min. The resulting green mixture was stirred for 40 min and was filtered over alumina, which was rinsed with thf (40 mL). Volatiles were then evaporated under vacuum, and crystallization from a thf/pentane solution (1/3) at room temperature afforded **3c** as green crystals (40 mg, 0.103 mmol, 23%). Anal. Calcd for $C_{22}H_{25}N_3Ni$: C, 67.73; H, 6.46; N, 10.77. Found: C, 67.67; H, 6.61; N, 10.76. ^{1}H NMR ($CDCl_3$, 300 K, 300.13 MHz): δ 7.05 (d, 1H, NC*H*, ^3J = 1.7); 7.05 (s, 2H, *m*-H_{Ar}); 6.79 (d, 1H, NC*H*, ^3J = 1.7); 4.70 (s, 5H, C_5H_5); 4.70 (vb, 2H, NCH_2); 2.39 (s, 3H, *p*-Me); 2.10 (bs, 6H, *o*-Me); 2.00 and 1.67 (2 m, 2 × 1H, CH_2); 1.54 (bd, 1H, C*H*CN, ^3J = 8.3); 1.15 and 0.97 (2vb, 2 × 1H, CH_2CH). ^{13}C{^{1}H} NMR ($CDCl_3$, 300 K, 75.47 MHz): δ 174.3 (*N*CN); 138.2 and 135.9 (*ipso*-/*p*-C_{Ar}); 134.8 and 134.7 (*o*-C_{Ar}); 132.5 (*C*N); 128.4 and 128.3 (*m*-C_{Ar}); 122.2 and 120.7 (NCH); 90.1 (C_5H_5); 47.5 (NCH_2); 27.2 (NCH_2CH_2); 26.0 (CH_2CH); 20.4 (*p*-Me); 17.5 and 17.3 (*o*-Me); −27.1 (*C*HCN). IR (ATR): ν(C_{sp^2}—H) 3147 (w), 3117 (w); ν(C_{sp^3}—H) 2945 (m), 2856 (w); ν(CN) 2176 (m).

Synthesis of [Ni{Mes-NHC-$(CH_2)_4$CH(CN)}Cp] (3d). To a suspension of KO*t*Bu (48 mg, 0.428 mmol) in toluene (9 mL) at room temperature was added **1d** (210 mg, 0.432 mmol) with vigorous stirring over a period of 10 min. The resulting mixture was stirred for 1 h and filtered over alumina, which was then rinsed with thf (60 mL). The solvent was then evaporated under vacuum, and crystallization from a thf/pentane solution (1:3) at room temperature afforded **3d** as brown crystals (15 mg, 0.037 mmol, 9%). ^{1}H NMR ($CDCl_3$, 300 K, 300.13 MHz): δ 7.09 (d, 1H, NC*H*, ^3J = 1.9); 7.07 and 7.04 (2bs, 2 × 1H, *m*-H_{Ar}); 6.85 (d, 1H, NC*H*, ^3J = 1.9); 5.23 and 4.47 (2 m, 2 × 1H, NCH_2); 4.85 (s, 5H, C_5H_5); 2.41 (s, 3H, *p*-Me); 2.20 and 1.93 (2 m, 2 × 1H, NCH_2CH_2); 2.01 and 1.89 (2s, 2 × 3H, *o*-Me); 1.51 (m, 2H, CH_2CH_2CH); 1.30 (m, 1H, C*H*CN); 1.11 and 0.94 (2 m, 2 × 1H, CH_2CH). ^{13}C{^{1}H} NMR ($CDCl_3$, 300 K, 75.47 MHz): δ 177.3 (*N*CN); 139.0 and 136.8 (*ipso*-/*p*-C_{Ar}); 135.8 and 135.5 (*o*-C_{Ar}); 134.2 (*C*N); 129.4 and 129.2 (*m*-C_{Ar}); 124.1 and 121.9 (NCH); 91.4 (C_5H_5); 52.4 (NCH_2); 31.0 (NCH_2CH_2); 29.9 (CH_2CH_2CH); 27.6 (CH_2CH_2CH); 21.3 (*p*-Me); 18.2 and 18.1 (*o*-Me); −18.7 (*C*HCN).

X-ray Diffraction Studies: Structure Determination and Refinement. Single crystals of **1a,b** suitable for X-ray diffraction studies were selected from batches of crystals obtained at −28 °C from dichloromethane/diethyl ether and toluene solutions, respectively. Crystals of complex **3d** were harvested from thf at room temperature. Diffraction data for all crystals were collected at 173(2) K on a Nonius Kappa-CCD area detector diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). A summary of crystal data, data collection parameters, and structure refinement details is given in Table S1 in the Supporting Information. Cell parameters were determined from reflections taken from a set of 10 frames (1.0° steps in ψ angle), each at 20 s exposure. All structures were solved using direct methods with SHELXS-97 and refined against F^2 for all reflections using the SHELXL-97 software.[35] Multiscan absorption corrections (MULscanABS in PLATON) were applied.[36] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were generated according to stereochemistry and refined as fixed contributors using a riding model in SHELXL-97.

DFT Computational Details. All calculations were performed using the Gaussian 03 software package,[37] and the PBE1PBE functional, without symmetry constraints. That functional uses a hybrid generalized gradient approximation (GGA), including a 25% mixture of Hartree−Fock[38] exchange with DFT[39] exchange correlation, given by the Perdew, Burke, and Ernzerhof functional (PBE).[40] The optimized geometries were obtained with a VDZP basis set (basis b1) consisting of the LanL2DZ basis set[41] augmented with an f-polarization function[42] for Ni and a standard 6-31G(d,p) basis set[43] for the remaining elements. Transition state optimizations were performed with the synchronous transit-guided quasi-Newton Method (STQN) developed by Schlegel et al.,[44] after a thorough search of the potential energy surfaces (PES). Frequency calculations were performed to confirm the nature of the stationary points, yielding one imaginary frequency for the transition states and none for the minima. Each transition state was further confirmed by following its vibrational mode downhill on both sides and obtaining the minima presented on the energy profiles. The energy values reported result from single-point calculations using a standard 6-311++G(d,p)[45] basis set and the geometries optimized at the PBE1PBE/b1 level. Solvent (toluene) effects were considered in the PBE1PBE/6-311++G(d,p)//PBE1PBE/b1 energy calculations using the polarizable continuum model (PCM) initially devised by Tomasi and co-workers[46] as implemented on Gaussian 03.[47] The molecular cavity was based on the united atom topological model applied on UAHF radii, optimized for the HF/6-31G(d) level.

■ ASSOCIATED CONTENT

Supporting Information. Table S1, giving X-ray crystallographic data and data collection parameters for complexes **1a,b** and **3b,d** and CIF files giving X-ray structural data, including data collection parameters, positional and thermal parameters, and bond distances and angles, for complexes **1a,b** and **3d**, as well as atomic coordinates for all optimized species. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data (excluding structure factors) have also been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication Nos. CCDC 812544 (**1a**), 812545 (**1b**), and 812546 (**3d**), respectively. Copies of the data can be obtained free of charge from the CCDC via www.ccdc.cam.ac.uk/data_request/cif.

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