Synthesis, Structure, and Solution Dynamics of Pentamethylcyclopentadienyl Nickel Complexes Bearing N-Heterocyclic Carbene Ligands

Vincent Ritleng, Caroline Barth, Eric Brenner, Sandra Milosevic, and Michael J. Chetcuti*

Laboratoire de Chimie Organométallique Appliquée, UMR CNRS 7509, Ecole Européenne de Chimie,
Polymères et Matériaux (ECPM), Université Louis Pasteur, 25 Rue Becquerel, 67087 Strasbourg, France

Received April 29, 2008

Neutral pentamethylcyclopentadienyl nickel complexes of general formula [Ni(NHC)X(η^5-C_5Me_5)] [NHC = 1,3-dimethylimidazol-2-ylidene (Me-NHC), 1,3-bis(2,4,6,-trimethylphenyl)imidazol-2-ylidene (Mes-NHC), 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (iPr-NHC); X = Cl, I] were prepared from the reaction of pentamethylcyclopentadienyl acetylacetonate nickel(II) with 1 equiv of the corresponding imidazolium salt (NHC•HX). The new complexes [Ni(Me-NHC)I(η^5-C_5Me_5)] **1a**, [Ni(Mes-NHC)Cl(η^5-C_5Me_5)] **2**, and [Ni(iPr-NHC)Cl(η^5-C_5Me_5)] **3** were obtained in moderate to good yields and were fully characterized by ^{13}C and ^{1}H NMR spectroscopy, and in the cases of **1a** and **2** by single-crystal X-ray crystallography. The related cyclopentadienyl complex [Ni(Me-NHC)I(η^5-C_5H_5)] **1b** was also synthesized and structurally characterized; its geometry and spectroscopic data are comparable to those of complex **1a**. The variable-temperature (VT) ^{1}H NMR spectra of the sterically constrained complexes **2** and **3** are consistent with restricted rotation about the nickel−carbene carbon bond. The free energy of activation for the dynamic processes, in both cases, was determined to be on the order of 65−67 kJ mol^{-1} by VT NMR experiments.

Introduction

The synthesis and isolation of the first N-heterocyclic carbene (NHC), or imidazol-2-ylidene, was reported in 1991.[1] Since then, NHCs have become an important class of ligands in organometallic chemistry.[2–6] These ligands are often compared to tertiary phosphines because of similarities in their bonding to transition metals. Nevertheless, substantial differences do exist, notably in their electron-donating power. In general NHCs are stronger Lewis bases[7,8] and have reduced π-back-bonding with respect to tertiary phosphines.[9–12] Consequently, complexes that incorporate these ligands are more stable toward dissociative[13–16] and degradative cleavage.[17–20] Applications of organometallic complexes bearing NHC ligands in catalysis are now well recognized.[2,4–6,21–24]

Nickel−NHC complexes and their catalytic applications have attracted some recent attention.[25–38] The utility of nickel−NHC complexes in catalysis has been eclipsed by the far wider range of applications found for their palladium and ruthenium analogues.[2,39] Nevertheless, nickel complexes offer significant potential advantages in contrast to palladium NHC species, most notably in their much lower cost and in their reduced tendency to deposit nanoparticles of metallic nickel.[39] Despite the relative diversity of ligand frameworks found in NHC nickel complexes, no examples of such species bearing electron-rich and sterically demanding η^5-pentamethylcyclopentadienyl, η^5-C_5Me_5 (Cp*), ligands have been reported to date. An electron-rich and bulky Cp* ligand linked to an electron-rich nickel(NHC) group may impart substantial benefits in a catalytic cycle. Such Ni(NHC)-Cp* complexes should be capable of (i) better stabilizing

---

* To whom correspondence should be addressed. E-mail: chetcuti@chimie.u-strasbg.fr. Tel: + 33 3 90 24 26 31. Fax: + 33 3 90 24 26 39.

(1) Arduengo, A. J.; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, *113*, 361.

(2) Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1290.

(3) Bourissou, D.; Guerret, O.; Gabbai, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39.

(4) Herrmann, W. A.; Köcher, C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2163.

(5) See issues 5 and 6 of , *Coord. Chem. Rev.* **2007**, *251*, 595.

(6) César, V.; Bellemin-Laponnaz, S.; Gade, L. H. *Chem. Soc. Rev.* **2004**, *33*, 619.

(7) Dorta, R.; Stevens, E. D.; Scott, N. M.; Costabile, C.; Cavallo, L.; Hoff, C. D.; Nolan, S. P. *J. Am. Chem. Soc.* **2005**, *127*, 2485.

(8) Chianese, A. R.; Li, X.; Janzen, M. C.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2003**, *22*, 1663.

(9) Penka, E. F.; Schläpfer, C. W.; Atanasov, M.; Albrecht, M.; Daul, C. *J. Organomet. Chem.* **2007**, *692*, 5709.

(10) Khramov, D. M.; Lynch, V. M.; Bielawski, C. W. *Organometallics* **2007**, *26*, 6042.

(11) Fantasia, S.; Petersen, J. L.; Jacobsen, H.; Cavallo, L.; Nolan, S. P. *Organometallics* **2007**, *26*, 5880.

(12) Díez-González, S.; Nolan, S. P. *Coord. Chem. Rev.* **2007**, *251*, 874.

(13) Milosevic, S.; Brenner, E.; Ritleng, V.; Chetcuti, M. J. *Dalton Trans.* **2008**, 1973.

(14) Allen, D. P.; Crudden, C. M.; Calhoun, L. A.; Wang, R. *J. Organomet. Chem.* **2004**, *689*, 3203.

(15) Dorta, R.; Stevens, E. D.; Hoff, C. D.; Nolan, S. P. *J. Am. Chem. Soc.* **2003**, *125*, 10490.

(16) Simms, R. W.; Drewitt, M. J.; Baird, M. J. *Organometallics* **2002**, *21*, 2958.

(17) Hong, S. H.; Chlenov, A.; Day, M. W.; Grubbs, R. H. *Angew. Chem., Int. Ed.* **2007**, *46*, 5148.

(18) Galan, B. R.; Gembicky, M.; Dominiak, P. M.; Keister, J. B.; Diver, S. T. *J. Am. Chem. Soc.* **2005**, *127*, 15702.

(19) Cabeza, J. A.; Del Rio, I.; Miguel, D.; Sánchez-Vega, M. G. *Chem. Commun.* **2005**, 3956.

(20) Jazzar, R. F.; MacGregor, S. A.; Mahon, M. F.; Richards, S. P.; Whittlesey, M. K. *J. Am. Chem. Soc.* **2002**, *124*, 4944.

(21) Navarro, O.; Kelly, R. A., III; Nolan, S. P. *J. Am. Chem. Soc.* **2003**, *125*, 16194.

(22) Vasquez-Serrano, L. D.; Owens, B. T.; Buriak, J. M. *Chem. Commun.* **2002**, 2518.

(23) Markò, I. E.; Stérin, S.; Buisine, O.; Mignani, G.; Branlard, P.; Tinant, B.; Declerq, J.-P. *Science* **2002**, *298*, 204.

(24) Trnka, T. M.; Grubbs, R. H. *Acc. Chem. Res.* **2001**, *34*, 18.

10.1021/om800376q CCC: $40.75

coordinatively unsaturated sites through steric protection and electronic donation and (ii) subsequently enhancing a reductive elimination step via the steric bulkiness of the Cp* ligand.[36] We believed that it was of interest to develop a convenient route to Ni(NHC)Cp* complexes.

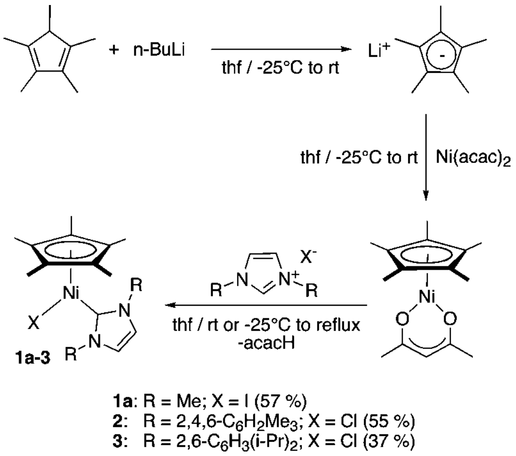
Herein, we report the facile "one-pot" synthesis of [Ni(NHC)XCp*] (X = Cl, I) complexes by reaction of the corresponding imidazolium salt with [NiCp*(acac)] (acac = acetylacetonate), prepared *in situ*. The structures of two of the resulting species were established by single-crystal X-ray diffraction studies. The synthesis and structure of the new related cyclopentadienyl complex [Ni(Me-NHC)ICp] is also described. Bulky aryl-substituted NHC ligands lead to complexes in which there is hindered rotation about the nickel−carbene bond at room temperature. The activation free energy of rotation for these processes was established by VT ^{1}H NMR spectroscopy.

Results and Discussion

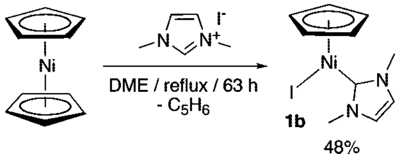
Synthesis of the Neutral Complexes [Ni(NHC)XCp*]. Most common methods of attaching a NHC onto a metal center require the prior synthesis of either the free carbene[40–42] or a NHC silver complex,[8,42,43] before subsequent complexation or transmetalation. This procedure is avoided here by the direct addition of the imidazolium salt onto the nickel precursor.[44,45]

The cyclopentadienyl complexes [Ni(NHC)XCp] can be prepared from nickelocene and the corresponding imidazolium salt.[44,45] Nevertheless, attempts to prepare the Ni(NHC)Cp* complexes, using a parallel synthetic method, with NiCp*$_2$ were not fruitful. We therefore developed a new synthesis for the Ni(NHC)Cp* complexes.

Scheme 1. Syntheses of Complexes 1a, 2, and 3



Scheme 2. Synthesis of Complex 1b



The nickel precursor used was [Ni(acac)Cp*], prepared by the reaction of anhydrous [Ni(acac)$_2$] with LiCp* in THF according to the procedure outlined by Manriquez.[46] It proved to be unnecessary to isolate the moderately stable [Ni(acac)Cp*],[47] and a suspension of the *in situ* prepared nickel complex was reacted with the imidazolium salts in THF, in a "one-pot" procedure shown in Scheme 1. The neutral complexes [Ni(Me-NHC)ICp*] **1a**, [Ni(Mes-NHC)ClCp*] **2**, and [Ni(iPr-NHC)ClCp*] **3** (Me-NHC = 1,3-dimethylimidazol-2-ylidene, Mes-NHC = 1,3-bis(2,4,6,-trimethylphenyl)imidazol-2-ylidene, iPr-NHC = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) were all isolated as air-stable red-violet solids in moderate to good yields (37−57% after workup).[48]

The hitherto unknown complex [Ni(Me-NHC)ICp] **1b** was obtained from nickelocene and the imidazolium salt (see Experimental Section) by modification of a previously reported synthesis that yielded other Ni(NHC)Cp complexes,[44,45] but not this one. The synthesis is shown in Scheme 2. All compounds were characterized by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy (*vide infra*).

Structural Studies. Crystals of **1a**, **1b**, and **2** suitable for X-ray structure determination were grown from cold THF/diethyl ether (**1a**, **1b**) or toluene (**2**) solutions. The molecular structures of **1a** and **1b** are shown in similar orientations in parts a and b of Figure 1, respectively. Figure 2 shows the geometry of complex **2**. Crystallographic data and data collection parameters are listed in Table 1, and a list of selected bond lengths and angles for all three complexes appear in Table 2.

The molecular structures of these complexes are similar. All feature a nickel atom bonded to a η^5-Cp (**1b**) or Cp* (**1a**, **2**) group, a NHC moiety, and a halide ligand. If one considers the Cp or Cp* group as a single ligand, the nickel atom lies at the center of a trigonal plane formed by the ring centroid, the halide, and the carbenoid carbon atom C(1) of the NHC ligand ($\sum$(bond angles) = 360°). However, there are significant departures from

---

(25) Lee, C.-C.; Ke, W.-C.; Chan, K.-T.; Lai, C.-L.; Hu, C.-H.; Lee, H. M. *Chem.−Eur. J.* **2007**, *13*, 582.

(26) Ng, S.-S.; Jamison, T. F. *J. Am. Chem. Soc.* **2005**, *127*, 7320.

(27) Duong, H. A.; Cross, M. J.; Louie, J. *J. Am. Chem. Soc.* **2004**, *126*, 11438.

(28) Mahandru, G. M.; Liu, G.; Montgomery, J. *J. Am. Chem. Soc.* **2004**, *126*, 3698.

(29) Sawaki, R.; Sato, Y.; Mori, M. *Org. Lett.* **2004**, *6*, 1131.

(30) Omar-Amrani, R.; Thomas, A.; Brenner, E.; Schneider, R.; Fort, Y. *Org. Lett.* **2003**, *5*, 2311.

(31) Böhm, V. P. W.; Weskamp, T.; Gstöttmayr, C. W. K.; Herrmann, W. A. *Angew. Chem., Int. Ed.* **2000**, *39*, 1602.

(32) McGuinness, D. S.; Cavell, K. J.; Skelton, B. W.; White, A. H. *Organometallics* **1999**, *18*, 1596.

(33) Xi, Z.; Zhang, X.; Chen, W.; Fu, S.; Wang, D. *Organometallics* **2007**, *26*, 6636.

(34) Inamoto, K.; Kuroda, J.-I.; Hiroya, K.; Noda, Y.; Watanabe, M.; Sakamoto, T. *Organometallics* **2006**, *25*, 3095.

(35) Chiu, P. L.; Lai, C.-L.; Chang, C.-F.; Hu, C.-H.; Lee, H. M. *Organometallics* **2005**, *24*, 6169.

(36) Matsubara, K.; Ueno, K.; Shibata, Y. *Organometallics* **2006**, *25*, 3422.

(37) Matsubara, K.; Ueno, K.; Koga, Y.; Hara, K. *J. Org. Chem.* **2007**, *72*, 5069.

(38) Malyshev, D. A.; Scott, N. M.; Marion, N.; Stevens, E. D.; Ananikov, V. P.; Beletskaya, I. P.; Nolan, S. P. *Organometallics* **2006**, *25*, 4462.

(39) Sommer, W. J.; Weck, M. *Coord. Chem. Rev.* **2007**, *251*, 874.

(40) Jafarpour, L.; Nolan, S. P. *Organometallics* **2000**, *19*, 2055.

(41) Herrmann, W. A.; Elison, M.; Fischer; J.; Köcher, C.; Artus, G. R. J. *Chem.−Eur. J.* **1996**, *2*, 772.

(42) Peris, E. *Top. Organomet. Chem.* **2007**, *21*, 83.

(43) Wang, H. M. J.; Lin, I. J. B. *Organometallics* **1998**, *17*, 972.

(44) Kelly, R. A.; Scott, N. M.; Díez-González, S.; Stevens, E. D.; Nolan, S. P. *Organometallics* **2005**, *24*, 3442.

(45) Abernethy, C. D.; Cowley, A. H.; Jones, R. A. *J. Organomet. Chem.* **2000**, *596*, 3.

(46) Bunel, E. E.; Valle, L.; Manriquez, J. M. *Organometallics* **1985**, *4*, 1680.

(47) Smith, M. E.; Andersen, R. A. *J. Am. Chem. Soc.* **1996**, *118*, 11119.

(48) Palladium(II) acetylacetonate has been used to prepare Pd(NHC) species, but in this case, the free NHC was used, rather than the imidazolium salt. Navarro, O.; Marion, N.; Scott, N. M.; Gonzalez, J.; Amoroso, D.; Bell, A.; Nolan, S. P. *Tetrahedron* **2005**, *61*, 9716–9722.

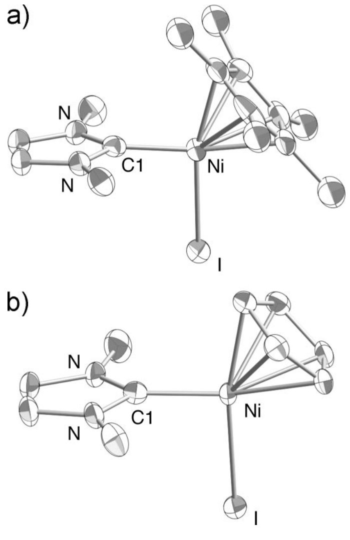


Figure 1. (a) ORTEP plot showing the molecular structure of [Ni(Me-NHC)I(η^5-C$_5$Me$_5$)] **1a**. Key atoms are labeled. Ellipsoids are shown at the 50% probability level. Only one of the two (disordered) positions of the Cp* methyl carbon atoms is shown; hydrogen atoms are omitted for clarity. (b) ORTEP plot showing the molecular structure of [Ni(Me-NHC)I(η^5-C$_5$H$_5$)] **1b**. Ellipsoids are are shown at the 50% probability level. Key atoms are labeled and hydrogen atoms are omitted for clarity.

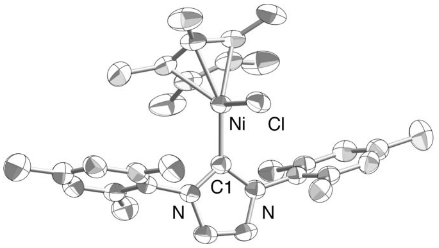


Figure 2. ORTEP plot showing the molecular structure of [Ni(Mes-NHC)Cl(η^5-C$_5$Me$_5$)] **2**. Ellipsoids are shown at the 50% probability level. Key atoms are labeled and hydrogen atoms are omitted for clarity. The molecule of toluene, found in the unit cell, is not shown.

the idealized 120° angles of a trigonal structure for all three molecules (Table 2). In all three structures, the X−Ni−NHC angles are 94.5 ± 1°.

The nickel−carbene carbon bond lengths are not significantly different from each other [Ni−C(1) = 1.887(3), 1.880(4), and 1.906(3) Å for **1a**, **1b**, and **2**, respectively]. The value for **2** is comparable to those reported for the related analogues [Ni(1,3-bis(2,4,6,-trimethylphenyl)dihydroimidazol-2-ylidene)-ClCp] (1.85(2)−1.89(2) Å)[44] and [Ni(Mes-NHC)ClCp] (1.917(9) Å).[45]

The nickel−halide distances are normal in all three complexes: the Ni−I bond length of 2.5212(5) Å in **1a** is marginally longer than the value 2.5006(6) Å found in the less sterically congested Cp complex **1b**. Both values are similar to the value of 2.5269(9) Å found in [Ni(1,3,4,5-tetramethylimidazol-2-ylidene)I(η^3-C$_3$H$_5$)].[49] The Ni−Cl distance of 2.1962(9) in **2** is also close to the Ni−Cl distances observed in the related nickel NHC complexes bearing mesityl substituents, where values of 2.199(5)−2.183(6) Å[44] and 2.185(2) Å[45] have been registered.

One significant difference between structures **1** and **2** is the angle subtended between the plane formed by the Cp/Cp* centroid, the nickel atom, and the halide atom and the plane that contains the five-membered imidazolylidene ring. Molecules of **1b** sit on a crystallographically imposed mirror plane in which this interplanar angle is set by symmetry at 90°. In **1a**, the two planes are also practically perpendicular (interplanar angle = 87°). In the more sterically demanding bis-mesityl NHC complex **2**, the imidazolylidene ring is tilted at an angle of 73.5° with respect to the Cp*$_{\text{cent}}$−Ni−Cl plane, presumably because of the steric congestion present in the molecule.

The angle formed between the two least-squares mesityl ring planes in **2** is 34°; that is, the two rings are twisted with respect to each other, presumably to minimize steric interactions with other ligands. This interplanar angle is comparable to the values observed in the two other NHC complexes bearing mesityl substituents, in which the values found are 34.7(8)−33.34(70)[44] and 39.0°.[45] The two mesityl rings both make angles of 78° with respect to the five-membered imidazolylidene ring.

The molecular structure of **2** suggests that free rotation about the nitrogen−mesityl bonds is not feasible. A space-filling molecular model of **2** clearly shows that complete rotation about the nitrogen−mesityl bonds is not allowed without severe molecular deformations, due to the steric bulk of the Cp* ligand and its interaction with the NHC group.

VT NMR Studies. The ^{1}H and ^{13}C{^{1}H} NMR spectra of complexes **1** at ambient temperature are straightforward: both show the presence of one η^5-Cp or Cp* group and the Me-NHC ligand. The spectra reveal that an effective plane of symmetry that bisects the molecule exists in solution on the NMR time scale. This effective mirror plane, rigorously present in the solid-state structure of **1b**, contains the halogen, the nickel, and the NHC carbene carbon atom, as well as the Cp or Cp* centroid. It is also revealed in the NMR spectra of the more sterically congested complexes **2** and **3**, but the ^{1}H NMR spectra of these molecules are more complex and deserve further comment.

The ^{1}H NMR spectrum of **2** at ambient temperature displays two singlets in a 1:1 integrated ratio for the four *meta*-hydrogen atoms of the two mesityl groups, as well as three singlets, in a 3:3:3 relative integrated ratio, for the four *ortho-* and the two *para*-methyl groups. The two alkene protons of the carbene ligand are isochronous, indicating that a molecular mirror plane is present on the ^{1}H NMR time scale. If one considers the molecular structure of **2**, only a moderate rotation about the Ni−NHC carbene−carbon bond, coupled with a minor twist about the two nitrogen−aryl carbon bonds, is required to generate the mirror plane that bisects the molecule on the ^{1}H NMR time scale. We believe that these motions best explain the observed symmetry in the spectrum.

Nevertheless, the two *ortho*-methyl and the two *meta*-hydrogen signals are somewhat broad at ambient temperature. A variable-temperature ^{1}H NMR experiment was thus performed on a toluene-d_8 solution of **2** between 299 and 373 K. As the temperature was increased, the *ortho*-methyl resonances became even broader and eventually coalesced at a temperature (T_C) of ca. 353 K. Similar coalescence was observed for the aromatic *meta*-hydrogen atom signals at 323 K. The free energy of activation ($\Delta G^\ddagger$) for this fluxional process (based on the coalescence temperature of the *ortho*-methyl groups and, independently, of the *meta*-aromatic protons) is 67 ± 2 kJ mol^{-1}.[50]

The ^{1}H NMR spectrum of complex **3** also displays a single signal for the two alkene protons of the NHC double bond and

---

(49) Silva, L. C.; Gomes, P. T.; Veiros, L. F.; Pascu, S. I.; Duarte, M. T.; Namorado, S.; Ascenso, J. R.; Dias, A. R. *Organometallics* **2006**, *25*, 4391.

(50) Gutowsky, H. S.; Holm, C. H. *J. Chem. Phys.* **1956**, *25*, 1228.

Table 1. X-ray Crystallographic Data and Data Collection Parameters for Complexes 1 and 2

parameter	**1a**	**1b**	**2**[a]
empirical formula	$C_{15}H_{23}IN_2Ni$	$C_{10}H_{13}IN_2Ni$	$C_{31}H_{39}ClN_2Ni \cdot C_7H_8$
fw	416.96	346.83	625.94
cryst syst	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/m$	$P2_1/c$
unit cell dimens			
a (Å)	8.2210(5)	7.1384(5)	16.3570 (7)
b (Å)	8.3762(6)	8.9168(6)	14.2962 (6)
c (Å)	14.2071(5)	9.3335(4)	16.8901 (7)
α (deg)	86.125(4)	90	90
β (deg)	77.031(3)	103.872(4)	118.715 (2)
γ (deg)	62.850(2)	90	90
V (Å^3)	847.63(9)	576.77(6)	3463.9(3)
Z	2	2	4
D_{calcd} (g cm^{-3})	1.634	1.997	1.200
radiation, λ (Å)	Mo Kα, 0.71073	Mo Kα, 0.71073	Mo Kα, 0.71073
absorp coeff (mm^{-1})	2.956	4.321	0.664
temperature (K)	173(2)	173(2)	173(2)
cryst size (mm)	0.20 × 0.15 × 0.10	0.20 × 0.15 × 10	0.40 × 0.35 × 0.15
h, k, l_{max}	10, 10, 18	9, 11, 12	21, 18, 21
$T_{\text{min}}, T_{\text{max}}$	0.568, 0.784	0.452, 0.662	0,770, 0.868
no. of reflns collected	3892	1396	7937
R (reflections)	0.0393 (3095)	0.0270 (1234)	0.0617 (4731)
wR^2 (reflections)	0.0899 (3892)	0.0609 (1396)	0.1742 (7937)
GOF on F^2	1.023	1.121	1.036

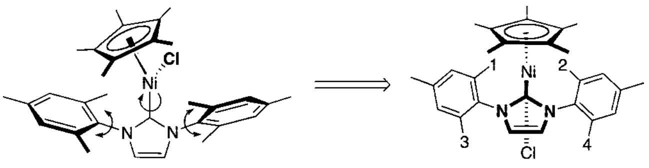
[a] One molecule of toluene is present in the asymmetric unit.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 1a, 1b, and 2

bond length or angle	**1a**	**1b**	**2**
Ni−C1	1.887(3)	1.880(4)	1.906(3)
Ni−X[a]	2.5212(5)	2.5006(6)	2.1962(9)
Ni−Cp$^{\dagger}_{\text{cent}}$	1.758	1.755	1.782
C1−Ni−X[a]	94.53(11)	93.63(13)	95.27(9)
C1−Ni−Cp$^{\dagger}_{\text{cent}}$[a]	136.0	134.6	142.0
X−Ni−Cp$^{\dagger}_{\text{cent}}$[a]	129.4	131.7	122.7
(NHC)[b] − (X−Ni−Cp$^{\dagger}_{\text{cent}}$)[a]	87.2	90	73.5

[a] X = I for **1a**, **1b** and Cl for **2**. Cp† = Cp (**1b**) or Cp* (**1a**, **2**). [b] (NHC) = best least-squares plane through five-membered imidazolyidene ring.

Scheme 3. Dynamic Behavior of Complex 2[a]



2 **2A**

[a] Rotation about the Ni−C$_{\text{carbene}}$ bond coupled with oscillations of the mesityl groups about the N−C$_{\text{Ar}}$ bond of **2** leads to conformation **2a** (shown from a different perspective to emphasize its symmetry). In **2a**, the mirror plane renders Me groups 1 and 2 and also 3 and 4 equivalent; rotation about the Ni−C$_{\text{carbene}}$ bond equalizes Me groups 1 and 4 and, hence, all *ortho*-Me groups.

for the *para* protons of the aromatic rings. Thus an effective mirror plane also bisects this molecule on the ^{1}H NMR time scale. Two doublets (for the *meta* aromatic ring protons) and two pseudoseptets (for the C*H* protons of the isopropyl groups) are observed. The central carbon atoms of the isopropyl groups are diastereotopic, and this results in four doublets being observed for the two sets of isopropyl methyl signals. All signals are sharp at 263 K.

Variable-temperature ^{1}H NMR data, from 263 to 373 K, were collected on a toluene-d_8 solution of **3**. As the temperature increased, the resonances of the two sets of *meta* aromatic ring protons and those of the two isopropyl groups broadened. Four distinct signal coalescences were observed as the temperature was raised. These all gave the same free energy of activation ($\Delta G^{\ddagger}$) of ca. 65 ± 2 kJ mol^{-1}, which strongly suggests that all four coalescences are linked to the same dynamic process in compound **3**.[50]

These results indicate that there is an effective mirror plane of symmetry present in solution for all these molecules. In addition, in complexes **2** and **3**, the *ortho* substituents of the aromatic rings, which are not equivalent at room temperature, become equivalent on the NMR time scale when the solutions of these species are heated moderately. The same effect is seen for the *meta* aromatic ring protons.

The most likely dynamic process that could account for these signal equivalences on the ^{1}H NMR time scale at elevated temperatures is free rotation about the Ni−C$_{\text{carbene}}$ bond, coupled with oscillations about the N−C$_{\text{Ar}}$ axes, as shown in Scheme 3. Space-filling models clearly show that even in complex **2** full rotation of the aryl rings about the N−C$_{\text{Ar}}$ axis is not possible owing to the strong steric interactions between the *ortho* substituents and the Cp* group. This steric effect is enhanced in complex **3**, which contains larger isopropyl groups in the *ortho* positions of its phenyl rings. However, small-angle oscillations of the two rings are certainly possible, and this, coupled with rotation about the Ni−C$_{\text{carbene}}$ bonds, would make the two *ortho* groups of the aromatic rings equivalent; the two *meta* substituents also become equivalent. The activation energies of the dynamic processes for complexes **2** and **3** are essentially the same. As these energies are unlikely to be equal if the dynamic processes involved full rotation about the N−C$_{\text{Ar}}$ axes (the steric footprints of the aryl groups in **2** and **3** are quite different), this also suggests that the dynamic process involves Ni−C$_{\text{carbene}}$ rotation and not full N−C$_{\text{Ar}}$ rotation.

In summary, it appears that the sterically constrained complexes **2** and **3** both exhibit oscillations about the N−C$_{\text{Ar}}$ bonds and a comparable rotational barrier about the Ni−C$_{\text{carbene}}$ bond. The absence of rotation about the nitrogen−aryl bonds is clearly due to steric effects. Conjugation with the aromatic ring may also result in the N−C$_{\text{Ar}}$ bond having partial double-bond character.[51] However, the origin of the restricted rotation observed about the metal−NHC bond, which is seen here and has also been observed elsewhere, is less obvious. Restricted rotation about the metal carbene carbon bond was not observed in the closely related Cp analogues [Ni(NHC)ClCp].[44,45] Previous studies on the nature of the rotational barrier initially invoked steric rather than electronic effects, since the metal−carbene bond was believed to have predominantly single-bond character.[8,49,52–55] However, more recent studies suggest that π-back-bonding in NHC−metal bonds may not be negligible,[9,10] and indeed π-back-donation was found to make around a 10% contribution to the Pt−NHC bond in [*cis*-Pt(NHC)(DMSO)Cl_2] complexes.[11]

It is noteworthy that the carbene carbon atoms in complexes **1a**, **2**, and **3** appear at 175 (in $CDCl_3$) and 177 and 180 ppm (both in C_6D_6), respectively, in the ^{13}C NMR spectrum of these complexes. These signals are downfield of the signals seen at 165, 166,[45] and 169[44] ppm, respectively (all in $CDCl_3$), for their corresponding Cp derivatives, and likely indicate increased π-back-donation from the more electron-rich nickel atoms in the Cp* complexes as compared to their Cp analogues.[56] The rotational barrier about the Ni−$C_{carbene}$ bond of **2** and **3** is thus probably mainly steric in nature, but there is possibly a minor electronic component.

Conclusion

Neutral Cp* complexes of formula [Ni(NHC)XCp*] (NHC = Me-NHC, X = I, **1a**; NHC = Mes-NHC, X = Cl, **2**; NHC = iPr-NHC, X = Cl, **3**) were isolated from the reaction of [NiCp*(acac)], prepared *in situ*, with the corresponding imidazolium halides. The previously unreported complex [Ni(Me-NHC)ICp] **1b** was also prepared starting from nickelocene. Single-crystal X-ray diffraction studies established the molecular geometries of complexes **1a**, **1b**, and **2**. Complexes **2** and **3** show a barrier to nickel−carbene bond rotation ($\Delta G^{\ddagger} = 65-67$ kJ. mol^{-1}) that was elucidated from VT ^1H NMR studies. The barrier is believed to be predominantly steric in nature. Studies of the reactivity of these complexes are currently under way.

Experimental Section

General Comments. 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 obtained for all complexes 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. The ^1H NMR variable-temperature experiments were recorded at 400 MHz in toluene-d_8, from 26 to 100 °C for complex **2** and from −10 to 100 °C for complex **3**. Elemental analyses were performed by the Service Central de Microanalyse du CNRS, at the Institut de Chimie, Université Louis Pasteur in Strasbourg. Commercial compounds were used as received. 1,3-Dimethylimidazolium iodide,[57] 1,3-bis(2,4,6,-trimethylphenyl)imidazolium chloride,[58,59] 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride,[58] and bis(2,4-pentanedionato)nickel(II)[60,61] were prepared according to published methods.

Synthesis of [Ni(Me-NHC)ICp*], 1a. *n*-Butyllithium (6.25 mL, 1.6 M solution in hexanes, 10.0 mmol) was added dropwise at −25 °C to a solution of pentamethylcyclopentadiene (1.61 mL, 10.0 mmol) in tetrahydrofuran (20 mL). After a few minutes, the resulting white suspension was added to a green suspension of bis(2,4-pentanedionato)nickel(II) (2.57 g, 10.0 mmol) in tetrahydrofuran (20 mL) at −25 °C. The reaction mixture was allowed to reach room temperature and was stirred for 1 h at this temperature to afford a dark red suspension of [NiCp*(acac)].[46] The reaction medium was again cooled to −25 °C, and a suspension of 1,3-dimethylimidazolium iodide (2.24 g, 10.0 mmol) in tetrahydrofuran (20 mL) was added. The mixture was again allowed to reach room temperature and was then refluxed for 2 h. The resulting red-violet suspension was filtered on Celite, and this was rinsed with dichloromethane until the solvent ran colorless. The solvents were removed under vacuum. The residue was washed with pentane (3 × 5 mL) to afford **1a** as a red solid (2.37 g, 57% yield). Anal. Calcd for $C_{15}H_{23}N_2INi$: C, 43.21; H, 5.56; N, 6.72. Found: C, 42.89; H, 5.43; N, 6.34. ^1H NMR (toluene-d_8, 298 K, 300.13 MHz): δ 6.04 (s, 2H, NC*H*); 3.58 (s, 6H, *Me*); 1.60 (s, 15H, C_5Me_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 298 K, 75.47 MHz): δ 175.1 (N*C*N); 123.1 (N*C*H); 100.9 (C_5Me_5); 38.8 (Me); 10.8 (C_5Me_5).

Synthesis of [Ni(Me-NHC)ICp], 1b. A solution of nickelocene (567 mg, 3.00 mmol) in DME (30 mL) was added to 1,3-dimethylimidazolium iodide (699 mg, 3.12 mmol). The mixture was refluxed for 63 h, during which time the solution color slowly turned from a dark green to a dark red. The solvent was then removed under vacuum and the reddish-black residue dissolved in thf (20 mL), filtered on a Celite pad, and rinsed with tetrahydrofuran (3 × 15 mL). The solvent was then removed under vacuum, and the residue redissolved in dichloromethane and filtered on a 4 × 5 cm column of silica. Solvent was removed from the red filtrate, and the resulting powder was washed with pentane (3 mL), dried, and recrystallized from a diethylether/tetrahydrofuran mixture at −28 °C to afford pure **1b** (501 mg, 48% yield). Anal. Calcd for $C_{10}H_{13}N_2INi$: C, 34.63; H, 3.78; N 8.08. Found: C 34.87; H 3.93; N 7.98. ^1H NMR ($CDCl_3$, 298 K, 300.13 MHz): δ 6.91 (s, 2H, NC*H*); 5.34 (s, 5H, C_5H_5), 4.15 (s, 6H, *Me*). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 298 K, 75.47 MHz): δ 165.1 (N*C*N); 123.9 (N*C*H); 91.9 (C_5H_5); 39.8 (Me).

Synthesis of [Ni(Mes-NHC)ClCp*], 2. [NiCp*(acac)][46] was prepared as described for **1a** using pentamethylcyclopentadiene (161 μL, 1.00 mmol) and *n*-butyllithium (625 μL of a 1.60 M hexanes solution) in tetrahydrofuran (2 mL), followed by cold addition of this slurry to a suspension of bis(2,4-pentanedionato)nickel(II) (257 mg, 1.00 mmol) in tetrahydrofuran (2 mL). The resulting dark red reaction medium was maintained at room temperature, and a suspension of 1,3-bis(2,4,6,-trimethylphenyl)imidazolium chloride (341 mg, 1.00 mmol) in tetrahydrofuran (5 mL) was added. The mixture was stirred at room temperature for 1 h, during which time the color changed to violet. The solvent was then removed under vacuum, and the resulting residue was extracted with toluene (10 mL) and filtered through a Celite pad. This was rinsed with toluene (3 × 5 mL) until the washings were colorless. Concentration to ~3 mL under vacuum followed by addition of pentane (10 mL)

---

(51) Gallagher, M. M.; Rooney, A. D.; Rooney, J. J. *J. Organomet. Chem.* **2008**, *693*, 1252.

(52) Newman, C. P.; Deeth, R. J.; Clarkson, G. J.; Rourke, J. P. *Organometallics* **2007**, *26*, 6225.

(53) Enders, D.; Gielen, H. *J. Organomet. Chem.* **2001**, *617*, 70.

(54) Weskamp, T.; Schattenmann, W. C.; Spiegler, M.; Herrmann, W. A. *Angew. Chem., Int. Ed.* **1998**, *37*, 2490.

(55) Doyle, M. J.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1974**, 679.

(56) Demerseman, B.; Mbaye, M. D.; Sémeril, D.; Toupet, L.; Bruneau, C.; Dixneuf, P. H. *Eur. J. Inorg. Chem.* **2006**, 1174.

(57) Schaub, T.; Backes, M.; Radius, U. *Organometallics* **2006**, *25*, 4196.

(58) Arduengo, A. J., III; Krafczyk, R.; Schmutzler, R.; Craig, H. A.; Goerlich, J. R.; Marshall, W. J.; Unverzagt, M. *Tetrahedron* **1999**, *55*, 14523.

(59) Voges, M. H.; Rømming, C.; Tilset, M. *Organometallics* **1999**, *18*, 529.

(60) Charles, R. G.; Pawlikowski, M. A. *J. Phys. Chem.* **1958**, *62*, 440.

(61) Cotton, F. A.; Fackler, J. P. *J. Am. Chem. Soc.* **1961**, *83*, 218.

afforded a violet solid when the solution was allowed to stand overnight at −28 °C. The mother liquor was removed via syringe and the solid washed with pentane (2 × 1 mL) and dried under vacuum to give spectroscopically pure **2** (291 mg, 55% yield). ^{1}H NMR (toluene-d_8, 298 K, 400.13 MHz): δ 6.92 (br, 2H, *m-H*); 6.80 (br, 2H, *m-H*); 6.22 (s, 2H, NC*H*); 2.69 (br, 6H, *o-Me*); 2.21 (s, 6H, *p-Me*); 1.81 (br, 6H, *o-Me*); 1.17 (s, 15H, C_5Me_5). $^{13}C\{^1H\}$ NMR (C_6D_6, 298 K, 75.47 MHz): δ 177.1 (NCN); 138.6, 134.8 (*o*-C, $C_6H_2Me_3$); 138.4 (*p*-C, $C_6H_2Me_3$); 137.8 (*ipso*-C, $C_6H_2Me_3$); 130.5, 128.4 (*m*-C, $C_6H_2Me_3$); 124.1 (N*C*H); 102.1 (C_5Me_5); 21.4 (*p-Me*); 20.6 (*o-Me*); 18.6 (*o-Me*); 9.9 (C_5Me_5). A satisfactory elemental analysis could not be obtained for complex **2**; ^{1}H and $^{13}C\{^1H\}$ spectra are included in the Supporting Information.

[Ni(iPr-NHC)ClCp*], 3. [NiCp*(acac)][46] was prepared as described for **1a**, using pentamethylcyclopentadiene (258 μL, 1.60 mmol) and *n*-butyllithium (1.00 mL, 1.6 M solution in hexanes) in tetrahydrofuran (3 mL), followed by cold addition of this slurry to a suspension of bis(2,4-pentanedionato)nickel(II) (411 mg, 1.60 mmol) in tetrahydrofuran (3 mL). The resulting dark red reaction medium was cooled to −25 °C, and a suspension of 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride (679 mg, 1.60 mmol) in tetrahydrofuran (8 mL) was added. The mixture was allowed to reach room temperature and was then refluxed for 1 h. A color change to violet occurred. The solvent was removed under vacuum, and the resulting residue was extracted with toluene (15 mL) and filtered over Celite. Concentration to dryness and several washings with pentane gave **3** as a violet solid (365 mg, 37% yield). Analytically pure solid was obtained by recrystallization from a toluene/pentane solution. Anal. Calcd for $C_{37}H_{51}N_2ClNi$: C, 71.91; H, 8.32; N, 4.53. Found: C, 71.93; H, 8.10; N, 4.49. ^{1}H NMR (toluene-d_8, 263 K, 400.13 MHz): δ 7.39 (d, 2H, *m-H*, $^3J = 7.6$); 7.30 (t, 2H, *p-H*); 7.08 (d, 2H, *m-H*); 6.64 (s, 2H, NC*H*); 4.19 (m, 2H, C*H*Me$_2$); 2.29 (m, 2H, C*H*Me$_2$); 1.61 (d, 6H, $^3J = 6.8$, CH*Me*$_2$); 1.23 (d, 6H, $^3J = 6.8$, CH*Me*$_2$); 1.12 (s, 15H, C_5Me_5); 1.06 (d, 6H, $^3J = 6.8$, CH*Me*$_2$); 0.88 (d, 6H, $^3J = 6.8$, CH*Me*$_2$). $^{13}C\{^1H\}$ NMR (C_6D_6, 298 K, 75.47 MHz): δ 180.0 (N*C*N); 149.6 and 145.8 (*o*-C_{Ar}); 138.0 (*ipso*-C_{Ar}); 130.1 and 125.9 (*m*-C_{Ar}); 125.7 (*p*-C_{Ar}); 123.1 (N*C*H); 102.1 (C_5Me_5); 28.7 (*C*HMe$_2$); 27.2 and 26.9 (CH*Me*$_2$); 23.9 and 22.7 (CH*Me*$_2$); 10.1 (C_5Me_5).

X-ray Diffraction Studies. Structure Determination and Refinement. Single crystals of **1a** and **1b** suitable for X-ray diffraction studies were selected from batches of crystals obtained from thf/diethyl ether solutions at −25 °C. Crystals of complex **2** where harvested from toluene at −25 °C. Diffraction data for all crystals were collected on a Kappa CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). A summary of crystal data, data collection parameters, and structure refinements is given in Table 1. Cell parameters were determined from reflections taken from one set of 10 frames (1.0° steps in phi angle), each at 20 s exposure. The structures were solved using direct methods (SHELXS97) and refined against F^2 for all reflections using the SHELXL97 software. Multiscan absorptions corrections (MULscanABS in PLATON) were applied. All non-hydrogen atoms were refined anisotropically in structures. The Cp* rings in complex **1a** exhibit disorder, and the Me groups of this ligand were refined using a double-occupancy site model. Complex **1b** lies on a crystallographic mirror plane, and there is only half of the molecule in the asymmetric unit. Complex **2** contains a slightly disordered molecule of toluene in the crystal lattice, and this part of the structure was refined using fixed C−C distances. Hydrogen atoms in all structures were generated according to stereochemistry and refined as fixed contributors using a riding model in SHELXL97.[62,63]

Acknowledgment. We thank the CNRS and the Université Louis Pasteur (University of Strasbourg) for financial support. C.B. and S.M. thank the CNRS for M.Sc. research scholarships. Mr. Michel Schmitt is gratefully acknowledged for his assistance in obtaining the VT NMR data, and we appreciate the work of Dr. Lydia Brelot in the X-ray structure resolutions.

Supporting Information Available: Assigned ^{1}H and $^{13}C\{^1H\}$ and ^{13}C DEPT NMR spectra of **2**. CIF files giving X-ray structural data, including data collection parameters, positional and thermal parameters, and bond distances and angles for complexes **1a**, **1b**, and **2**. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data (excluding structure factors) have also been deposited in the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 686287, 686288, and 686289, respectively. Copies of the data can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk; www:http://www.ccdc.cam.ac.uk).

OM800376Q

---

(62) *Kappa CCD Operation Manual*; Delft, The Netherlands, 1997.

(63) Sheldrick, G. M. *SHELXL97, Program for the refinement of crystal structures*; University of Gottingen: Germany, 1997.