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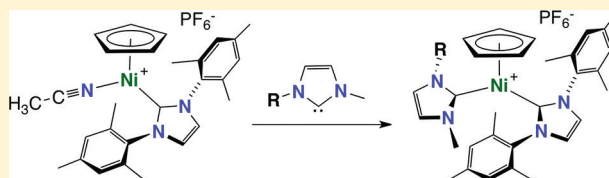
Synthesis and Structural Characterization of Half-Sandwich Nickel Complexes Bearing Two Different N-Heterocyclic Carbene Ligands

Anna Magdalena Oertel, Vincent Ritleng,* Loïc Burr, and Michael J. Chetcuti*

Laboratoire de Chimie Organométallique Appliquée, UMR CNRS 7509, Ecole Européenne de Chimie, Polymères et Matériaux, Université de Strasbourg, 25 rue Becquerel, 67087 Strasbourg, France

Supporting Information

ABSTRACT: Cationic cyclopentadienyl mixed bis-N-heterocyclic carbene (NHC) nickel complexes of the general formula $[\text{Ni}(\text{NHC})(\text{NHC}')\text{Cp}](\text{PF}_6^-)$ ($\text{NHC}/\text{NHC}' = 1,3\text{-bis}(2,4,6\text{-trimethylphenyl})\text{imidazol-2-ylidene}$ (Mes_2NHC) **a**, $1,3\text{-dimethylimidazol-2-ylidene}$ (Me_2NHC) **b**, $1\text{-isopropyl-3-methylimidazol-2-ylidene}$ ($i\text{Pr-NHC-Me}$) **c**; $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$) were prepared by the reaction of the cationic monocarbene complex $[\text{Ni}(\text{Mes}_2\text{NHC})(\text{NCMe})\text{Cp}](\text{PF}_6^-)$ **1a** or $[\text{Ni}(\text{Me}_2\text{NHC})(\text{NCMe})\text{Cp}](\text{BF}_4^-)$ **1b** with the appropriate free carbene. The new mixed bis(carbene) complexes $[\text{Ni}(\text{Mes}_2\text{NHC})(\text{Me}_2\text{NHC})\text{Cp}](\text{PF}_6^-)$ **2ab**, $[\text{Ni}(\text{Mes}_2\text{NHC})(i\text{Pr-NHC-Me})\text{Cp}](\text{PF}_6^-)$ **2ac**, and $[\text{Ni}(\text{Me}_2\text{NHC})(i\text{Pr-NHC-Me})\text{Cp}](\text{BF}_4^-)$ **2bc** were obtained in moderate-to-high yields and were fully characterized by ^1H and ^{13}C NMR spectroscopies, elemental analyses, and, in the case of **2ab**, by a single-crystal X-ray diffraction study. The monocarbene precursor **1b** was also structurally characterized. The mixed bis-NHC complexes **2ab** and **2ac** were tested as catalysts for the Suzuki–Miyaura cross-coupling of phenylboronic acid with 4'-bromoacetophenone, and their activities were compared to that of related monocarbene CpNi complexes.



INTRODUCTION

Since the first isolation of a stable imidazol-2-ylidene,¹ N-heterocyclic carbenes (NHCs) have become an important class of ligands in organometallic chemistry.² The easy preparation and handling of their precursors, their high modularity, and their strong σ -donor properties,³ which allow them to form strong NHC–metal bonds that prevent ligand dissociation,⁴ have rendered them extremely popular as supporting ligands in transition-metal catalysis: NHC complexes have shown unprecedented catalytic activity in many important organic reactions.^{2,5}

Nickel–NHC systems are somewhat less developed than palladium–, ruthenium–, or even rhodium–NHC systems.^{2b} Nevertheless, the past decade has seen the emergence of a number of NHC–nickel catalytic systems that have now found applications in a vast number of organic transformations, including, notably, traditional C–C cross-coupling reactions;^{6–10} the amination¹¹ and dehalogenation^{11b,12} of aryl halides; the oxidation of secondary alcohols;^{13,14} C–S couplings;¹⁵ the activation of C–F bonds;^{16,17} the hydrosilylation of internal alkynes;¹⁸ three-component couplings of unsaturated hydrocarbons, aldehydes, and silyl derivatives;¹⁹ and $[2 + 2 + 2]$ cycloadditions.^{20–22}

Following our ongoing interest in NHC–Ni compounds,²³ we have recently reported that the neutral $[\text{Ni}(\text{Ar}_2\text{NHC})\text{ClCp}^+]$ and cationic $[\text{Ni}(\text{Ar}_2\text{NHC})(\text{NCCH}_3)\text{Cp}^+](\text{PF}_6^-)$ [$\text{Ar}_2\text{NHC} = 1,3\text{-diarylimidazol-2-ylidene}$; $\text{Cp}^+ = \text{Cp}(\eta^5\text{-C}_5\text{H}_5)$, $\text{Cp}^*(\eta^5\text{-C}_5\text{Me}_5)$] half-sandwich complexes are efficient pre-catalysts for the fast Suzuki coupling of aryl halides.²⁴ These catalysts function without the addition of a reductant or a

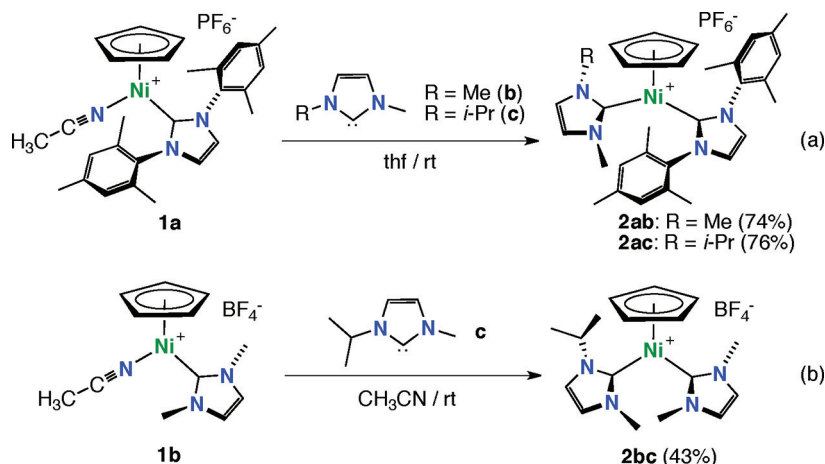
cocatalyst, and TOFs of up to 190 h^{-1} , a high rate for Ni(II) complexes under similar conditions,^{7,25} have been observed. However, fast deactivation of the active (presumably a Ni(0)) species remained an issue. As the presence of a second NHC unit on the nickel center may stabilize a coordinatively unsaturated intermediate that could appear during the catalytic cycle (metal–NHC bonds are regarded as especially stable⁴), and as bis-NHC–nickel(0)^{7i,8a,d,11c,15,16a,18a,26} or bis-NHC–nickel(I)²⁷ species are proposed to be either the active catalysts or intermediates in some of the above-cited organic reactions, we decided to investigate the stability and catalytic activity of half-sandwich nickel complexes that bear two NHC ligands.

Despite the relative diversity of NHC–Ni complexes bearing two NHC ligands,^{7e,f,i,8a,e–g,10,16a,18a,26–28} only one example of a cyclopentadienyl-bis-NHC–nickel complex, $[\text{Ni}(\text{Me}_4\text{NHC})_2\text{Cp}]^+\text{Cp}^-$, has hitherto been reported; this species was obtained by the direct reaction of 1,3,4,5-tetramethylimidazol-2-ylidene (Me_4NHC) with nickelocene.²⁹ Moreover, the first nickel complexes bearing two different NHCs have only just appeared.³⁰ It was, therefore, of interest to develop a general procedure that allows the successive attachment of two different NHC ligands onto one metal center, and we have developed a synthetic route that allows the facile generation of cationic mixed bis-NHC complexes of the general formula $[\text{Ni}(\text{NHC})(\text{NHC}')\text{Cp}]^+$. Herein, we report the synthesis of three such complexes by the reaction of a cationic acetonitrile complex $[\text{Ni}(\text{NHC})(\text{NCCH}_3)\text{Cp}]^+$ with the appropriate free

Received: September 15, 2011

Published: November 28, 2011

Scheme 1. Formation of the Mixed Bis(carbene) Nickel Complexes 2



NHC'. The molecular structure of one of these mixed bis-NHC complexes was established by a single-crystal X-ray diffraction study and is compared to those of its monocarbene precursors, $[\text{Ni}(\text{NHC})(\text{NCCH}_3)\text{Cp}]^+$ and $[\text{Ni}(\text{NHC}')(\text{NCCH}_3)\text{Cp}]^+$. Finally, limited studies into the catalytic activity of two of these species in Suzuki–Miyaura cross-coupling are presented and show that the coordination of a second NHC unit to an already crowded CpNi-NHC moiety dramatically stabilizes the resulting complex.

RESULTS AND DISCUSSION

Synthesis of the Mixed Bis-NHC–Nickel Complexes. We have recently described the synthesis and structure of several cationic acetonitrile complexes, $[\text{Ni}(\text{Ar}_2\text{NHC})(\text{NCCH}_3)\text{Cp}]^+\text{PF}_6^-$, including $[\text{Ni}(\text{Mes}_2\text{NHC})(\text{NCCH}_3)\text{Cp}]^+\text{PF}_6^-$ **1a**,^{23b,24} which is depicted in Scheme 1 (Mes_2NHC = 1,3-bis-2,4,6-trimethylphenylimidazol-2-ylidene, **a**). These complexes are readily accessible via reaction of their corresponding neutral chloro complexes $[\text{Ni}(\text{Ar}_2\text{NHC})\text{ClCp}]^+$ with KPF_6 in acetonitrile at room temperature.²⁴ The acetonitrile ligands in these complexes are labile, and free exchange is observed between free and coordinated CH_3CN , as shown by ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR studies in CD_3CN . The hitherto unreported complex, $[\text{Ni}(\text{Me}_2\text{NHC})(\text{NCCH}_3)\text{Cp}]^+\text{BF}_4^-$ **1b**, which contains the much less sterically demanding 1,3-dimethylimidazol-2-ylidene (Me_2NHC) **b**, was prepared according to a similar procedure by reacting the neutral iodo complex $[\text{Ni}(\text{Me}_2\text{NHC})\text{ICp}]^{23c}$ with AgBF_4 , and its structure was established by a single-crystal X-ray diffraction study (vide infra).

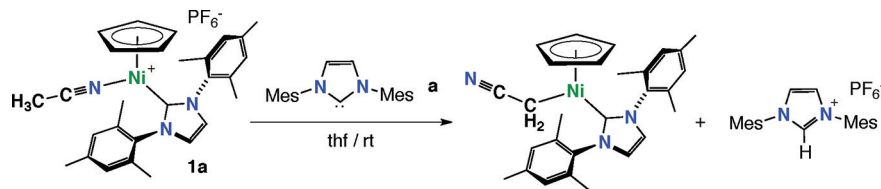
When a solution of complex **1a** in tetrahydrofuran was treated at room temperature with a freshly prepared solution of the free carbene Me_2NHC **b** (see the Experimental Section), the labile acetonitrile ligand was rapidly displaced and the half-sandwich mixed bis(carbene) complex $[\text{Ni}(\text{Mes}_2\text{NHC})(\text{Me}_2\text{NHC})\text{Cp}]^+\text{PF}_6^-$ **2ab** could be isolated in 74% yield (Scheme 1a). Similarly, the reaction between a solution of **1a** and a freshly prepared solution of 1-isopropyl-3-methylimidazol-2-ylidene (*i*Pr-NHC-Me), **c**, afforded the mixed bis(carbene) complex $[\text{Ni}(\text{Mes}_2\text{NHC})(i\text{Pr-NHC-Me})\text{Cp}]^+\text{PF}_6^-$ **2ac** in good yield as well (Scheme 1a). Finally a third member of this series, $[\text{Ni}(\text{Me}_2\text{NHC})(i\text{Pr-NHC-Me})\text{Cp}]^+\text{BF}_4^-$ **2bc**, could be obtained in moderate yield by reaction in acetonitrile of the less-bulky (and THF insoluble)

monocarbene nickel complex precursor **1b** with the asymmetrically substituted free carbene **c**. All compounds were isolated as air-stable green solids. They were characterized by ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy and by elemental analysis. The molecular structure of **2ab** was established by a single-crystal X-ray diffraction study (vide infra).

The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of the mixed bis(carbene) complexes **2** at ambient temperature present no anomalies: all show the presence of one $\eta^5\text{-Cp}$ group and of two NHC ligands. The carbene carbons are observed in the 158–168 ppm range in the ^{13}C NMR spectra, whereas the Cp carbon atoms appear at ca. 92 ppm, as is the case for closely related monoidimidazol-2-ylidene nickel Cp species, such as **1a** and **1b**,^{23a–d,24,31} and for the only other known half-sandwich bis-NHC–nickel complex, $[\text{Ni}(\text{Me}_4\text{NHC})_2\text{Cp}]^+\text{Cp}^-$.²⁹ Interestingly, in the ^1H NMR spectra, the Cp protons of the mixed alkyl- and aryl-substituted-NHC compounds **2ab** and **2ac** resonate as a singlet in the same range as observed for the Cp protons of aryl-substituted complexes, such as **1a**, at 4.6–4.8 ppm,^{24,31} rather than in the range observed for alkyl-substituted complexes, such as **1b**, **2bc**, or $[\text{Ni}(\text{Me}_4\text{NHC})_2\text{Cp}]^+\text{Cp}^-$, at 5.3–5.5 ppm.^{23a,c,29}

As for the cationic monocarbene compounds **1a**²⁴ and **1b**, the spectra of **2ab** reveal that an effective plane of symmetry that bisects the molecule exists in solution on the NMR time scale. This effective mirror plane contains the nickel atom, both NHC carbene carbons, and the Cp ring centroid. The protons of the Me_2NHC ring and the NMe groups thus resonate as two singlets in a 1:3 integrated ratio, in the molecule's ^1H NMR spectrum. The protons of the Mes_2NHC ring, the *ortho*-methyl groups, the *meta*-hydrogens, and the *para*-methyl groups of the mesityl groups all appear as four singlets in a 1:6:2:3 integrated ratio in the ^1H NMR signals of this molecule. This indicates that no apparent rotational barrier is present on the NMR time scale at ambient temperature in **2ab**.

Despite the absence of an effective molecular mirror plane, a similar situation in the asymmetric complex **2bc** leads to a single resonance for the two protons of the NHC ring and for the two NMe groups of the Me_2NHC ligand, respectively. However, in the ^1H NMR spectrum of the sterically more congested complex **2ac**, the four *meta*-hydrogen atoms of the two mesityl groups are displayed as two singlets in a 1:1 integrated ratio and the four *ortho*- and the two *para*-methyl groups as three singlets in a 3:3:3 relative integrated ratio; the

Scheme 2. Deprotonation of Coordinated CH₃CN by the Bulky Free Carbene **a**

corresponding protons of the Mes₂NHC ring remain isochronous. These results likely indicate that rotation is restricted about the N–mesityl bonds in **2ac**, as we observed previously in sterically congested neutral monocarbene Cp* complexes [Ni(Ar₂NHC)ClCp*]^{23c}.

It is not coincidental that all the bis(carbene) complexes synthesized contain at least one NHC ligand with small- to medium-sized substituents on the two nitrogen atoms. Despite repeated attempts, we were unable to synthesize the bis-Mes₂NHC complex [Ni(Mes₂NHC)₂Cp]⁺ by reacting free Mes₂NHC **a**³² with **1a**. Massive decomposition occurred instead, and small amounts of the imidazolium salt (Mes₂NHC–H)⁺PF₆[–] were isolated, together with less than 5% of the neutral cyanomethyl complex [Ni(Mes₂NHC)–(CH₂CN)Cp] (Scheme 2), which we recently reported to be readily obtained by reaction of **1a** with KOtBu.^{23a,b} The bulky free carbene **a** thus behaves here not as a two-electron donor ligand, but as a strong base, and in this role, it promotes the base-assisted C–H activation of the acetonitrile ligand. This result indicates that two Mes₂NHC groups are too voluminous to simultaneously bind to the nickel atom. A similar observation was made by Cowley and co-workers, who reported the formation of the half-sandwich bis(carbene) complex [Ni(Me₄NHC)₂Cp]⁺Cp[–] when nickelocene was treated with the medium-sized carbene Me₄NHC, but observed the formation of the monocarbene complex [Ni(Mes₂NHC)(η¹-C₅H₅)Cp] when nickelocene was treated with the more bulky Mes₂NHC **a**.²⁹ Presumably, steric congestion approaches critical proportions in bis-Mes₂NHC nickel cyclopentadienyl systems, and such species cannot be made.

Structural Studies of [Ni(Me₂NHC)(NCMe)Cp](BF₄) (1b**) and [Ni(Mes₂NHC)(Me₂NHC)Cp](PF₆) (**2ab**).** The structures of the monocarbene complex **1b**³³ and of the mixed bis-NHC complex **2ab**³⁴ were established by X-ray diffraction studies. Crystals suitable for X-ray structure determination were grown from solutions of acetonitrile/diethylether (**1b**) and CH₂Cl₂/diethylether (**2ab**). The molecular structures of the cationic parts of **1b** and of **2ab** are shown in similar orientations in Figures 1 and 2, respectively. A list of selected bond lengths and angles for **1b** and **2ab**, as well as for **1a**^{23b} (for comparison purposes), appear in Table 1.

The structure of the cationic part of **1b** is similar to that of its related neutral analogues [Ni(Me₂NHC)ICp]⁺ (Cp⁺ = Cp, Cp*), which have been fully discussed earlier.^{23c} It can also be compared to the cationic part of the monocarbene complex **1a**, namely, [Ni(Mes₂NHC)(NCMe)Cp]⁺.^{23b} The acetonitrile ligand in both structures is essentially linear [C4–C3–N = 178.6(2)° in **1b** and 177.9(2)° for **1a**]^{23b} and is also linearly coordinated to the nickel atom [the Ni–N–C3 angles are 175.6(2)° in **1b** and 174.5(2)° for **1a**]. Cp carbon distances, to each other and to the nickel atom, exhibit significant variations, but most of this is doubtless a result of the significant thermal motion and relatively poor localization of the Cp carbon atoms. A number of weak H–interactions may be present between

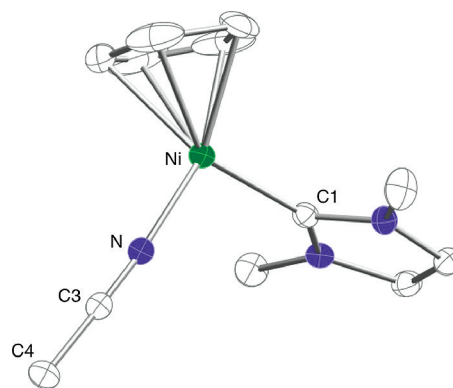


Figure 1. Molecular structure of the cation of [Ni(Me₂NHC)–(NCMe)Cp]⁺(BF₄)[–], **1b**, showing all non-H atoms. Ellipsoids are shown at the 50% probability level, and key atoms are labeled.

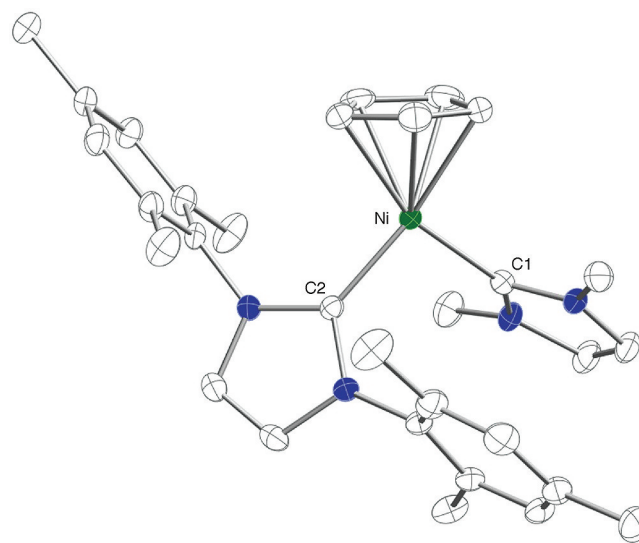


Figure 2. Molecular structure of the cation of [Ni(Mes₂NHC)–(Me₂NHC)Cp]⁺(PF₆)[–], **2ab**, showing all non-H atoms. Ellipsoids are shown at the 50% probability level, and key atoms are labeled.

various hydrogen atoms from acetonitrile, NHC, and Cp groups all with fluorine atoms in the BF₄[–] anions (the H⋯F distances range from 2.380 to 2.666 Å).

The molecular structure of the cation of **2ab** features a nickel atom bonded to a η⁵-Cp group, a Mes₂NHC, and a Me₂NHC moiety in a two-legged piano stool geometry. The coordination is globally similar to that of other half-sandwich complexes of the general formula [Ni(NHC)LCp]⁺,^{23a–c,24,31,35} such as **1a**^{23b} and **1b**, and is directly comparable to that of [Ni(Me₄NHC)₂Cp]⁺.²⁹ If one considers the Cp group as a single ligand, the nickel atom lies at the center of a pseudotrigonal plane formed by the ring centroid, the carbene carbon atom C(1) of the Me₂NHC ligand **b**, and the carbene carbon atom

Table 1. Selected Bond Lengths (Å) and Angles (°) for Complexes 1a, 1b, and 2ab with esd's in Parentheses^a

	1a ^{23b}	1b	2ab
Ni–C(1) and/or Ni–C(2)	1.902(2)	1.888(2)	1.906(3), 1.899(3)
Ni–N (1a, 1b)	1.869(2)	1.857(2)	
Ni–Cp _{cent}	1.760	1.751	1.772
Ni–C _{Cp} av	2.131	2.094	2.136
Ni–N–C _{CN}	174.5(2)	175.6(2)	
N–C _{CN} –C _{Me}	177.9(2)	178.6(2)	
C _{NHC} –Ni–N (1a, 1b) or C(1)–Ni–C(2) (2ab)	96.93(8)	98.86(7)	96.91(11)
C(1)–Ni–Cp _{cent} and/or C(2)–Ni–Cp _{cent}	131.8	129.8	136.0, 126.9
N–Ni–Cp _{cent} (1a, 1b)	131.2	131.3	

^aC(1) = carbene carbon of the Me₂NHC ligand. C(2) = carbene carbon of the Mes₂NHC ligand. N = acetonitrile nitrogen. Cp_{cent} = centroid of the Cp group.

C(2) of the Mes₂NHC ligand **a**; the sum of the angles subtended by these atoms is indeed almost exactly 360°. However, there are significant departures from the idealized 120° angles of a trigonal structure (Table 1). Thus, the carbenoid carbons C(1) and C(2) of **2ab** subtend an angle of 96.91(11)° at the nickel atom, a value that is typical of CpNiL₂ (or CpNiL'L') complexes: the L–Ni–L' angles observed for **1a**,^{23b} **1b**, and [Ni(Me₄NHC)₂Cp]⁺²⁹ are 96.93(8), 98.86(7) and 97.07(2)°, respectively.

Despite the different steric footprints of the two NHC ligands, the two nickel–carbene carbon bond lengths of **2ab** are not significantly different from each other [Ni–C(1) = 1.899(3) Å; Ni–C(2) = 1.906(3) Å]. Moreover, these values are remarkably close to those observed for the Mes₂NHC- and Me₂NHC-containing monocarbene analogues **1a** [Ni–C(2) = 1.902(2) Å]^{23b} and **1b** [Ni–C(1) = 1.888(2) Å] and are in the range of those reported for [Ni(Me₄NHC)₂Cp]⁺,²⁹ in which values of 1.883(2) Å were observed for both nickel–carbene carbon distances. However, the bigger carbene subtends a larger angle at the nickel with the Cp centroid (126.9° and 136.0° for Me₂NHC and Mes₂NHC, respectively).

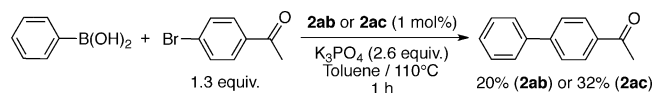
The planes defined by the two five-membered imidazol-2-ylidene rings of **2ab** are almost orthogonal to each other (74.6°), and the two mesityl rings are close to perpendicular to the Mes₂NHC ring plane (the plane of each aryl ring makes angles of 74.5° and 84° with the imidazol-2-ylidene plane), presumably to minimize steric interactions. The plane that contains the Me₂NHC ring in **2ab** makes an angle of 73° to the C(1)–Ni–Cp_{cent} plane (compared with 88.2°, **1b**), but the plane that contains the Mes₂NHC ring makes a much smaller angle of 34° with the C(2)–Ni–Cp_{cent} plane.

The Cp ring of the mixed bis(carbene) complex **2ab** exhibits structural distortions, as there are significant variations in the Ni–C_{Cp} distances, as well as fluctuations in the C_{Cp}–C_{Cp} distances. Similar distortions have been previously observed and studied in other Cp or Cp*Ni systems.³⁶ Some of the imidazolylidene hydrogen atoms are relatively close and interact weakly with some F atoms of the PF₆[−] anion (H...F distances lie in the 2.35–2.55 Å range). The Me₂NHC ring and one of the mesityl rings are close to coplanar (interplanar angle = 9.5°), suggesting that there might be some π -stacking interactions between the rings.

Short Study of the Catalytic Activities of (2ab) and (2ac) in Suzuki–Miyaura Cross-Coupling. The catalytic activity of the mixed bis(carbene) complexes **2ab** and **2ac** in the cross-coupling of phenylboronic acid with 4'-bromoacetophenone was examined under the standard conditions we have established with related monocarbene complexes [Ni(NHC)–LCp[†]] (L = Cl[−], or NCMe, PF₆[−]), that is, with 1.3 equiv of

PhB(OH)₂ and 2.6 equiv of K₃PO₄ as the sole additive in toluene at 90–110 °C.²⁴ Under these conditions, **2ab** and **2ac** (1 mol %) give the desired product, 4-acetylbiphenyl, in, respectively, 20% and 32% yield after 1 h of reaction (Scheme 3).

Scheme 3. Suzuki–Miyaura Cross-Coupling of 4'-Bromoacetophenone with Phenylboronic Acid Catalyzed by **2ab** and **2ac**



No homocoupling product, 4,4'-diacetylbiphenyl, is detected. Compared to the very high rate seen for a Ni(II)-based catalyst in the absence of a cocatalyst or reductant with the monocarbene half-sandwich catalyst [Ni{(iPr₂Ph)₂NHC}–(NCMe)Cp*]⁺PF₆[−] [(iPr₂Ph)₂NHC = 1,3-bis-2,6-diisopropyl-phenylimidazol-2-ylidene] (95% conversion after 10 min at 90 °C with 3 mol % loading, or 60% conversion after 1 h at 110 °C with 1 mol % loading),²⁴ these results were clearly disappointing.

To establish whether these low reactivities were due to an intrinsic stability of **2ab** and **2ac**, several reactivity tests were conducted on both species. They all demonstrated the high intrinsic stability of these cationic bis(carbene) complexes: for example, both complexes **2ab** and **2ac** species are unaffected by added acid; neither reaction nor decomposition was observed.³⁷ Thus, it appears that the coordination of a second NHC ligand onto a Cp–Ni(Mes₂NHC) moiety stabilizes the catalyst precursor to such an extent that the complex is almost catalytically inert. One reasonable explanation may be that the demanding steric footprints of the bulky Mes₂NHC, the smaller Me₂NHC or *i*Pr–NHC–Me, and the Cp ligand all together probably render the nickel center almost inaccessible. Preliminary studies into the reactivity of the much less sterically congested species **2bc** tend to confirm this diagnostic.

CONCLUSION

In summary, a general methodology for the synthesis of half-sandwich Ni(II) complexes bearing two *different* NHC ligands has been developed. Thus, the mixed bis(carbene) complexes [Ni(Mes₂NHC)(Me₂NHC)Cp]⁺PF₆[−] **2ab**, [Ni(Mes₂NHC)–(*i*Pr–NHC–Me)Cp]⁺PF₆[−] **2ac**, and [Ni(Me₂NHC)(*i*Pr–NHC–Me)Cp]⁺BF₄[−] **2bc** were isolated in moderate-to-high yields from the reaction of the cationic acetonitrile complex [Ni(Mes₂NHC)(CH₃CN)Cp]⁺PF₆[−] **1a** or [Ni(Me₂NHC)–(CH₃CN)Cp]⁺BF₄[−] **1b** with the appropriate free NHC.

A single-crystal X-ray diffraction study established the molecular structure of the sterically congested **2ab**, which was compared to those of its monocarbene analogues, **1a** and **1b**, and to that of its less sterically encumbered homologue $[\text{Ni}(\text{Me}_4\text{NHC})_2\text{Cp}]^+\text{Cp}^-$. It is not coincidental that all the bis(carbene) complexes synthesized contain at least one NHC ligand with small- to medium-sized substituents on the two nitrogen atoms. The repeated failures in synthesizing the bis- Mes_2NHC complex $[\text{Ni}(\text{Mes}_2\text{NHC})_2\text{Cp}]^+$ by reacting free Mes_2NHC with **1a**, and the deprotonation of the acetonitrile ligand of **1a** instead, indeed, strongly suggest that two Mes_2NHC groups together with a Cp ligand are too voluminous to bind simultaneously to the nickel atom. The important steric congestion of the half-sandwich mixed bis(carbene) complexes **2ab** and **2ac**, which contain the bulky Mes_2NHC and a smaller Me_2NHC or $i\text{Pr-NHC-Me}$ ligand, is most probably responsible for their great stability and hence the low reactivity of **2ab** and **2ac** in the Suzuki–Miyaura cross-coupling of 4'-bromoacetophenone with phenylboronic acid. The reactivity of **2bc**, which bears two small NHCs, is more promising and is currently under investigation.

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 at 298 K 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 $^{13}\text{C}\{^1\text{H}\}$. The assignments of the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were made with the aid of DEPT ^{13}C spectra for all complexes and of $^1\text{H}/^{13}\text{C}$ HSQC correlation for complex **2ac**. The chemical shifts are referenced to residual deuterated solvent peaks. Chemical shifts (δ) and coupling constants (J) are expressed in parts per million and hertz, respectively. Elemental analysis for complexes **2** were performed by the Service d'Analyses, de Mesures Physiques et de Spectroscopie Optique, UMR CNRS 7177, at the Institut de Chimie, Université de Strasbourg. Commercial compounds were used as received. 1-Isopropyl-1H-imidazole,³⁸ Mes_2NHC **a**,³⁹ $[\text{Ni}(\text{Me}_2\text{NHC})\text{ICp}]^{23c}$ and $[\text{Ni}(\text{Mes}_2\text{NHC})(\text{NCMe})\text{Cp}](\text{PF}_6)$ **1a**²⁴ were prepared according to published methods. The preparations of 1,3-dimethylimidazolium iodide⁴⁰ and 1-isopropyl-(3-methyl)imidazolium iodide⁴¹ were adapted from published syntheses, and the improved procedures are given below.

Synthesis of 1,3-Dimethylimidazolium Iodide. Iodomethane (1.64 mL, 20.0 mmol) was added to a solution of 1-methyl-1H-imidazole (1.6 mL, 20.0 mmol) in toluene (80 mL). The mixture was stirred at 50 °C overnight. The overlaying solution was removed by syringe, and the resulting white solid was washed with diethyl ether (3 \times 7 mL) and dried in vacuo for 2 h. 1,3-Dimethylimidazolium iodide was obtained as a white solid in 97% yield (4.37 g, 19.5 mmol). ^1H NMR (CDCl_3 , 300.13 MHz): δ = 10.01 (s, 1H, NCHN), 7.41 (s, 2H, NCH), 4.09 (s, 6H, Me).

Synthesis of 1-Isopropyl-3-methylimidazolium Iodide. Iodomethane (1.42 g, 0.62 mL, 10.0 mmol) was added dropwise over a 5 min period to a solution of 1-isopropyl-1H-imidazole (1.102 g, 10.0 mmol) in toluene (20 mL). The solution was heated at 50 °C and stirred at this temperature for 8 h. The overlaying solution was removed by syringe, and the resulting white solid was washed with diethyl ether (3 \times 7 mL) and dried in vacuo for 2 h. 1-Isopropyl-(3-methyl)imidazolium iodide was obtained as a white solid in 95% yield (2.40 g, 9.5 mmol). ^1H NMR (CDCl_3 , 300.13 MHz): δ = 10.20 (s, 1H, NCHN), 7.43 and 7.40 (s, 1H, NCH), 4.83 (septet, 3J = 6.6, 1H, CH), 4.13 (s, 3H, Me), 1.66 (d, 3J = 6.6, CHMe_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 75.47 MHz): δ = 136.0 (NCHN), 123.9 and 120.2 (NCH), 53.6 (CH), 37.2 (Me), 23.3 (CHMe_2).

Synthesis of $[\text{Ni}(\text{Me}_2\text{NHC})(\text{NCMe})\text{Cp}]^+\text{BF}_4^-$ (1b**).** AgBF_4 (509 mg, 2.61 mmol) was added to a solution of $[\text{Ni}(\text{Me}_2\text{NHC})\text{ICp}]$ (905 mg, 2.61 mmol) in acetonitrile (30 mL). The color immediately changed from red to green. After 10 min, the reaction medium was filtered through Celite, which, in turn, was rinsed with acetonitrile (4 \times 5 mL), and the solvent was then concentrated to ca. 1 mL. Treatment with diethylether gave green crystals after standing at -32 °C overnight. The mother liquor was removed by syringe and the solid washed with diethylether (3 \times 5 mL) and dried under vacuum to give **1b** (730 mg, 2.10 mmol, 80%). ^1H NMR (CD_3CN , 300.13 MHz): δ = 7.20 (s, 2H, NCH), 5.44 (s, 5H, $\eta^5\text{-C}_5\text{H}_5$), 4.07 (s, 6H, Me). Free CH_3CN that results from exchange with CD_3CN is seen as a singlet (at 1.96 ppm) on the downfield side of the multiplet due to residual CHD_2CN observed at 1.94 ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_3CN , 75.47 MHz): δ = 156.2 (NCN), 125.8 (NCH), 93.8 ($\eta^5\text{-C}_5\text{H}_5$), 39.2 (Me). Free CH_3CN that results from exchange with CD_3CN is seen as two singlets (at 1.77 and 118.3 ppm) overlapping with the multiplet due to residual CHD_2CN at 1.32 ppm and with the singlet due to CD_3CN at 118.3 ppm.

Synthesis of $[\text{Ni}(\text{Mes}_2\text{NHC})(\text{Me}_2\text{NHC})\text{Cp}]^+\text{PF}_6^-$ (2ab**).** *n*-Butyllithium (0.20 mL, 0.32 mmol, 1.6 M in hexanes) was added dropwise to a suspension of 1,3-dimethylimidazolium iodide (222 mg, 0.32 mmol) in THF (3 mL) and stirred for 10 min at room temperature. The reaction mixture was filtered through Celite, and the resulting solution of **b** was added to a solution of **1a** (211 mg, 0.32 mmol) in THF (5 mL) under vigorous stirring. The mixture was stirred at this temperature for 15 min, and then the volatiles were evaporated under vacuum. The residue was extracted with CH_2Cl_2 (3 \times 5 mL) and filtered through Celite, which was rinsed with CH_2Cl_2 (3 \times 5 mL). The solvent was evaporated under vacuum, and **2ab** crystallized from a cold solution of CH_2Cl_2 and diethyl ether. **2ab** was isolated as green crystals (170 mg, 0.25 mmol, 74%). Anal. Calcd for $\text{C}_{31}\text{H}_{37}\text{F}_6\text{N}_4\text{NiP}$: C, 55.63; H, 5.57; N, 8.37. Found: C, 55.48; H, 5.62; N, 8.38. ^1H NMR (CDCl_3 , 400.13 MHz): δ = 7.03 (s, 4H, *m*-H), 6.98 and 6.93 (2s, 2 \times 2H, NCH), 4.76 (s, 5H, C_5H_5), 3.42 (s, 6H, NMe), 2.39 (s, 6H, *p*-Me), 1.98 (s, 12H, *o*-Me). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100.61 MHz): δ = 168.2 and 160.3 (NCN), 140.0 and 136.3 (*ipso*-/*p*- C_{Ar}), 135.1 (*o*- C_{Ar}), 129.8 (*m*- C_{Ar}), 125.8 and 124.8 (NCH), 91.9 (C_5H_5), 38.9 (NMe), 21.2 (*p*-Me), 18.1 (*o*-Me).

Synthesis of $[\text{Ni}(\text{Mes}_2\text{NHC})(i\text{-Pr-NHC-Me})\text{Cp}]^+\text{PF}_6^-$ (2ac**).** *n*-Butyllithium (0.3 mL, 0.48 mmol, 1.6 M in hexanes) was added dropwise to a suspension of 1-isopropyl-(3-methyl)imidazolium iodide (109 mg, 0.43 mmol) in THF (5 mL) and stirred for 10 min at room temperature. The reaction mixture was filtered through Celite, and the resulting solution of **c** was added to a solution of **1a** (267 mg, 0.43 mmol) in THF (5 mL) under vigorous stirring. The mixture was stirred at this temperature for 15 min, and then the volatiles were evaporated under vacuum. The residue was dissolved in CH_3CN (5 mL) and filtered through alumina, which was rinsed with CH_3CN (3 \times 10 mL). The solvent was evaporated under reduced pressure, and **2ac** was crystallized from a cold solution of THF and pentane. **2ac** was isolated as green crystals (228 mg, 0.33 mmol, 76%). Anal. Calcd for $\text{C}_{33}\text{H}_{41}\text{F}_6\text{N}_4\text{NiP}$: C, 56.84; H, 5.93; N, 8.03. Found: C, 56.74; H, 6.17; N, 7.94. ^1H NMR (CDCl_3 , 300.13 MHz): δ = 7.15 (bs, 2H, *m*-H), 7.05 and 6.96 (2d, 2 \times 1H, NCH-*c*, 3J = 2.1), 7.00 (s, 2H, NCH-*a*), 6.94 (bs, 2H, *m*-H), 5.43 (sept, 1H, CHMe_2 , 3J = 6.8), 4.72 (s, 5H, C_5H_5), 2.87 (s, 3H, NMe), 2.40 (s, 6H, *p*-Me), 2.28 and 1.58 (2s, 2 \times 6H, *o*-Me), 1.30 and 1.29 (2d, 3H, $\text{CH}(\text{CH}_3)_2$, 3J = 6.8). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 75.47 MHz): δ = 168.1 and 158.1 (NCN), 140.3 and 136.2 (*ipso*-/*p*- C_{Ar}), 135.4 and 135.3 (*o*- C_{Ar}), 129.9 and 129.6 (*m*- C_{Ar}), 126.1 (NCH-*a*), 125.7 and 119.5 (NCH-*b*), 91.8 (C_5H_5), 53.2 ($\text{CH}(\text{CH}_3)_2$), 37.3 (NMe), 24.5 and 22.8 ($\text{CH}(\text{CH}_3)_2$), 21.1 (*p*-Me), 18.5 and 17.4 (*o*-Me).

Synthesis of $[\text{Ni}(\text{Me}_2\text{NHC})(i\text{-Pr-NHC-Me})\text{Cp}]^+\text{BF}_4^-$ (2bc**).** *n*-Butyllithium (1 mL, 1.60 mmol, 1.6 M in hexanes) was added dropwise to a suspension of 1-isopropyl-(3-methyl)imidazolium iodide (403 mg, 1.60 mmol) in THF (16 mL) and stirred for 10 min at room temperature. The reaction mixture was filtered through Celite, and the resulting solution of **c** was added to a solution of **1b** (540 mg, 1.55 mmol) in acetonitrile (20 mL) under vigorous stirring. The mixture

was stirred at this temperature for 15 min, and then the volatiles were evaporated under vacuum. The residue was then dissolved in acetonitrile (5 mL) and filtered on alumina, which was rinsed with acetonitrile (3 × 5 mL). The solvent was concentrated under reduced pressure, and **2bc** was precipitated by addition of diethylether. **2bc** was isolated as a green powder (290 mg, 0.67 mmol, 43%). Anal. Calcd for $C_{17}H_{25}BF_4N_4Ni$: C, 47.38; H, 5.85; N, 13.00. Found: C, 47.52; H, 6.30; N, 12.49. 1H NMR (CD_3CN , 300.13 MHz): δ = 7.17 and 7.15 (2d, 2 × 1H, NCH-c, 3J = 2.0), 7.08 (s, 2H, NCH-b), 5.45 (s, 5H, C_5H_5), 5.41 (sept, 1H, $CHMe_2$, 3J = 6.8), 3.98 (s, 3H, NMe-c), 3.85 (s, 6H, NMe-b), 1.20 (d, 6H, $CH(CH_3)_2$, 3J = 6.77). $^{13}C\{^1H\}$ NMR (CD_3CN , 75.47 MHz): δ = 164.2 and 162.5 (NCN), 126.4 and 120.0 (NCH-c), 125.4 (NCH-b), 92.3 (C_5H_5), 54.2 ($CH(CH_3)_2$), 39.7 (NMe-c), 39.3 (NMe-b), 23.1 ($CH(CH_3)_2$).

Procedure for the Suzuki–Miyaura Cross-Coupling Reactions. A Schlenk tube, placed under an argon atmosphere, was charged with 4'-bromoacetophenone (1.0 mmol), phenylboronic acid (1.3 mmol), K_3PO_4 (2.6 mmol), **2ab** or **2ac** (0.01 mmol, 1 mol %), and toluene (3 mL) and was immediately heated with vigorous stirring by placing it into an oil bath at 110 °C. After 60 min, the reaction was stopped by cooling the reaction to room temperature and allowing air to enter the Schlenk tube. NMR yields were determined by removing a sample with a syringe, drying it under vacuum, extracting the residue with $CDCl_3$, and filtering the solution in an NMR tube. The obtained yields are the average values of three runs.

X-ray Diffraction Studies. Structure Determination and Refinement. Single crystals of **1b** and **2ab** suitable for X-ray diffraction studies were selected from batches of crystals obtained at −32 °C from acetonitrile/diethylether and CH_2Cl_2 /diethylether solutions, respectively. Diffraction data for all crystals were collected on a Nonius Kappa-CCD area detector diffractometer using graphite-monochromated Mo- $K\alpha$ radiation (λ = 0.71073 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 ϕ angle), each at 20 s exposure. The structures were solved using direct methods with SHELXS-97 and refined against F^2 for all reflections using the SHELXL-97 software.⁴² Multiscan absorption corrections (MULSCANABS in PLATON) were applied.⁴³ 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.

■ ASSOCIATED CONTENT

■ Supporting Information

CIF files giving X-ray structural data, including data collection parameters, positional and thermal parameters, and bond distances and angles for complexes **1b** and **2ab**. 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 publications nos. CCDC 824508 (**1b**) and 824507 (**2ab**), respectively. Copies of the data can be obtained free of charge from the CCDC via www.ccdc.cam.ac.uk/data_request/cif.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: vrileng@unistra.fr (V.R.), michael.chetcuti@unistra.fr (M.J.C.). Tel: + 33 3 68 85 26 31.

■ ACKNOWLEDGMENTS

A.M.O. thanks the Ministère de l'Enseignement Supérieur et de la Recherche for a doctoral fellowship. We are grateful to the CNRS and the University of Strasbourg for their financial help. Dr. Lydia Brelot is gratefully acknowledged for her work with the X-ray structure resolutions. We appreciate the assistance of

Mr. Michel Schmitt in obtaining the $^1H/^{13}C$ HSQC correlation for complex **2ac**.

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- (32) Isolated free carbene Mes₂NHC **a** was used. The formation of the cyanomethyl complex [Ni(Mes₂NHC)(CH₂CN)Cp] can, therefore, not result from the reaction with unreacted base.
- (33) Crystal data for **1b**: C₁₂H₁₆N₃Ni·BF₄, FW = 347.80; triclinic, $P\bar{1}$; $a = 6.8787(6)$ Å, $b = 10.1410(8)$ Å, $c = 10.8037(9)$ Å; $\alpha = 97.351(2)^\circ$, $\beta = 93.501(2)^\circ$, $\gamma = 93.098(2)^\circ$; $V = 744.59(11)$ Å³; $Z = 2$; $D_{\text{calcd}} = 1.551$ mg·m⁻³; $\mu = 1.340$ mm⁻¹; $T = 173(2)$ K; crystal form, color = block, green; crystal size = $0.48 \times 0.40 \times 0.30$, $h_{\text{max}} = 9$, $k_{\text{max}} = 14$, $l_{\text{max}} = 12$; $T_{\text{min}} = 0.5655$, $T_{\text{max}} = 0.6893$; 10 183 collected reflns, 4643 independent, 4182 with $I > 2\sigma(I)$, $R = 0.0392$, $wR^2 = 0.0986$; GOF = 1.060.
- (34) Crystal data for **2ab**: C₃₁H₃₇N₄Ni·F₆P, FW = 669.33; monoclinic, $P2_1/c$; $a = 9.1782(2)$ Å, $b = 18.5195(6)$ Å, $c = 18.6420(6)$ Å, $\beta = 97.070(2)^\circ$; $V = 3144.59(16)$ Å³; $Z = 4$; $D_{\text{calcd}} = 1.414$ mg·m⁻³; $\mu = 0.731$ mm⁻¹; $T = 173(2)$ K; crystal form, color = prism, green; crystal size = $0.46 \times 0.22 \times 0.15$, $h_{\text{max}} = 11$, $k_{\text{max}} = 24$, $l_{\text{max}} = 24$; 23 130 collected reflns, 7155 independent, 5568 with $I > 2\sigma(I)$, $R = 0.0510$, $wR^2 = 0.1450$; GOF = 1.042.
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