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Synthesis and Catalytic Activity in Suzuki Coupling of Nickel Complexes Bearing *n*-Butyl- and Triethoxysilylpropyl-Substituted NHC Ligands: Toward the Heterogenization of Molecular Catalysts

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Supporting Information

ABSTRACT: Cyclopentadienyl N-heterocyclic carbene (NHC) nickel complexes of general formula [Ni(R-NHC-*n*Bu)XCp] [R-NHC-*n*Bu = 1-butyl-3-methyl-, 1-isopropyl-3-butyl-, 1-(2,4,6-trimethylphenyl)-3-butyl-, 1-(2,6-diisopropylphenyl)-3-butyl-imidazol-2-ylidene; X = Cl or I; Cp = η^{5} -C₅H₅], which bear an *n*-butyl side-chain attached to one of the nitrogen



atoms of the NHC ring, were synthesized as models for trialkoxysilylpropyl-substituted complexes. They were prepared by the direct reactions of nickelocene with the corresponding imidazolium salts (R-NHC-nBu·HX). The new complexes [Ni(Me-NHCnBu)ClCp] (1a), [Ni(*i*Pr-NHC-nBu)ClCp] (1b), [Ni(Ph-NHC-nBu)ICp] (1c), [Ni(Mes-NHC-nBu)ICp] (1d), and [Ni(iPr2Ph-NHC-nBu)ICp] (1e) were obtained in moderate to good yields and were fully characterized by standard spectroscopic techniques, and in the cases of 1a,b,d,e by single-crystal X-ray crystallography. The bulky electron-rich pentamethylcyclopentadienyl derivatives, [Ni(Mes-NHC-*n*Bu)ICp*] (2d) and [Ni(*i*Pr₂Ph-NHC-*n*Bu)ICp*] (2e) (Cp* = η^{5} -C₅Me₅), were prepared from reactions of *in situ* prepared [Ni(acac)Cp*] with the corresponding carbene precursors. Both Cp* complexes were also fully characterized spectroscopically, and their structures were established by single-crystal X-ray crystallography. All new complexes catalyzed the Suzuki-Miyaura cross-coupling of phenylboronic acid with aryl halides in the absence of cocatalysts or reductants. However, the small dialkyl-substituted species 1a and 1b proved to be the least efficient. In addition, in contrast to our previous results with the closely related diaryl-substituted species $[Ni(Ar_3NHC)LCp^{\dagger}]$ (L = Cl⁻, NCMe (PF_6^-); $Cp^\dagger = Cp$, Cp^*), in which complexes that bear the electron-rich Cp^* ligand were much more active than those bearing the Cp ligand, no substantial catalytic behavior differences were observed between the Cp complexes 1d,e and their Cp* counterparts 2d,e. A TOF of up to 352 h^{-1} , a so far unprecedented rate for nickel(II) complexes under similar conditions, was even observed with the Cp complex 1d. In view of these encouraging results, the triethoxysilylpropyl-substituted analogue of 1d, [Ni(Mes-NHC-TES)ClCp] (1d-TES) (Mes-NHC-TES = 1-(2,4,6-trimethylphenyl)-3-[3-(triethoxysilyl)propyl]imidazol-2ylidene), was prepared, fully characterized, and tested catalytically. As it showed similar catalytic activity to 1d, it was heterogenized on alumina to give 1d-Al. The latter species, however, exhibited a greatly reduced catalytic activity compared to 1d and 1d-TES. Possible reasons for both the excellent activities of 1d and 1d-TES and the disappointing activity of 1d-Al are discussed.

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}

Although nickel offers significant potential advantages compared to its more widely used d^{10} counterpart, palladium, including a much lower cost⁶ and a reduced tendency to aggregate and agglomerate into less active large metallic nanoclusters,⁷ its chemistry with NHC ligands has been much less studied than that of palladium.^{2b} Nevertheless, the

past decade has seen the emergence of a number of NHCnickel-based catalytic systems that have now found applications in a vast number of organic transformations, including notably in traditional C–C cross-coupling reactions,^{8–12} the amination¹³ and dehalogenation^{13b,14} of aryl halides, the oxidation of secondary alcohols,^{15,16} C–S couplings,¹⁷ the activation of C– F bonds,^{18,19} the hydrosilylation of internal alkynes,²⁰ threecomponent couplings of unsaturated hydrocarbons, aldehydes, and silyl derivatives,²¹ and [2+2+2] cycloadditions.^{22–24} In this context, we have recently reported that the neutral [Ni-(Ar₂NHC)ClCp[†]] and cationic [Ni(Ar₂NHC)(NCCH₃)Cp[†]]-(PF₆) [Ar₂NHC = 1,3-diarylimidazol-2-ylidene, Cp[†] = Cp (η^{5} -

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Received: November 9, 2011 Published: February 2, 2012 C_5H_5), Cp^* (η^5 - C_5Me_5)] half-sandwich complexes are efficient precatalysts for the fast Suzuki coupling of aryl halides.^{25,26} 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,^{9,27} have been observed.

The relative dearth of effective, nonpolluting, truly recyclable and inexpensive catalysts for the syntheses of fine organic chemicals on large scales²⁸ generates an increasing demand for supported versions of homogeneous catalysts.²⁹ Among the possible practical strategies for separating and recycling active catalysts,³⁰ the immobilization of homogeneous catalysts on solid supports appears particularly attractive because it should combine the advantages of heterogeneous catalysis (i.e., easy product isolation and catalyst recycling) with the versatility of homogeneous catalysis. Compared to expensive organic polymers,³¹ inorganic metal oxide materials are common supports for the heterogenization of molecular catalysts due to their excellent thermal and chemical stability.³² In addition, they possess high surface areas, and organic groups can be robustly anchored on to the surface hydroxyl groups. As a Nbonded *n*-butyl side arm could serve as a model for a threecarbon linker between a carbene ring and a trialkoxysilane functional group condensed on the surface of a metal oxide (Scheme 1), we believed it was of interest (i) to replace one of

Scheme 1. *n*-Butyl Side Arm As a Model for a Three-Carbon Linker between a NHC Ring and a Si(OR)₃ Anchoring Group



the NHC-aryl substituents of our complexes²⁵ by an *n*-butyl group and study its influence on the catalytic activity of the resulting complexes and (ii) if the results were satisfying, to prepare a trialkoxysilyl-functionalized analogue of the best *n*-butyl-substituted catalyst precursor and then heterogenize the latter.

Herein, we describe the synthesis of a series of cyclopentadienyl [Ni(R-NHC-*n*Bu)XCp] (R = Me, *i*Pr, Ph, Mes, *i*Pr₂Ph; X = Cl, I) and pentamethylcyclopentadienyl [Ni(Ar-NHC-*n*Bu)ICp^{*}] (Ar = Mes, *i*Pr₂Ph) complexes that bear an *n*-butyl side chain attached to one of the nitrogen atoms of the NHC ring and discuss their structural and spectroscopic features. Their catalytic activity in the Suzuki–Miyaura cross-coupling of aryl halides with phenylboronic acid is then presented and compared to the results we have previously obtained under similar conditions with the related symmetrically substituted [Ni(Ar₂NHC)LCp[†]] species.²⁵ The best TOF reported for Ni(II) complexes in the absence of reductant and cocatalyst^{9,25} was observed with one of the new complexes. We also present the synthesis and catalytic activity of its

triethoxysilylpropyl-substituted derivative, the immobilization of the latter onto alumina, and the catalytic activity of the resulting heterogenized catalyst.

RESULTS AND DISCUSSION

a. Synthesis of [Ni(R-NHC-*n*Bu)XCp] Complexes. The Cp complexes [Ni(Me-NHC-*n*Bu)ClCp] (1a), [Ni(*i*Pr-NHC-*n*Bu)ClCp] (1b), [Ni(Ph-NHC-*n*Bu)ICp] (1c), [Ni(Mes-NHC-*n*Bu)ICp] (1d), and [Ni(*i*Pr₂Ph-NHC-*n*Bu)ICp] (1e) all bear a dangling *n*-butyl side arm on their NHC ligands and were obtained in respectable yields (49–68%) from the reaction of nickelocene and the imidazolium salts $\mathbf{a}-\mathbf{e}^{33,34}$ by using the standard synthetic methods that were established for other Ni(NHC)Cp complexes (Scheme 2).^{35–37} All complexes were isolated as air-stable dark red to violet solids and were characterized by ¹H and ¹³C{¹H} NMR spectroscopy, elemental analysis, or electrospray mass spectroscopy, and in the cases of 1a,b,d,e by X-ray crystallography.

The spectroscopic features of complexes 1a-e are typical of neutral [Ni(NHC)XCp] species previously characterized by us³⁵ and others.^{36,37} The carbene carbon is observed in the 158-168 ppm range in the ¹³C NMR spectrum, while the Cp carbon atoms appear at ca. 91-92 ppm, as it is the case for the other neutral complexes of this type. 35-37 The Cp protons resonate as a singlet in the ¹H NMR spectra of 1a and 1b, in the same range as is observed for the Cp protons of the other known alkyl-substituted complexes [Ni(Me₂NHC)ICp]³⁸ $(Me_2NHC = 1,3-dimethylimidazol-2-ylidene)$ and $[Ni{Me-$ NHC- $(CH_2)_2CN$ [ICp] (Me-NHC- $(CH_2)_2CN = 1$ -propylnitrile-3-methylimidazol-2-ylidene),^{35b} at 5.2–5.3 ppm. The Cp protons of 1c-e appear between 4.8 and 4.9 ppm, as do those of their mixed alkyl-aryl-substituted analogues, 35b,37 and are slightly downfield of the signals seen between 4.5 and 4.6 ppm for [Ni(Ar₂NHC)CpX] complexes that bear symmetrically substituted diarylimidazol-2-ylidene ligands.^{35a,36} While the ¹H and ${}^{13}C{}^{1}H$ NMR spectra of 1a-c are straightforward, it is noteworthy that 1b and 1c exhibit signals for diastereotopic NCH₂ and NCH₂CH₂ protons at ambient temperature. The room-temperature ¹H NMR spectra of the more sterically congested compounds 1d and 1e are more complex and feature a number of broad signals. For example, the two meta-hydrogen atoms of the mesityl ring of 1d are isochronous but are displayed as a broad singlet, while the two ortho-methyl groups are not equivalent and appear as two broad singlets in a 3:3 relative integrated ratio, and the NCH₂ protons are diastereotopic and appear as two broad signals. At 263 K, all signals are sharp: the meta-protons of the aromatic ring resonate as two separate singlets in a 1:1 integrated ratio, and the three methylene groups appear as three pairs of nonequivalent multiplets. In the case of 1e, all signals are sharp at 253 K. At this temperature, the methylene protons resonate as three pairs of nonequivalent multiplets, the metaprotons of the aromatic ring appear as two doublets in a 1:1 integrated ratio, and the two isopropyl groups are displayed as four doublets in a 3:3:3:3 integrated ratio and two septets in a

Scheme 2. Preparation of the Cyclopentadienyl Nickel-NHC Complexes



Scheme 3. Preparation of the Pentamethylcyclopentadienyl Nickel-NHC Complexes



1:1 relative integrated ratio. We can therefore conclude that complexes 1d and 1e exist as single rotamers at low temperature.

Similar dynamic behavior and temperature-dependent ¹H NMR spectra have been previously observed for the very closely related [Ni(Mes-NHC-nBu)BrCp]³⁷ and [Ni{Mes- $NHC-(CH_2)_4CN ICp]^{35b} (Mes-NHC-(CH_2)_4CN = 1-(2,4,6$ trimethylphenyl)-3-(butylnitrile)imidazol-2-ylidene) complexes, as well as for the symmetrically substituted and sterically congested Cp* complex [Ni(Mes₂NHC)ClCp*] (Mes₂NHC = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene),³⁸ and have been attributed to restricted rotation about the Ni-carbene and N-C bonds. The origin of these restricted rotations is not obvious, and hydrogen bonding between the halide and one of the NCH₂ protons has been invoked as a possible explanation for [Ni(Mes-NHC-nBu)BrCp].³⁷ However, such restricted rotation is not observed in the closely related analogue $[Ni{Mes-NHC-(CH_2)_3CN}ClCp]$ (Mes-NHC-(CH_2)_3CN = 1-(2,4,6-trimethylphenyl)-3-(propylnitrile)imidazol-2-ylidene),³⁹ which bears a small but more electronegative chloride instead of a more bulky bromide or iodide, and with [Ni(Mes₂NHC)ClCp],^{36,40} which bear the less bulky Cp ligand instead of the large Cp*. Furthermore, there are no especially short H...X interactions in any of the solid-state structures reported here (vide infra). Thus, in the cases of 1d and 1e, it is probably the presence of the voluminous iodide and its steric interactions with the Ar-NHC-nBu and Cp groups that hamper the free rotation about the Ni-carbene and N-C bonds. As regards the Ni-carbene bond in particular, a minor electronic component cannot be excluded since a number of studies show that π -bonding with NHC ligands may be far from negligible.41

b. Synthesis of [Ni(Ar-NHC-*n*Bu)ICp*] Complexes. The Cp* complexes [Ni(Mes-NHC-*n*Bu)ICp*] (2d) and [Ni- $(iPr_2Ph-NHC-nBu)ICp^*$] (2e) were obtained from the reaction of *in situ* prepared [Ni(acac)Cp*]⁴² with the imidazolium iodides d and e by using the procedure recently developed in our laboratory (Scheme 3).³⁸ Both complexes were isolated as dark red crystals in moderate yields (30–34%). Good spectroscopic data were obtained, and both molecular structures were established by X-ray diffraction studies.

The spectroscopic features of complexes **2d** and **2e** are similar to those of the neutral [Ni(NHC)XCp*] species previously characterized by us.³⁸ Thus, in their ¹³C NMR spectra, the signals of the carbene carbons are downfield of the signals seen for their corresponding Cp derivatives **1d**,**e** and are observed in the 175–178 ppm range. The Cp* carbon atoms appear at ca. 101–102 (C_5 Me₅) and 10–11 (C_5 Me₅) ppm, as is the case for the other complexes of this type.³⁸ In their ¹H NMR spectra, the Cp* protons resonate as a singlet at ca. 1.3– 1.5 ppm and are located in between the signals seen at ca. 1.1– 1.2 ppm for [Ni(Ar₂NHC)ClCp*] complexes and at 1.60 ppm for [Ni(Me₂NHC)ICp*].³⁸

Both compounds exhibit diastereotopic NCH₂ and NCH₂CH₂ protons at ambient temperature, and all signals are sharp. The two meta-hydrogen atoms and the two orthomethyl groups of the mesityl ring of 2d are not equivalent on the NMR time scale and appear as four singlets in a 1:1 and 3:3 relative integrated ratio. Similarly, the ¹H NMR spectrum of 2e at room temperature displays four doublets and two pseudoseptets in a 3:3:3:3 and 1:1 relative integrated ratio for the ortho-isopropyl groups of the aromatic ring, as well as two doublets in a 1:1 ratio for the meta-hydrogen atoms. Hence, in contrast to their Cp analogues 1d and 1e, which exist as single rotamers at low temperature, the sterically congested Cp* complexes 2d and 2e already exist as single rotamers at ambient temperature. This tends to confirm that the observed restricted rotation about the Ni-carbene and N-C bonds in 1d,e and 2d,e are mainly due to steric factors. Nevertheless a minor electronic component to this increased hindrance to free rotation in 2d,e cannot be excluded since the downfield shift of the ¹³C signal of the carbone carbons of 2d,e may indicate increased $\bar{\pi}$ -back-donation from the more electron-rich nickel atoms in these complexes.^{38,43}

c. Structural Studies. The structures of [Ni(Me-NHC*n*Bu)ClCp] (1a), [Ni(*i*Pr-NHC-*n*Bu)ClCp] (1b), [Ni(Mes-NHC-*n*Bu)ICp] (1d), [Ni(*i*Pr₂Ph-NHC-*n*Bu)ICp] (1e), [Ni-(Mes-NHC-*n*Bu)ICp*] (2d), and [Ni(*i*Pr₂Ph-NHC-*n*Bu)-ICp*] (2e), each containing an asymmetric NHC ligand with an *n*-butyl arm, were established by X-ray diffraction studies. Crystals suitable for X-ray structure determination were grown from toluene/pentane solutions at -32 °C for all complexes. Crystallographic data and data collection parameters are listed in Table S1 for complexes 1a,b and in Table S2 for complexes 1d,e and 2d,e (see the Supporting Information). Key bond lengths and bond angles are collected in Table 1 for complexes

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

	1a	1b (molecule A)	1b (molecule B)
Ni-C(1)	1.878(2)	1.887(5)	1.863(5)
Ni-Cl	2.1947(6)	2.1926(15)	2.1859(18)
Ni-Cp _{cent} ^a	1.768	1.769	1.759 ^b
Ni $-C_{Cp}$ av ^c	2.126	2.133	2.137 ^b
C(1)–Ni–Cl	95.26(7)	93.66(16)	93.86(17)
C(1)–Ni–Cp _{cent}	132.8	133.8	134.2
Cl-Ni-Cp _{cent}	131.9	132.4	131.9

 ${}^{a}Cp_{cent}$ = centroid of the Cp group. ${}^{b}The$ Cp ring in molecule B is rotationally disordered over two equally populated sites, and the positional esd's are relatively large. The centroid and the average Ni– C_{cp} distance is based on all 10 Cp carbons. ${}^{c}Average$ Ni–C distance to the Cp ring.

1a,b and in Table 2 for complexes 1d,e and 2d,e. Complex 1b

crystallizes in the $P2_1/c$ space group with two independent

Table 2.	Select	ed Bond	l Length	s (Å) a	and Ar	ngles	(deg)	for
Complex	xes 1d,	1e, 2d,	and 2e v	vith Es	sd's in	Pare	nthese	es

	1d	1e	2d	2e
Ni-C(1)	1.886(4)	1.884(3)	1.891(3)	1.888(6)
Ni-I	2.5222(7)	2.5099(5)	2.5187(5)	2.5374(9)
Ni $-Cp^{\dagger}_{cent}^{a}$	1.761	1.759	1.761	1.765
Ni–C _{Cp†} av ^b	2.124	2.131	2.139	2.138
C(1)-Ni-I	97.28(13)	95.53(10)	96.43(11)	95.18(19)
$C(1)$ -Ni- Cp_{cent}	134.8	134.7	135.7	137.0
I-Ni-Cp _{cent}	127.9	129.7	127.5	127.1
$^{a}Cp^{\dagger}_{cent} = centroid$	of the Cp or	Cp* group.	^b Average Ni-	-C distance

to the Cp or Cp* ring.

molecules (A and B) in the unit cell; one of these (molecule A) exhibits some disorder of the *n*-butyl arm and the other (molecule B) some rotational disorder of the Cp* ligand, but the general geometric features of both molecules are similar. Figure 1 shows molecule A of **1b** with only one position of the



Figure 1. Molecular structures of [Ni(Me-NHC-nBu)ClCp] (1a) and of [Ni(iPr-NHC-nBu)ClCp] (1b) showing all non-H atoms. Ellipsoids are shown at the 50% probability level, and key atoms are labeled. Only molecule A of 1b, with one position of the *n*-butyl arm, is shown.

n-butyl arm. The structure of 1a is also depicted in Figure 1. The molecular structures of 1d and 1e are shown in Figure 2, and those of complexes 2d and 2e in Figure 3. Note that complex 2e exhibits some disorder of the *n*-butyl arm: only one position is depicted in Figure 3.

The molecular structures of these complexes are closely related to each other and to those established for similar $[Ni(NHC)XCp^{\dagger}]$ complexes,^{35b,36–39} in particular for the asymmetrically substituted $[Ni\{Me-NHC-(CH_2)_2CN\}ICp]^{35b}$ and $[Ni\{Mes-NHC-(CH_2)_3CN\}CICp]$.^{35b,39} The nickel atom is bonded to a η^5 -Cp (1a,b,d,e) or Cp* (2b,d) group, a NHC



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Figure 2. Molecular structures of [Ni(Mes-NHC-nBu)ICp] (1d) and of $[Ni(iPr_2Ph-NHC-nBu)ICp]$ (1e) showing all non-H atoms. Ellipsoids are shown at the 50% probability level, and key atoms are labeled.



Figure 3. Molecular structures of $[Ni(Mes-NHC-nBu)ICp^*]$ (2d) and of $[Ni(iPr_2Ph-NHC-nBu)ICp^*]$ (2e) showing all non-H atoms. Ellipsoids are shown at the 50% probability level, and key atoms are labeled. Only one position of the *n*-butyl arm of 2e is shown.

moiety, and a halide ligand in all molecules; if one consider the Cp or Cp* group as a single ligand, the metal lies at the center of a pseudotrigonal plane. The sum of the angles subtended at the nickel atom by the Cp or Cp* ligand centroid, the halogen

,	B(OH) ₂ + Br	1a-2e K₃PO₄ Toluene / 110°C	A	\prec°
entry	cat. (mol %)	$t \pmod{t}$	conversion $(\%)^b$	A/B ratio ^b
1	1a (1)	60	81 ^c	80/20
2	1b (1)	60	87 ^c	80/20
3	1d (3)	60	$78^{d,e}$	B n.d. ^f
4	1d (3)	60	86 ^{<i>d</i>}	B n.d. ^f
5	1d (1)	60	91 ^{<i>d</i>}	B n.d. ^f
6	1d (1)	60	99 ^c	B n.d. ^f
7	1d (1)	15	88 ^c	B n.d. ^f
8	1d (0.5)	60	53 ^c	B n.d. ^f
9	1e (3)	60	88 ^d	B n.d. ^f
10	2e (1)	60	88 ^d	B n.d. ^f
11	1d-TES (1)	60	97 ^c	B n.d. ^f
12	1d-Al (3)	60	43^c	B n.d. ^f

Table 3. Suzuki–Miyaura Cross-Coupling of 4'-Bromoacetophenone with Phenylboronic Acid Catalyzed by Complexes 1a-2e, 1d-TES, and 1d-Al^a

^{*a*}Reaction conditions: 4'-bromoacetophenone (1.0 mmol), phenylboronic acid (1.3 mmol), K_3PO_4 (2.6 mmol), catalyst (1–3 mol %), toluene (3.0 mL), 110 °C. ^{*b*}NMR yield, average value of three runs. ^{*c*}Schlenk tube loaded in a glovebox with $H_2O < 0.5$ ppm, $O_2 < 0.5$ ppm. ^{*d*}Reaction run under Schlenk tube techniques. ^{*e*}Run at 90 °C. ^{*f*}n.d. = not detected.

atom, and the carbene carbon atom of the NHC ligand is indeed almost exactly 360°. There are, however, significant departures from the idealized 120° angles of a trigonal-planar structure for all six molecules (Tables 1 and 2). The carbenoid carbon C(1) and the halide Cl (1a,b) or I (1d,e and 2d,e) subtend an angle of 95.5 \pm 2° at the nickel atom. These values are in the range of those observed for the closely related [Ni{Me-NHC-(CH₂)₂CN}ICp]^{35b} and [Ni{Mes-NHC-(CH₂)₃CN}ClCp],^{35b,39} for which values of 93.4(2)°/92.9(2) ° and 98.41(9)° have been determined, respectively.

The nickel-carbene bond lengths lie in the narrow ranges of 1.863(5) - 1.886(6) Å for the complexes with R = alkyl and X = Cl (1a,b, Table 1) and of 1.884(3)-1.891(4) Å for the complexes with R = aryl and X = I (1d,e and 2d,e, Table 2), and are therefore not significantly different from each other. These values are comparable to those reported for [Ni{Me-NHC- $(CH_2)_2CN$ ICp $(1.884(6)/1.866(7) \text{ Å})^{35b}$ and $[Ni-{Mes-NHC-(CH_2)_3CN}CICp]$ $(1.882(3) \text{ Å})^{35b}$ as well as for [Ni(NHC)XCp*] complexes (1.880(4)-1.906(3) Å).³⁸ The Ni-Cl distances of 2.1947(6) Å in 1a and of 2.1926(6)/ 2.1859(18) Å in 1b are close to the Ni-Cl distances observed in related [Ni(NHC)ClCp] complexes.^{35b,36a-c,37} The Ni–I distances in 1d and 1e (2.5222(7) and 2.5099(5) Å) are comparable to those observed in the more sterically congested Cp* complexes 2d and 2e (2.5187(5) and 2.5374(9) Å) and to those reported for [Ni(Me₂NHC)ICp],³⁸ [Ni{Me-NHC-(CH₂)₂CN}ICp],^{35b} and [Ni(Me₂NHC)ICp*],³⁸ where values of 2.5006(6), 2.5083(10)/2.4979(10), and 2.5212(5) Å were observed, respectively.

In all six structures, the η^{5} -C₅R₅ rings exhibit structural distortions with significant variations in both the C_{Cp†}-C_{Cp†} and Ni-C_{Cp†} distances. Such variations have been occasionally observed in other Ni(η^{5} -C₅R₅) systems and arise from "allyl-ene", "diene", or intermediate distortions (between "ally-ene" and "diene") of the η^{5} -C₅R₅ ring.^{44,45} Thus, "diene" distortions are observed in complexes **1a**, **1b**, **1e**, **2d**, and **2e**, and intermediate distortions are seen in complex **1d** (see Scheme S1 in the Supporting Information).

In contrast to what has been observed in some related complexes,³⁷ there are no short intramolecular contacts in any

of these complexes and thus no evidence of any intramolecular hydrogen bonding. In addition there is no evidence of any intermolecular hydrogen bonding in any of the unit cells. The crystal structure of **1e** exhibits unusually large channels that nevertheless appear to be void of potential solvent molecules.

d. Suzuki–Miyaura Cross-Coupling of Aryl Halides. The catalytic activities of the new half-sandwich nickel(II) complexes 1a–2e, which bear an *n*-butyl arm on their NHC ligand, were examined for the coupling of 4'-bromoacetophenone with phenylboronic acid under the standard conditions established with their symmetrically substituted analogues $[Ni(Ar_2NHC)LCp^{\dagger}]$,²⁵ i.e., with 1.3 equiv of PhB(OH)₂ and 2.6 equiv of K₃PO₄ in toluene at 90–110 °C (Table 3). No additive such as PPh₃ was necessary, as is often the case in other systems.^{9c-f,27a,c} All complexes are catalytically active and give the desired product 4-acetylbiphenyl in good to excellent yield in 15 to 60 min, which are fast reaction times for nickelcatalyzed Suzuki couplings. Typical reaction times, indeed, usually range under similar conditions from 1–2 h at best to 12–24 h at worst.^{9,27}

Relatively good conversion to the coupling product was observed with 3 mol % of 1d at 90 °C (Table 3, entry 3). Increasing the temperature to 110 °C slightly improved the yield (entry 4), but more interestingly, decreasing the catalyst loading 1 mol % did not affect the reaction and 91% conversion could be observed after 60 min with 1d (entry 5). This is in sharp contrast to what had been observed with the symmetrically substituted analogues [Ni(Ar₂NHC)LCp^{\dagger}], which bear a small chloride or acetonitrile ligand instead of a voluminous iodide, and for which decreasing the catalyst loading led to decreased conversions, thereof indicating fast catalyst deactivation.²⁵ Nevertheless, it is worth mentioning that significant yield variations were observed between each of the three catalytic runs that were conducted for these table entries (entries 3-5). Since these reactions had been conducted by using standard Schlenk techniques, we presumed that these variations were due to small amounts of O₂, which was entering the catalytic reactor when the solvent was added (see Experimental Section) and which was progressively deactivating the highly air-sensitive active species. To prevent such O₂ contamination, we then decided to load the catalytic reactors in a glovebox with H_2O and O_2 levels below 0.5 ppm (see Experimental Section). Under these conditions, no irregular yield variations were observed. Indeed, we even observed significant improvements. Thus, with a catalyst loading of 1 mol % of 1d, the coupling reaction was almost quantitative after 60 min (entry 6), and a conversion of 88% was observed after only 15 min of reaction (entry 7), leading to a turnover frequency (TOF) of 352 h^{-1} . This is even better than the TOF of 190 h^{-1} we recently reported with $[Ni{(iPr_2Ph)_2NHC}(NCMe)Cp^*]$ - (PF_6) [(*i*Pr₂Ph)₂NHC = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene]²⁵ and is, to our knowledge, the best TOF observed so far in Suzuki-Miyaura cross-coupling catalyzed by a Ni(II) complex in the *absence* of reductant and cocatalyst.^{9,25,27,46} Nevertheless, we note that further decreasing the catalyst loading to 0.5 mol % led to a conversion of only 53% after 60 min (entry 8), which indicates that the limits of our system in terms of turnovers lie close to the 1 mol % range.

In contrast to $[Ni{(iPr_2Ph)_2NHC}ClCp]$, which bears bulky iPr_2Ph groups and gave better results than $[Ni(Mes_2NHC)-ClCp]$,²⁵ no improvement was observed with 1e compared to 1d (entry 9 vs entry 4). In addition, in contrast to the bulky, electron-rich $[Ni(Ar_2NHC)LCp^*]$ complexes, which gave much better results than their Cp analogues,²⁵ no enhanced catalysis was registered with the Cp* complex 2e (entry 10 vs entry 5). Finally, a greatly decreased selectivity was noted with the small species, 1a and 1b, that bear an alkyl instead of an aryl substituent on the NHC ring, and a chloride instead of an iodide on the nickel atom. Significant amounts of the homocoupling product, 4,4'-diacetylbiphenyl, were indeed formed with these complexes (entries 1 and 2).

A few comments concerning the reaction mechanism can be made. We have suggested²⁵ that the active catalytic species is a Ni(0) complex that is generated by initial reduction of the Ni(II) precursor by homocoupling of phenylboronic acid.^{27,47} Such initial reduction to a highly air-sensitive Ni(0) species is further corroborated by the observed catalyst deactivation when small amounts of O2 accidentally entered the Schlenk tubes. Also, in our previous report, the absence of a significant reactivity difference between the neutral [Ni(Ar₂NHC)ClCp[†]] complexes and the cationic $[Ni(Ar_2NHC)(NCMe)Cp^{\dagger}](PF_6)$ species, which bear labile acetonitrile ligands, suggested that the necessary generation of a vacant site might arise through Cp or Cp* ring slippage rather than halide or acetonitrile dissociation.^{25,48} The significant stabilization of the active species with the bulky iodide-containing catalyst precursors 1d-2e tends to confirm this hypothesis. The n-butyl arm indeed seems too small and too far from the metal center to exert such an influence. Moreover, the absence of improvement with 1e and 2e (with respect to 1d) shows that neither a possible faster reduction from the starting Ni(II) complex to the active Ni(0)species (as may be expected with the more electron-rich Cp* species) nor an even better steric protection of the active center (as expected with a *i*Pr₂Ph substituent instead of a Mes substituent and/or a Cp* ligand instead of a Cp ligand) seems to play a significant role anymore in the presence of the highly protecting iodide ligand.

In view of these unexpected but interesting results, some aspects of the catalytic potential of the new [Ni(Ar-NHC-*n*Bu)ICp] catalyst precursors **1d**,**e** were examined with a short series of aryl bromides and chlorides bearing electron-withdrawing and electron-donating substituents (Table 4). Good yields of 4-acetylbiphenyl were obtained from 4'-

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$\langle \rangle$	-B(OH) ₂ + X-	R Holuene / 110°C	
Entry	Cat (mol%)	Aryl halide	Conversion $(\%)^b$
1	1d (3)	CI-CI-CO	76
2	1e (3)	ci	77
3	1d (1)	Br	46
4	1d (1)	CI-	23
5	1d (1)	Br	27
6	1e (1)	ci	10 ^c
7	1d (1)	Br-NH ₂	$28^{c,d}$
8	1d (3)	Br-NO2	0
9	1d (1)	Br	$67^{e_{f,g}}$

Table 4. Suzuki–Miyaura Cross-Coupling of Aryl Chlorides and Bromides with Phenylboronic Acid Catalyzed by 1d and $1e^{a}$

^{*a*}Reaction conditions: aryl halide (1.0 mmol), phenylboronic acid (1.3 mmol), K_3PO_4 (2.6 mmol), 1d or 1e (1–3 mol %), toluene (3 mL), 110 °C, 1 h. ^{*b*}NMR yield. ^{*c*}Isolated yield. ^{*d*}22% of biphenyl. ^{*e*}12% of dehalogenation product. ^{*f*}GC-MS yield. ^{*g*}2 h of reaction.

chloroacetophenone with both catalysts (entries 1 and 2). The electron-donating substrates 4-bromotoluene and 4chlorotoluene were however converted to the desired coupling products in lower yields (entries 3 and 4), and even lower yields were observed with the sterically hindered 2-bromo- and 2-chlorotoluene (entries 5 and 6), which is rather disappointing since other Ni(II)-based catalysts convert these substrates very efficiently.^{9,27} Nevertheless, good conversion was obtained for the cross-coupling of bromonaphthalene with phenylboronic acid (entry 9). In the case of 4'-bromoaniline (entry 7), side reactions occurred in addition to the desired coupling, as large amounts of biphenyl (resulting from the homocoupling of phenylboronic acid) and of aniline (resulting from the dehalogenation of 4'-bromoaniline) were detected. Finally, no reaction occurred with the electronically deactivated 1-bromo-4-nitrobenzene (entry 8).

This short series of electronically activated and deactivated aryl halides shows that the reaction scope of the [Ni(Ar-NHC-n-Bu)ICp] catalyst precursors **1d** and **1e** is of the same order as that of the related symmetric complexes [Ni(Ar₂NHC)LCp^{*}] (Ar = Mes, L = Cl; Ar = iPr₂Ph, L = NCMe, PF₆⁻) species.²⁵ Thus, a decreased activity was noticed for both types of complexes with the electron-donating substrates. Nevertheless, compared to the active species generated by the symmetric catalysts [Ni(Ar₂NHC)LCp^{*}] bearing either a chloride or an acetonitrile ligand, those formed by the *n*-butyl compounds **1d**,e, bearing a voluminous iodide ligand, are much more stable

Organometallics

and allow the reduction of the catalyst loading, which is crucial in the perspective of a heterogenized version. Moreover, these species are able to catalyze Suzuki–Miyaura cross-coupling in the absence of additives, which is also a key point for a potential heterogenized version of this catalyst.

e. Synthesis and Catalytic Activity of Trialkoxysilylpropyl-Substituted Complexes. Since the presence of an iodide ligand bound to the nickel atom seemed crucial for a stable catalytically active species, initial studies focused on the syntheses of the iodo complexes [Ni(Ph-NHC-TMS)ICp] (1c-TMS), [Ni(Mes-NHC-TMS)ICp] (1d-TMS), and [Ni(*i*Pr₂Ph-NHC-TMS)ClCp] (1e-TMS). These were obtained by direct reaction, in refluxing DME, of nickelocene with 1-phenyl-3-[3-(trimethoxysilyl)propyl]imidazolium iodide,³³ 1-(2,4,6-trimethylphenyl)-3-[3-(trimethoxysilyl)propyl]imidazolium iodide,³³ or 1-(2,6-diisopropylphenyl)-3-[3-(trimethoxysilyl)propyl]-imidazolium iodide, respectively.³³ Unfortunately, purification of the trimethoxysilyl-functionalized 1c-, 1d-, and 1e-TMS complexes proved to be very difficult, as neither crystallization nor column chromatography could be employed for these species. The complexes remained immobilized onto the silica or alumina by condensation of the trimethoxysilyl groups with the surface hydroxyl groups. Thus, their ¹H NMR spectra always revealed important traces of the ligand precursor and of several hydrolysis products.

Consequently, subsequent studies focused on the synthesis of triethoxysilyl-functionalized complexes, which proved to be more robust toward hydrolysis than trimethoxysilyl-substituted compounds. Thus, reaction of nickelocene with $1-(2,4,6-trimethylphenyl)-3-[3-(triethoxysilyl)propyl]imidazolium chloride (d-TES)⁴⁹ in DME at reflux afforded [Ni(Mes-NHC-TES)ClCp] (1d-TES), which was isolated as a violet oil of satisfying purity in 71% yield after column chromatography (Scheme 4). The new complex was characterized by ¹H and ¹³C{¹H} NMR spectroscopy and electrospray mass spectroscopy.$

Scheme 4. Preparation of the Triethoxysilyl-Functionalized Nickel-NHC Complex 1d-TES



The ¹H and ¹³C{¹H} NMR spectra of complex 1d-TES at ambient temperature present no anomalies and show the presence of one η^5 -Cp group and of the functionalized NHC ligand. The carbene carbon is observed at 162.9 ppm in the ¹³C NMR spectrum, while the Cp carbon atoms appear at 91.8 ppm. The Cp protons resonate at 4.72 ppm in the ¹H NMR spectrum. These values are close to those observed for its nbutyl-substituted analogue 1d (vide supra). Nevertheless, in contrast to the room-temperature ¹H NMR spectrum of 1d, in which the two meta-hydrogen atoms of the mesityl ring are equivalent on the NMR time scale and are displayed as one broad singlet, the two ortho-methyl groups appear as two broad singlets in a 3:3 relative integrated ratio, and the NCH₂ protons are diastereotopic, the room-temperature ¹H NMR spectrum of 1d-TES displays the two meta-hydrogen atoms of the mesityl ring as a sharp singlet, the two ortho-methyl groups as one

broad singlet, and the NCH₂ protons as one broad signal. Thus, in comparison to 1d, which bears a bulky iodide ligand, the triethoxysilvl-functionalized complex 1d-TES, which carries a smaller chloride ligand, shows greatly reduced rotational barriers at room temperature. This result confirms the prevalent role played by the voluminous iodide ligand in complexes 1d,e in hampering free rotation about the Ni-carbene and N-C bonds. However, since the very closely related complex [Ni{Mes-NHC-(CH₂)₃CN}ClCp],^{35b,39} which bears an alkylnitrile side arm, and the symmetric compound [Ni- $(Mes_2NHC)ClCp$]³⁶ do not show any rotational barrier at all on the NMR time scale at room temperature, this also demonstrates that despite its far-off position to the nickel atom, the bulky dangling triethoxysilylpropyl arm is noninnocent with respect to the dynamic processes in 1d-TES and may to some extent play a protecting role. Thus, although 1d-TES does not carry a protecting iodide ligand, we still decided to investigate its catalytic activity. Satisfyingly, 1d-TES also shows good activity for the coupling of phenylboronic acid with 4'bromoacetophenone; 97% conversion to 4-acetylbiphenyl was observed after 60 min of reaction at 110 °C with a catalyst loading of 1 mol % (Table 3, entry 11). In light of these results, we decided to heterogenize it and study the catalytic activity of the resulting supported complex.

f. Immobilization of [Ni(Mes-NHC-TES)CICp] (1d-TES) onto Alumina and Catalytic Activity of the Heterogenized Complex. The complex [Ni(Mes-NHC-TES)CICp] (1d-TES) was covalently grafted onto alumina by condensation of the triethoxysilyl groups with the surface hydroxyls by refluxing 1d-TES in the presence of alumina in toluene for 4 h. The alumina-tethered complex 1d-AI was obtained as a pink solid, which was characterized by standard solid-state spectroscopies (see the Experimental Section). The data suggested that complex 1d-TES was intact and had been successfully immobilized onto the alumina surface.

The catalytic activity of the immobilized complex 1d-Al was next evaluated for the coupling of 4'-bromoacetophenone with phenylboronic acid under the standard conditions established for its nongrafted analogues. The desired product, 4acetylbiphenyl, was obtained in only 43% yield after 1 h of reaction with 3 mol % of 1d-Al (Table 3, entry 12). This conversion is markedly lower than those observed with 1-3 mol % of the nongrafted analogues 1d-2e, which bear an iodide ligand (Table 3, entries 3-10). It is also much lower than that observed with 1d-TES, which does not bear an iodide ligand but bears the very bulky dangling triethoxysilylpropyl arm (Table 3, entry 11). The disappointing activity observed with 1d-Al may thus be attributed to the instability of the active species generated by 1d-Al in the absence of any protecting group; 1d-Al indeed does not bear an iodide ligand, and the bulky dangling anchoring arm of 1d-TES may have lost its (supposed) protecting properties in 1d-Al, as it is now condensed to the alumina surface and is therefore less mobile. However, the activity of 1d-Al is also lower than that observed for [Ni(Mes₂NHC)ClCp], for which 68% conversion were observed after 30 min of reaction with a catalyst loading of 3 mol %.²⁵ Moreover, despite a better selectivity, it is also lower than what is seen for the alkyl-substituted and chloridecontaining species 1a,b (Table 3, entries 1 and 2). This disappointing activity may thus also be attributed (at least partially) to the heterogenization itself, which may render the active sites more difficult to reach by the substrates.

CONCLUSION

Direct reaction of imidazolium salts bearing a N-bound *n*-butyl or triethoxysilylpropyl arm with nickelocene or *in situ* prepared [Ni(acac)Cp*] allowed the preparation of the corresponding [Ni(R-NHC-*n*Bu)XCp] (1a-e), [Ni(Ar-NHC-*n*Bu)ICp*] (2d,e), and [Ni(Mes-NHC-TES)ClCp] (1d-TES) complexes in moderate to good yields. The latter was grafted onto alumina.

Single-crystal X-ray diffraction studies of complexes 1a,b,d,e and 2d,e revealed that these compounds have geometric features common to all $[Ni(R_2NHC)XCp^{\dagger}]$ compounds. Nevertheless, ¹H NMR data of the iodide-containing complexes $[Ni(Ar-NHC-nBu)ICp^{\dagger}]$ 1d,e and 2d,e revealed restricted rotation about the Ni–carbene and N–C bonds at room temperature. The origin of these hampered rotations is believed to be mainly steric in nature and is attributed to the presence of the voluminous iodide ligand. Accordingly, in contrast to 1d, its triethoxsilylpropyl analogue, [Ni(Mes-NHC-TES)CICp] (1d-TES), which carries a smaller chloride ligand, shows greatly reduced (but not equal to zero) rotation barriers at room temperature.

The new complexes $[Ni(Ar-NHC-nBu)ICp^{\dagger}]$ **1d,e** and **2e** efficiently catalyze the cross-coupling of phenylboronic acid with aryl halides in the absence of cocatalysts or reductants.²⁵ Moreover, in contrast to the results observed with their symmetric analogues $[Ni(Ar_2NHC)LCp^{\dagger}]$ (L = Cl⁻; NCMe, PF₆⁻),²⁵ no substantial activity difference was observed between the Cp complexes **1d,e** and their Cp* counterpart **2e**, and a TOF of up to 352 h⁻¹ was even observed with the Cp complex **1d**. The significant stabilization of the active species, which allowed this very high TOF for a nickel(II) complex under similar conditions, is attributed to the presence of the voluminous iodide ligand, which would play a highly protecting role.

Despite the absence of a protecting iodide ligand, the triethoxsilylpropyl-substituted complex **1d-TES** is as efficient as **1d**. This surprisingly high activity with respect to what is observed with other chloride-containing complexes²⁵ may be attributed to the presence of the bulky dangling triethoxsilylpropyl arm. This group may indeed play a protecting role, as suggested by its noninnocent behavior with respect to the dynamic processes in **1d-TES**. Accordingly, the activity drop observed with the alumina-tethered compound **1d-Al** may be attributed, at least partially, to the absence of a protecting group.

Thus, our quest to heterogenize half-sandwich NHCnickel(II) complexes $[Ni(NHC)LCp^{\dagger}]$ onto a metal oxide and to evaluate the effect of the substitution of one aryl substituent on the NHC ring by an *n*-butyl arm led us to the serendipidous discovery of the important role that may be played by the "spectator" ligand L or a bulky dangling NHC side arm in protecting the active species.

EXPERIMENTAL SECTION

General Comments. All reactions were carried out using standard Schlenk or glovebox techniques under an atmosphere of dry argon. Solvents were distilled from appropriate drying agents under argon prior to use. Unless otherwise specified, 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 ¹³C{¹H}. A ¹H 2D COSY spectrum was obtained for complex **2e** to help in the ¹H signal assignments. The assignments of the ¹³C{¹H} NMR spectra were

made with the aid of DEPT 13 C spectra for all complexes and $^{1}H/^{13}$ C HSQC correlation for complex 2e. The chemical shifts are referenced to residual deuterated solvent peaks. Chemical shifts (δ) and coupling constants (*J*) are expressed in ppm and Hz, respectively. The 1 H NMR variable-temperature experiments with complexes 1d and 1e were recorded at 400 MHz in CDCl₃ from 298 to 253 K. Electrospray mass spectra were recorded on a MicrOTOF 66 mass spectrometer. Elemental analyses were performed by the Service d'Analyses, de Mesures Physiques et de Spectroscopie Optique, UMR CNRS 7177, Institut de Chimie, Université de Strasbourg. DRIFT and ¹H MAS NMR were performed by the Unité de Catalyse et de Chimie du Solide, UMR CNRS 8181, Université de Lille I, France. Vibrational frequencies are expressed in cm⁻¹. ICP-AES was performed by the Laboratoire de Chimie Analytique et Minérale, UMR CNRS 7178, Institut Pluridisciplinaire Hubert Curien, Université de Strasbourg. Commercial compounds were used as received. The imidazolium salts $a_{j}^{33} b_{j}^{34} c-e_{j}^{33}$ and $c_{j} d_{j} e^{-TMS_{j}^{33}}$ nickelocene_j^{35a} and [Ni(acac)-Cp^{*}]³⁸ were prepared according to published procedures. The imidazolium salt d-TES was prepared according to a slightly modified version of microwave-assisted procedures that have been reported for the synthesis of other silane-substituted imidazolium halides.44

Synthesis of [Ni(Me-NHC-nBu)ClCp] (1a). Nickelocene (553 mg, 2.93 mmol) and 1-butyl-3-methylimidazolium chloride a (339 mg, 1.94 mmol) were refluxed for 4 h in thf (20 mL). The solvent was then removed in vacuo, the residue was extracted with hot toluene (20 mL), and the extract was filtered through Celite, which was subsequently rinsed with toluene $(3 \times 5 \text{ mL})$ until the washings were colorless. The resulting solution was then concentrated under vacuum and passed though a neutral silica chromatography column and eluted with ethyl acetate/pentane (8.5:1.5) to give a red solution. After solvent removal, crystallization from toluene/pentane (1:2) at -32 °C gave 1a (282 mg, 0.948 mmol, 49%) as dark red needles. ES-MS: m/z [M]⁺ calcd for C13H19N2Ni 261.090, found 261.089. ¹H NMR (CDCl3, 300.13 MHz): δ 6.91 (s, 2H, NCH), 5.22 (s, 5H, C₅H₅), 4.75 (br, 2H, NCH₂), 4.33 (s, 3H, NCH₃), 1.94 (br, 2H, NCH₂CH₂), 1.51 (m, 2H, CH₂CH₃), 1.05 (t, 3H, CH₃, ${}^{3}J$ = 7.4). ${}^{13}C{}^{1}H$ NMR (CDCl₃, 75.47 MHz): δ 159.8 (NCN), 123.5 (NCH), 121.8 (NCH), 91.7 (C₅H₅), 51.7 (NCH₂), 38.9 (NCH₃), 33.2 (NCH₂CH₂), 20.2 (CH₂CH₃), 14.0 (CH₂).

Synthesis of [Ni(*i***Pr-NHC-***n***Bu)ClCp] (1b). Nickelocene (176 mg, 0.932 mmol) and 1-isopropyl-3-butylimidazolium chloride b (189 mg, 0.932 mmol) were refluxed in DME (9 mL) for 2 h. The resulting dark red solution was cooled to room temperature, and the solvent removed** *in vacuo***. Column chromatography over neutral silica with diethyl ether as eluent afforded 1b** (175 mg, 0.538 mmol, 58%) as dark red crystals after solvent evaporation. ES-MS: m/z [M]⁺ calcd for C₁₅H₂₃N₂Ni 289.121, found 289.122. ¹H NMR (CDCl₃, 300.13 MHz): δ 6.96 (d, 1H, NCH, ³J = 2.1), 6.94 (d, 1H, NCH, ³J = 2.1), 6.47 (septet, 1H, NCHMe₂, ³J = 6.8), 5.22 (s, 5H, C₅H₅), 4.90 and 4.70 (2 m, 2 × 1H, NCH₂), 2.01 and 1.88 (2 m, 2 × 1H, NCH₂CH₂), 1.52 (d + m, 6 H+ 2H, NCHMe₂ and CH₂CH₃), 1.06 (t, ³J = 7.5, 3H, CH₃). ¹³C{¹H} NMR (CDCl₃, 75.47 MHz): δ 158.2 (NCN), 122.2 (NCH), 118.1 (NCH), 91.8 (C₅H₅), 53.8 (NCHMe₂), 51.7 (NCH₂), 33.3 (NCH₂CH₂), 23.8 (NCHMe₂), 20.3 (CH₂CH₃), 14.0 (CH₃).

Synthesis of [Ni(Ph-NHC-nBu)ICp] (1c). Nickelocene (123 mg, 0.651 mmol) and 1-phenyl-3-butylimidazolium iodide c (213 mg, 0.649 mmol) were refluxed for 16 h in DME (12 mL). The solution slowly turned from dark green to dark red. The solvent was then removed in vacuo, the residue was extracted with toluene (10 mL), and the extract was filtered through Celite, which was rinsed with toluene until the washings were colorless. The resulting solution was concentrated to dryness and recrystallized from toluene/pentane (1:4) to afford 1c (194 mg, 0.430 mmol, 66%) as red crystals, which were washed with pentane $(3 \times 3 \text{ mL})$ and dried under vacuum. Anal. Calcd for C₁₈H₂₁IN₂Ni: C, 47.94; H, 4.69; N, 6.21. Found: C, 48.00; H, 4.82; N, 6.06. ¹H NMR (CDCl₃, 300.13 MHz): δ 8.07 (d, 2H, Ph), 7.57 (m, 3H, Ph), 7.15 (d, 1H, NCH, ${}^{3}J = 1.9$), 7.11 (d, 1H, NCH, ${}^{3}J =$ 1.9), 5.17 (m, 1H, NCH₂), 4.90 (s, 5H, C₅H₅), 4.58 (m, 1H, NCH₂), 2.01 and 1.91 (2 m, 2 × 1H, NCH₂CH₂), 1.55 (m, 2H, CH₂CH₃), 1.07 (t, 3H, CH_3 , ${}^{3}J = 7.3$). ${}^{13}C{}^{1}H$ NMR (CDCl₃, 75.47 MHz): δ 165.9

(NCN), 140.9 (*ipso*- C_{Ar}), 129.1 and 126.5 (*o*-/*m*- C_{Ar}), 128.6 (*p*- C_{Ar}), 123.7 and 122.6 (NCH), 92.0 (C_5H_5), 53.2 (NCH₂), 32.9 (NCH₂CH₂), 20.3 (CH₂CH₃), 14.1 (CH₃).

Synthesis of [Ni(Mes-NHC-nBu)ICp] (1d). Nickelocene (380 mg, 2.01 mmol) and 1-(2,4,6-trimethylphenyl)-3-butylimidazolium iodide d (753 mg, 2.03 mmol) were refluxed for 20 h in DME (30 mL). The solution slowly turned from dark green to dark red. The solvent was then removed in vacuo, and unreacted nickelocene was extracted with pentane $(3 \times 5 \text{ mL})$. Column chromatography over neutral silica with diethyl ether/pentane (7:3) and then toluene as eluents afforded 1d (612 mg, 1.24 mmol, 62%) as a deep red-violet solid after solvent evaporation. ES-MS: m/z [M]⁺ calcd for C₂₁H₂₇N₂Ni 365.1522, found 365.1503. ¹H NMR (CDCl₃, 263 K, 400.14 MHz): δ 7.16 (s, 2H, m-H and NCH), 6.99 (s, 1H, m-H), 6.87 (s, 1H, NCH), 5.47 (m, 1H, NCH₂), 4.88 (s, 5H, C₅H₅), 4.36 (m, 1H, NCH₂), 2.47 (s, 3H, o-Me), 2.42 (s, 3H, p-Me), 2.01 and 1.90 (2 m, 2 × 1H, NCH₂CH₂), 1.74 (s, 3H, o-Me), 1.48 and 1.44 (2 m, 2×1 H, CH₂CH₃), 1.05 (t, 3H, CH₃) ${}^{3}J$ = 7.3). ¹H NMR (CDCl₃, 298 K, 400.14 MHz): δ 7.15 (s, 1H, NCH), 7.03 (br, 2H, m-H), 6.86 (s, 1H, NCH), 5.44 (br, 1H, NCH₂), 4.89 (s, 5H, C₅H₅), 4.42 (br, 1H, NCH₂), 2.49 (br, 3H, o-Me), 2.42 (s, 3H, p-Me), 2.00 (br, 2H, NCH₂CH₂), 1.74 (br, 3H, o-Me), 1.51 (br, 2H, CH₂CH₃), 1.07 (t, 3H, CH_{3} , ${}^{3}J$ = 7.3). ${}^{13}C{}^{1}H$ NMR (CDCl₃, 75.47 MHz): δ 166.4 (NCN), 139.1 and 136.9 (ipso-/p-C_{Ar}), 137.9 and 134.4 (o-CAr), 130.1 and 128.6 (br, m-CAr), 124.4 and 122.5 (NCH), 91.8 (C₅H₅), 53.6 (NCH₂), 33.1 (NCH₂CH₂), 21.3 (*p*-Me), 20.1 (CH₂CH₃), 18.0 (br, o-Me), 14.1 (CH₃).

Synthesis of [Ni(iPr₂Ph-NHC-nBu)ICp] (1e). Nickelocene (566 mg, 3.00 mmol) and 1-(2,6-diisopropylphenyl)-3-butylimidazolium iodide e (1.25 g, 3.03 mmol) were refluxed for 39 h in DME (40 mL). The solution slowly turned from dark green to dark red. The solvent was then removed in vacuo, and unreacted nickelocene was extracted with pentane $(4 \times 5 \text{ mL})$. Column chromatography over neutral silica with diethyl ether/pentane (7:3) as eluent afforded 1e (1.060 g. 1.98 mmol, 66%) as a violet solid after solvent evaporation. ES-MS: m/z $[M]^{\scriptscriptstyle +}$ calcd for $C_{24}H_{33}N_2Ni$ 407.1992, found 407.1946. 1H NMR $(CDCl_3, 253 \text{ K}, 400.14 \text{ MHz}): \delta 7.54 (t, 1H, p-H, ^3J = 6.8), 7.46 (d, 1H, 2000)$ 1H, m-H, ${}^{3}J = 6.8$), 7.26 (d, 1H, m-H, ${}^{3}J$ n.r.), 7.16 (d, 1H, NCH, ${}^{3}J =$ 1.7), 6.93 (d, 1H, NCH, ${}^{3}J$ = 1.7), 5.48 (m, 1H, NCH₂), 4.80 (s, 5H, C_5H_5), 4.37 (m, 1H, NCH₂), 3.41 (sept, 1H, CHMe₂, ³J = 6.8), 2.01 and 1.91 (2 m, 2 × 1H, NCH₂CH₂), 1.72 (sept, 1H, CHMe₂, ${}^{3}J$ = 6.8), 1.46 (d, 3H, CHMe₂, ${}^{3}J$ = 6.8 and m, 2H, CH₂CH₃), 1.20 (d, 3H, CHMe₂, ${}^{3}J$ = 6.8), 1.05 (d, 3H, CHMe₂, ${}^{3}J$ = 6.8 and t, 3H, CH₃, ${}^{3}J$ = 7.2), 0.97 (d, 3H, CHMe₂, ${}^{3}J$ = 6.8). ${}^{1}H$ NMR (CDCl₃, 298 K, 300.13 MHz): δ 7.54 (t, 1H, p-H, ${}^{3}J$ = 6.8), 7.47 (br, 1H, m-H), 7.26 (br, 1H, *m*-H), 7.15 (d, 1H, NCH, ³J = 1.7), 6.92 (d, 1H, NCH, ³J = 1.7), 5.49 (br, 1H, NCH₂), 4.82 (s, 5H, C₅H₅), 4.44 (br, 1H, NCH₂), 3.52 (br, 1H, CHMe₂), 2.01 (br, 2H, NCH₂CH₂), 1.78 (br, 1H, CHMe₂), 1.49 (br, 5H, CHMe₂ and CH₂CH₃), 1.22 (br, 3H, CHMe₂), 1.08 (t, 3H, CH_{3} , ${}^{3}J = 7.2$), 1.03 (br, 6H, CHMe₂). ${}^{13}C{}^{1}H$ NMR (CDCl₃, 75.47 MHz): δ 167.9 (NCN), 148.4 and 145.5 (br, o-C_{Ar}), 136.7 (ipso-C_{Ar}), 130.2 (p-C_{Ar}), 126.1 and 122.0 (NCH), 124.9 and 123.4 (br, m-C_{Ar}), 91.6 (C5H5), 54.0 (NCH2), 33.1 (NCH2CH2), 28.7 and 28.2 (b, CHMe₂), 26.9 and 26.1 (br, CHMe₂), 23.7 and 22.6 (br, CHMe₂), 20.1 (CH_2CH_3) , 14.1 (CH_3) .

Synthesis of [Ni(Mes-NHC-nBu)ICp*] (2d). To a freshly prepared suspension of [Ni(acac)Cp*]³⁸ (0.851 mmol) in thf (5 mL) was added 1-(2,4,6-trimethylphenyl)-3-butylimidazolium iodide d (315 mg, 0.851 mmol) suspended in thf (5 mL), and the reaction mixture was stirred at reflux for 3 h. The resulting deep violet suspension was cooled to room temperature, and the solvent removed in vacuo. The residue was extracted with toluene (5 mL) and filtered through silica, which was rinsed with toluene $(4 \times 5 \text{ mL})$ until the washings were colorless. Concentration to ca. 1 mL followed by addition of pentane (2 mL) and crystallization at -32 °C afforded 2d (145 mg, 0.257 mmol, 30%) as a dark red solid, which was washed with pentane $(3 \times 3 \text{ mL})$ and dried under high vacuum. ¹H NMR (C₆D₆, 300.13 MHz): δ 6.87 (s, 1H, m-H), 6.66 (s, 1H, m-H), 6.38 (s, 1H, NCH), 6.00 (d, 1H, NCH), 4.93 (m, 2H, NCH₂), 2.95 (s, 3H, o-Me), 2.14 (s, 3H, p-Me), 1.89 (m, 1H, NCH₂CH₂), 1.57 (s, 3H, o-Me), 1.46 (s, 15H, C₅Me₅), 1.39 (m, 1H, NCH₂CH₂ and m, 2H,

CH₂CH₃), 0.94 (t, 3H, CH₃, ${}^{3}J$ = 7.2). ${}^{13}C{}^{1}H$ NMR (C₆D₆, 75.47 MHz): δ 175.4 (NCN), 138.1 and 138.0 (o-C_{Ar}), 136.6 and 134.6 (*ipso-/p*-C_{Ar}), 130.1 and 128.3 (*m*-C_{Ar}), 124.6 and 119.9 (NCH), 101.3 (C₅Me₅), 53.7 (NCH₂), 32.3 (NCH₂CH₂), 23.7 (o-Me), 20.6 (*p*-Me), 20.3 (CH₂CH₃), 18.4 (o-Me), 13.8 (CH₃), 10.7 (C₅Me₅).

Synthesis of [Ni(iPr₂Ph-NHC-nBu)ICp*] (2e). To a freshly prepared suspension of [Ni(acac)Cp*]³⁸ (1.00 mmol) in thf (10 mL) was added 1-(2,6-diisopropylphenyl)-3-butylimidazolium iodide e (323 mg, 0.783 mmol) in a single portion, and the reaction mixture was stirred at reflux for 3 h. The resulting red-violet suspension was cooled to room temperature, and the solvent removed in vacuo. The residue was extracted with toluene (10 mL) and filtered through silica, which was rinsed with toluene $(3 \times 10 \text{ mL})$ until the washings were colorless. Concentration to ca. 1 mL followed by addition of pentane (10 mL) and crystallization at -32 °C afforded 2e (160 mg, 0.264 mmol, 34%) as a dark red solid, which was washed with pentane $(3 \times$ 3 mL) and dried under high vacuum. Anal. Calcd for C₂₉H₄₃IN₂Ni: C, 57.55; H, 7.16; N, 4.63. Found: C, 57.62; H, 7.06; N, 4.28. ¹H NMR $(CDCl_3, 300.13 \text{ MHz}): \delta 7.44 \text{ (m, 2H, m-H)}, 7,21 \text{ (dd, 1H, p-H, }^3J =$ 6.4), 7.13 (d, 1H, NCH, ${}^{3}J = 1.8$), 6.87 (d, 1H, NCH, ${}^{3}J = 1.8$), 5.38 and 4.78 (2 m, 2 × 1H, NCH₂), 4.28 (septet, 1H, CHMe₂-A, ${}^{3}J$ = 6.8), 2.05 and 1.83 (2 m, 2 × 1H, NCH₂CH₂), 1.98 (septet, 1H, CHMe₂-B, ${}^{3}J = 6.8$), 1.59 (m, 2H, CH₂CH₃), 1.42 (d, 3H, CHMe₂-A, ${}^{3}J = 6.8$), 1.30 (s, 15H, C_5Me_5), 1.24 (d, 3H, CHMe₂-B, ³J = 6.8), 1.12 (d, 3H, CHMe₂-B, ${}^{3}J = 6.8$), 1.08 (t, 3H, CH₂CH₃, ${}^{3}J = 7.4$), 0.87 (d, 3H, CHMe₂-A, ${}^{3}J = 6.8$). ${}^{13}C{}^{1}H$ NMR (CDCl₃, 75.47 MHz): δ 178.3 (NCN), 148.4 and 145.8 (o-CAr), 136.4 (ipso-CAr), 129.9 (m-CAr), 126.8 (NCH), 125.2 (m-C_{Ar}), 123.7 (p-C_{Ar}), 119.9 (NCH), 101.8 (C₅Me₅), 54.7 (NCH₂), 33.2 (NCH₂CH₂), 29.3 (CHMe₂-A), 28.2 (CHMe₂-B), 28.0 (CHMe₂-B), 25.9 (CHMe₂-A), 23.2 (CHMe₂-A), 23.0 (CHMe₂-B), 20.6 (CH₂CH₃), 14.3 (CH₃), 10.8 (C₅Me₅).

Synthesis of [Ni(Mes-NHC-TES)CICp] (1d-TES). Nickelocene (126 mg, 0.667 mmol) and 1-(2,4,6-trimethylphenyl)-3-[3-(triethoxysilyl)propyl]imidazolium chloride (d-TES) (285 mg, 0.667 mmol) were refluxed for 30 min in DME (10 mL). The resulting dark red suspension was cooled to room temperature, and the solvent removed in vacuo. Column chromatography over neutral silica with diethyl ether/pentane (7:3) as eluent afforded 1d-TES (261 mg, 0.474 mmol, 71%) as a violet oil after solvent evaporation. ES-MS: $m/z [M]^+$ calcd for C₂₆H₃₉N₂NiO₃Si 513.2078, found 513.2059. ¹H NMR (CDCl₃, 300.13 MHz): δ 7.17 (s, 1H, NCH), 7.08 (s, 2H, *m*-H), 6.82 (s, 1H, NCH), 5.00 (br, 2H, NCH₂), 4.72 (s, 5H, C₅H₅), 3.87 (q, 6H, $Si(OCH_2CH_3)_{3}$, ${}^{3}J = 6.9$), 2.43 (s, 3H, p-Me), 2.25 (m, 2H, CH₂), 2.11 (br, 6H, o-Me), 1.26 (t, 9H, Si(OCH₂CH₃)₃, ${}^{3}J$ = 6.9), 0.79 (m, 2H, CH₂Si). ¹³C{¹H} NMR (CDCl₃, 75.47 MHz): δ 162.9 (NCN), 139.2 and 137.0 (ipso-/p-C_{Ar}), 136.2 (br, o-C_{Ar}), 129.2 (m-C_{Ar}), 123.4 and 123.1 (NCH), 91.8 (C₅H₅), 58.7 (Si(OCH₂CH₃)₃), 54.3 (NCH₂), 25.2 (CH₂), 21.4 (p-Me), 18.5 (Si(OCH₂CH₃)₃), 18.4 (o-Me), 7.9 (CH₂Si).

Immobilization of [Ni(Mes-NHC-TES)ClCp] (1d-TES) onto Alumina. Alumina (3.70 g, 36.3 mmol) was introduced into a Schlenk tube and dried under vacuum overnight at 110 °C. A solution of 1d-TES (200 mg, 0.364 mmol) in toluene (15 mL) was added, and the resulting suspension refluxed for 4 h with vigorous stirring. After cooling the suspension to room temperature, toluene was removed by filtration and the solid washed with hot CH₂Cl₂ (6 × 10 mL). The resulting pink solid was then dried overnight under high vacuum to give the supported complex 1d-Al. ICP-AES: Ni, 2.84 mg·g⁻¹ (0.0484 mmol·g⁻¹). ¹H MAS NMR (400.14 MHz, 14 kHz, 128 transients): δ 6.9 (NCH and *m*-H), 4.6 (Cp and NCH₂), 3.4 (*p*-Me and Si(OCH₂CH₃)_{3-n}), 2.1 (*o*-Me), 1.3 (Si(OCH₂CH₃)_{3-n}). DRIFT (64 scans): ν (O-H); 3509 (s); ν (Csp²-H); 3131 (m), 3087 (m); ν (Csp³-H) 2979 (m), 2930 (s), 2890 (s), 2831 (m); ν (C=C) 1610 (w), 1565 (w), 1488 (m), 1456 (m).

General Procedure for Suzuki–Miyaura Cross-Coupling Reactions Using Standard Schlenk Techniques. A Schlenk tube equipped with a septum was charged with aryl halide (1.0 mmol), phenylboronic acid (1.3 mmol), K_3PO_4 (2.6 mmol), and catalyst (1.0–3.0 mol %) before being put under an atmosphere of argon. Toluene (3 mL) was injected, and the mixture immediately heated with

Organometallics

vigorous stirring by putting the Schlenk into an oil bath at 90 or 110 °C. After 15-120 min, the reaction was stopped by cooling the reaction to room temperature and allowing air to enter in the Schlenk tube. GC yields were calculated by using tetradecane as an internal standard. NMR yields were determined by removing a sample with a syringe, drying it under vacuum, extracting the residue with CDCl₃, and filtering the solution into the NMR tube. In a standard workup, the solvent was completely removed under vacuum. The residue was extracted with a 1:1 mixture of diethyl ether/water (20 mL). The organic layer was separated, and the aqueous layer extracted with another 10 mL portion of diethyl ether. The combined extracts were washed with water $(2 \times 10 \text{ mL})$ and dried over Na₂SO₄. The solvent was removed under reduced pressure, and the crude material was purified by column chromatography over SiO₂ with pentane/ethyl acetate as eluent to give the desired product. All yields are the average values of three runs.

General Procedure for Suzuki–Miyaura Cross-Coupling Reactions Using Standard Glovebox Techniques. In a glovebox with levels of H_2O and $O_2 < 0.5$ ppm, a Schlenk tube equipped with a glass stopper was charged with aryl halide (1.0 mmol), phenylboronic acid (1.3 mmol), K_3PO_4 (2.6 mmol), and a toluene solution (3 mL) containing 1.0–3.0 mol % of catalyst. The Schlenk tube was then taken outside the glovebox, and the mixture immediately heated with vigorous stirring by putting the Schlenk tube into an oil bath at 110 °C. After 15–120 min, the reaction was stopped by cooling the reaction to room temperature and allowing air to enter in the Schlenk tube. GC and NMR yields were determined as for the reactions carried out under standard Schlenk techniques. Standard workups were similar to those of the reactions carried out under standard Schlenk techniques.

X-ray Diffraction Studies. Structure Determination and Refinement. Single crystals of 1a,b,d,e and 2d,e suitable for X-ray diffraction studies were selected from batches of crystals obtained at -32 °C from toluene/pentane solutions for all compounds. Diffraction data for all crystals were collected at 173(2) K on a Nonius Kappa-CCD area detector diffractometer using graphitemonochromated Mo K α radiation ($\lambda = 0.71073$ Å). A summary of crystal data, data collection parameters, and structure refinements is given in Tables S1 and S2 (see the Supporting Information). Cell parameters were determined from reflections taken from one set of 10 frames $(1.0^{\circ} \text{ steps in phi angle})$, 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.⁵⁰ Multiscan absorption corrections (MULscanABS in PLATON) were applied.51 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

S Supporting Information

Scheme S1 illustrating the distortions in the η^{5} -C₅R₅ ligands of complexes **1a–2e**, Tables S1 and S2, giving X-ray crystallographic data and data collection parameters for complexes **1a,b,d,e** and **2d,e**, 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,d,e** and **2d,e**. 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 846657 (**1a**), 846658 (**1b**), 846659 (**1d**), 846660 (**1e**), 846661 (**2d**), and 846662 (**2e**). 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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DEDICATION

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