# Half-sandwich NHC-nickel(II) complexes as pre-catalysts for the fast Suzuki coupling of aryl halides: a comparative study† ‡

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Cationic half-sandwich nickel complexes of general formula  $[Ni(NHC)(NCMe)(\eta^5-C_5R_5)](PF_6)$ [NHC = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr) a, 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (IMes)  $\mathbf{b}$ ;  $\mathbf{R} = \mathbf{H}$ , Me] were prepared from the reaction of their neutral homologues  $[Ni(NHC)Cl(\eta^5-C_sR_s)]$  with 1 equiv. of KPF<sub>6</sub> in acetonitrile at room temperature. The new cationic complexes [Ni(IPr)(NCMe)( $\eta^{5}$ -C<sub>5</sub>Me<sub>5</sub>)](PF<sub>6</sub>) **3a**, [Ni(IMes)(NCMe)( $\eta^{5}$ -C<sub>5</sub>Me<sub>5</sub>)](PF<sub>6</sub>) **3b** and  $[Ni(IMes)(NCMe)(\eta^5-C_5H_5)](PF_6)$  **4b** were obtained in high yield and were fully characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy, IR spectroscopy, elemental analyses, and in the case of **3a** by a single-crystal X-ray diffraction study. The neutral analogue of **3a**,  $[Ni(IPr)Cl(\eta^5-C_5Me_5)]$  **1a** was also structurally characterized. Their geometries were compared and no significant structural differences were observed. Nevertheless solution NMR spectroscopy established that the acetonitrile ligand of the cationic species is labile in solution. This results in the absence of any rotational significant barrier about the nickel-carbone carbon bond at ambient temperature in solution in the sterically congested cationic complexes **3a** and **3b**, in contrast to their neutral analogues **1a** and  $[Ni(IMes)Cl(\eta^5-C_5Me_5)]$  **1b**. The neutral and the cationic complexes catalyzed the cross-coupling of phenylboronic acid with aryl halides in the absence of co-catalysts or reductants. Surprisingly, the neutral or cationic nature of the complexes proved to have almost no influence on the reaction yields and rates. However, complexes bearing the bulky electron-rich pentamethylcyclopentadienyl ligand were much more active than those bearing the cyclopentadienyl ligand, and TOF of up to 190 h<sup>-1</sup>, a high rate for nickel(II) complexes under similar conditions, were observed with these species.

# Introduction

Since the first isolation of a stable imidazol-2-ylidene,<sup>1</sup> Nheterocyclic carbenes (NHCs) have become a very important class of ligands in organometallic chemistry.<sup>2</sup> NHCs behave like typical strong  $\sigma$ -donor<sup>3</sup> ligands with non-negligible  $\pi$ -acceptor abilities.<sup>4</sup> These electronic characteristics are similar to those of tertiary phosphines, and they show similar abilities to stabilize the various oxidation states and coordinatively unsaturated intermediates that appear in catalytic reactions.<sup>2,5</sup> However, NHCs show superior performances in many aspects over traditional trialkyl- and triarylphosphine ligands, including versatility, ready preparation, thermal-, air- and moisture-stability, as well as nontoxicity. In addition, NHCs exhibit superior qualities regarding ligand dissociation<sup>6</sup> and degradative cleavage,<sup>7</sup> both of which are less likely as compared to tertiary phosphines.8 Both properties lead to a higher complex stability. Moreover, carbene complexes have shown unprecedented catalytic activity under homogeneous conditions in many important organic reactions.<sup>2</sup>

The chemistry of Ni-NHC complexes has been much less investigated than that of Pd-, Ru- or even Rh-NHC complexes.<sup>2</sup> However, the last decade has seen the emergence of a number of NHC-Ni(0) systems, generally generated in situ from a Ni(0) compound such as Ni(COD)2 and a NHC ligand, or from a Ni(II) compound, a NHC ligand and an excess of reductant. These species were shown to be efficient catalysts in the amination of aryl chlorides,9 C-S couplings,10 cross-coupling reactions of fluorinated arenes,11 three-component couplings of unsaturated hydrocarbons, aldehydes and silyl derivatives,<sup>12</sup> and [2+2+2] cycloadditions.13,14,15 The major disadvantages of these systems are the air-sensitivity of the Ni(0) species and/or the necessity of an excess of reductant,<sup>9b-d,12f,13d</sup> which generates large amounts of waste. To overcome this inconvenience, much recent effort has been devoted to the development of well-defined air-stable Ni(II) complexes bearing electron-rich NHC ligands<sup>3a,16</sup> that are able to catalyze organic reactions without external reductants. Such species catalyze the amination of aryl halides,<sup>17</sup> the hydrothiolation of alkynes,<sup>18</sup> the base-free Michael addition<sup>19</sup> and the  $\alpha$ arylation of acyclic ketones<sup>17a</sup> (where no organometallic partner is involved), as well as Suzuki,<sup>20</sup> Kumada<sup>20c,21</sup> and Negishi<sup>22</sup> C-C cross-couplings reactions, in which the organometallic reagent (ArB(OH)<sub>2</sub>, ArMgX, ArZnX) is known to help reduce Ni(II) to Ni(0).23,24

However, despite (i) the high importance of developing efficient syntheses of biaryl compounds that are found in natural products,<sup>25</sup> drugs<sup>26</sup> or materials,<sup>27</sup> (ii) the much lower cost and easier removal of nickel from the product<sup>28</sup> (with respect to its

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<sup>&</sup>lt;sup>‡</sup> Throughout this manuscript,  $Cp = \eta^{5}-C_{5}H_{5}$ ,  $Cp^{*} = \eta^{5}-C_{5}Me_{5}$ , IPr = a = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene, IMes = b = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene.

	$Cp^{\delta}$	NCH=CHN	Ar	Ref.
1a <sup>b</sup>	1.12 (Cp*)	6.64	7.39 (d, 2H, <i>m</i> -H, ${}^{3}J$ = 7.6), 7.30 (t, 2H, <i>p</i> -H), 7.08 (d, 2H, <i>m</i> -H), 4.19 (m, 2H, CHMe <sub>2</sub> ), 2.29 (m, 2H, CHMe <sub>2</sub> ), 1.61 (d, 6H, CHMe <sub>2</sub> , ${}^{3}J$ = 6.8), 1.23 (d, 6H, CHMe <sub>2</sub> ,	29
3a <sup>c</sup>	0.88 (Cp*)	7.51	${}^{3}J = 6.8$ , 1.06 (d, 6H, CH $Me_2$ , ${}^{3}J = 6.8$ ), 0.88 (d, 6H, CH $Me_2$ , ${}^{3}J = 6.8$ ) 7.62 (m, 2H, <i>p</i> -H), 7.50 (d, 4H, <i>m</i> -H, ${}^{3}J = 7.5$ ), 2.60 (br, 4H, CH $Me_2$ ), 1.37 (d, 12H,	This work
1b <sup>e</sup>	1.17 (Cp*)	6.22	CH $Me_2$ , ${}^{3}J = 6.9$ ), 1.13 (d, 12H, CH $Me_2$ , ${}^{3}J = 6.9$ ) <sup>d</sup> 6.92 (br. 2H, <i>m</i> -H), 6.80 (br. 2H, <i>m</i> -H), 2.69 (br s, 6H, <i>o</i> -Me), 2.21 (s, 6H, <i>p</i> -Me), 1.81	29
	···· (•F )		(br s, 6H, <i>o</i> - <i>Me</i> )	
3b <sup>c</sup>	0.96 (Cp*)	7.30	7.17 (s, 4H, m-H), 2.40 (s, 6H, p-Me), 2.12 (br s, 12H, $o$ -Me) <sup>d</sup>	This work
2b <sup>f</sup>	4.56 (Cp)	7.09	7.12 (s, 4H, m-H), 2.45 (s, 6H, p-Me), 2.18 (s, 12H, o-Me)	30
4b <sup>f</sup>	4.76 (Cp)	7.20	7.13 (s, 4H, m-H), 2.43 (s, 6H, p-Me), 2.12 (s, 3H, NCMe), 2.11 (s, 12H, o-Me)	This work
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Table 1  $^{1}$ H NMR data of the cationic complexes 3a, 3b and 4b and of their neutral counterparts 1a, 1b and  $2b^{a}$ 

<sup>*a*</sup>  $\delta$  in ppm and J in Hz. <sup>*b*</sup> In toluene- $d_8$  at 263 K. <sup>*c*</sup> In acetonitrile- $d_3$ . <sup>*d*</sup> Free CH<sub>3</sub>CN that results from exchange with CD<sub>3</sub>CN is seen as a singlet (at 1.96 ppm) on the downfield side of the multiplet due to residual CHD<sub>2</sub>CN observed at 1.94 ppm. <sup>*e*</sup> In toluene- $d_8$ . <sup>*f*</sup> In chloroform- $d_1$ .

more widely used d<sup>10</sup> counterpart, palladium), and (iii) the unique properties of NHC ligands in comparison to phosphines,<sup>2</sup> examples of NHC-Ni(II)-based catalysts for C–C coupling reactions remain scarce.<sup>20,21,22</sup>

Following our ongoing interest in NHC-Ni(II) compounds,<sup>6a</sup> we have recently described the synthesis and dynamic behavior of air and moisture stable neutral complexes [Ni(NHC)ClCp<sup>§</sup>] (Cp<sup>§</sup> = Cp, Cp\*)<sup>‡</sup> that bear aryl substituents on both NHC-nitrogen atoms.<sup>29,30</sup> Herein we report the high yield syntheses of some of their cationic derivatives, [Ni(NHC)(NCMe)Cp<sup>§</sup>](PF<sub>6</sub>) by reaction of the corresponding neutral species with KPF<sub>6</sub> in acetonitrile. The structure of one of these cationic complex was established by a single-crystal X-ray diffraction study and was compared to that of its neutral counterpart. No remarkable structural differences were observed in the solid state but solution NMR spectroscopy did reveal that the acetonitrile ligand in the cations is labile; this might lead to differences in the catalytic behaviour. Having all these complexes in hand, we thus decided to check the respective influence of (i) their cationic or neutral nature and (ii) the presence of the bulky electron-rich pentamethylcyclopentadienyl ligand or of the less bulky and electron poorer cyclopentadienyl on their activity in Suzuki-Miyaura couplings.

All the complexes catalyzed the cross-coupling of aryl halides with phenyl boronic acid in the absence of co-catalysts or reductants. Surprisingly, the neutral or cationic nature of the complexes proved to have almost no influence on the reaction yields and rates. However, complexes bearing the bulky electronrich pentamethylcyclopentadienyl ligand proved to be much more active than those bearing the cyclopentadienyl ligand, and among the best TOFs reported for Ni(II)-catalyzed Suzuki cross-coupling reactions under similar conditions were observed with these complexes.<sup>20</sup>

### **Results and discussion**

# Synthesis and characterization of the cationic complexes $[Ni(NHC)(NCMe)Cp^{\delta}]^+PF_{6}^-$

When acetonitrile solutions of the neutral complexes, [Ni(NHC)ClCp<sup>§</sup>] (Cp<sup>§</sup> = Cp<sup>\*</sup>, NHC = IPr, **1a**; Cp<sup>§</sup> = Cp<sup>\*</sup>, NHC = IMes, **1b**; Cp<sup>§</sup> = Cp, NHC = IMes, **2b**)<sup>‡</sup> were treated with 1 equivalent of KPF<sub>6</sub>, the chloride was abstracted and the cationic complexes, [Ni(NHC)(NCCH<sub>3</sub>)Cp<sup>§</sup>]<sup>+</sup>PF<sub>6</sub><sup>-</sup> (Cp<sup>§</sup> = Cp<sup>\*</sup>, NHC = IPr, **3a**;  $Cp^{\delta} = Cp^*$ , NHC = IMes, **3b**;  $Cp^{\delta} = Cp$ , NHC = IMes, **4b**) were isolated as yellow to green air-stable solids in 71–84% yield (eqn (1)). All complexes were fully characterized by <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopy (Tables 1 and 2), IR spectroscopy and elemental analyses.



The <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra of the cationic complexes **3a**, **3b** and **4b** at ambient temperature are straightforward: all show the presence of one  $\eta^5$ -Cp\* or -Cp group and of the IPr or IMes ligand. As for the neutral complexes **1a**,<sup>29</sup> **1b**<sup>29</sup> and **2b**,<sup>16e,30</sup> the spectra reveal that an effective plane of symmetry that bisects the molecule exists in solution on the NMR time scale. This effective mirror plane contains the acetonitrile ligand, the nickel and the NHC carbene carbon atom, as well as the Cp\* or Cp ring centroid.

Nevertheless, in contrast to the sterically congested neutral Cp\* species 1a and 1b, which possess a rotation barrier of 65-67 kJ mol<sup>-1</sup> about the nickel-carbene carbon bond,<sup>29</sup> the corresponding cationic complexes 3a and 3b show a greatly reduced rotation barrier at room temperature. Thus, the <sup>1</sup>H NMR spectrum of 1b at ambient temperature displays two singlets in a 1:1 integrated ratio for the four *meta*-hydrogen atoms of the two mesityl groups, as well as three singlets, in a 3:3:3 relative integrated ratio, for the four ortho- and the two para-methyl groups.<sup>29</sup> In contrast, its cationic analogue **3b** displays only one singlet for all the *meta*-hydrogen atoms and two singlets in a 3:6 relative integrated ratio for the ortho- and para-methyl groups (the bigger signal being slightly broadened, Table 1). Similarly, the <sup>1</sup>H NMR spectrum of **3a** displays only one doublet for the *meta* aromatic ring protons, one broad signal for the CH protons of the isopropyl groups and two doublets for the isopropyl methyls (the central carbon of each isopropyl group is diastereotopic). All these signals are doubled in the <sup>1</sup>H NMR spectrum of **1a** (Table 1). This doubling of the aryl substituent signals of **1a** and **1b** is also observed in their <sup>13</sup>C NMR spectra (Table 2). The <sup>1</sup>H and <sup>13</sup>C NMR spectra of the less bulky Cp species 2b and 4b are similar.

	Cp <sup>§</sup>	N <i>C</i> N	NCH=CHN	Ar	Ref.
1a <sup>b</sup>	102.1 ( <i>C</i> <sub>5</sub> ), 10.1 ( <i>Me</i> <sub>5</sub> )	180.0	123.1	149.6 and 145.8 ( $o$ -C <sub>Ar</sub> ), 138.0 ( <i>ipso</i> -C <sub>Ar</sub> ), 130.1 and 125.9 ( $m$ -C <sub>Ar</sub> ), 125.7 ( $p$ -C <sub>Ar</sub> ), 28.7 (CHMe <sub>2</sub> ) 27.2 and 26.9 (CHMe <sub>2</sub> ) 23.9 and 22.7 (CHMe <sub>2</sub> )	29
3a <sup>c</sup>	105.6 ( <i>C</i> <sub>5</sub> ), 9.8 ( <i>Me</i> <sub>5</sub> )	172.3	128.6	$(2.9 (CHMe_2)^{-1})^{-1}$ ( <i>ipso</i> -C <sub>Ar</sub> ), 131.6 ( <i>p</i> -C <sub>Ar</sub> ), 125.4 ( <i>m</i> -C <sub>Ar</sub> ), 29.5 ( <i>C</i> HMe <sub>2</sub> ), 27.1 and 22.9 ( <i>C</i> HMe <sub>2</sub> ) <sup><i>d</i></sup>	This work
1b <sup>b</sup>	102.2 ( <i>C</i> <sub>5</sub> ), 9.9 ( <i>Me</i> <sub>5</sub> )	177.2	124.1	138.6 and 134.8 $(o-C_{AT})$ , 138.4 $(p-C_{AT})$ , 137.8 $(ipso-C_{AT})$ , 130.5 and 129.3 $(m-C_{AT})$ , 21.4 $(o-Me)$ , 20.6 $(p-Me)$ , 18.6 $(o-Me)$	29
<b>3b</b> <sup>c</sup>	$105.6(C_5), 9.5(Me_5)$	170.2	126.8	140.4 ( <i>ipso</i> - $C_{Ar}$ or <i>p</i> - $C_{Ar}$ ), 137.0 ( <i>p</i> - $C_{Ar}$ or <i>ipso</i> - $C_{Ar}$ ), 136.4 ( <i>o</i> - $C_{Ar}$ ), 130.3 ( <i>m</i> - $C_{Ar}$ ), 21.1 ( <i>p</i> -Me), 18.9 ( <i>o</i> -Me) <sup><i>d</i></sup>	This work
2b <sup>e</sup>	92.3 ( $C_5$ H <sub>5</sub> )	167.2	124.6	139.3 ( $p$ -C <sub>Ar</sub> or <i>ipso</i> -C <sub>Ar</sub> ), 136.8 ( <i>ipso</i> -C <sub>Ar</sub> or $p$ -C <sub>Ar</sub> ), 136.1 ( $o$ -C <sub>Ar</sub> ), 129.4 ( $m$ -C <sub>Ar</sub> ), 21.4 ( $p$ -Me), 18.6 ( $o$ -Me)	This work
<b>4b</b> <sup>c</sup>	94.3 $(C_5H_5)$	160.2	127.1	140.9 ( $p$ -C <sub>Ar</sub> or <i>ipso</i> -C <sub>Ar</sub> ), 136.9 ( <i>ipso</i> -C <sub>Ar</sub> or $p$ -C <sub>Ar</sub> ), 136.4 ( $o$ -C <sub>Ar</sub> ), 130.3 ( $m$ -C <sub>Ar</sub> ), 21.3 ( $p$ -Me), 18.4 ( $o$ -Me) <sup>d</sup>	This work

Table 2  ${}^{13}C{}^{1}H$  NMR data of the cationic complexes 3a, 3b and 4b and of their neutral counterparts 1a, 1b and 2b<sup>a</sup>

<sup>*a*</sup>  $\delta$  in ppm. <sup>*b*</sup> In benzene- $d_6$ . <sup>*c*</sup> In acetonitrile- $d_3$ . <sup>*d*</sup> Free CH<sub>3</sub>CN that results from exchange with CD<sub>3</sub>CN is seen as two singlets (at 1.77 and 118.3 ppm) overlapping with the multiplet due to residual CHD<sub>2</sub>CN at 1.32 ppm and with the singlet due to CD<sub>3</sub>CN at 118.3 ppm. <sup>*e*</sup> In chloroform- $d_1$ .

Neither of them shows an observable rotational barrier at ambient temperature.

These results suggest that substitution of a bulky chloride by a smaller acetonitrile molecule would reduce the steric congestion in the cationic complexes bearing the bulky Cp\* and allow free rotation about the nickel–carbene carbon bond at ambient temperature. However a comparison of the molecular structures of **1a** and **3a** shows that they are very similar (*vide infra*). We thus tend to believe that this observed free rotation at room temperature in the cationic species is the direct result of ligand exchange and a dynamic process rather than of a purely dynamic process. Indeed, free CH<sub>3</sub>CN that results from exchange with CD<sub>3</sub>CN is seen in the <sup>1</sup>H and <sup>13</sup>C {<sup>1</sup>H} NMR spectra of **3a**, **3b**, and **4b**, indicating that the acetonitrile ligand of the cationic species is labile in solution. A dynamic rotational process would be much more facile for the two coordinate intermediate presumably present during the acetonitrile ligand exchange.

It is noteworthy that the carbene carbon atoms in complexes **3a**, **3b** and **4b** appear at 172.3, 170.2 and 160.2 ppm (in CD<sub>3</sub>CN), respectively, in the <sup>13</sup>C NMR spectrum of these complexes. These signals are slightly upfield of the signals seen at 180.0, 177.2 (both in C<sub>6</sub>D<sub>6</sub>) and 167.2 ppm (in CDCl<sub>3</sub>), respectively, for their neutral derivatives (Table 2). The apparent absence of a significant rotational barrier about the nickel–carbene carbon bond in the cationic Cp\* species **3a** and **3b** at ambient temperature is thus probably mainly due to the lability of acetonitrile in solution, but there may also be a minor electronic component.<sup>29</sup>

The IR spectra of the cationic complexes are rather surprising as weak v(CN) stretches are observed for solid samples of all three complexes at 2281 (**3a**), 2294 (**3b**) and 2299 cm<sup>-1</sup> (**4b**). These values are consistent with those reported for other Ni(II)–*N*-bound acetonitrile complexes.<sup>31</sup>

#### Structural studies of complexes 1a and 3a

Crystals of the cationic complex **3a** and of its neutral precursor **1a** suitable for X-ray structure determination were grown from cold acetonitrile-toluene (**3a**) and toluene (**1a**) solutions. The molecular structures of **1a** and of the cationic part of **3a** are shown in similar orientations in Fig. 1 and 2, respectively. Crystallographic data and data collection parameters are listed in Table 3, and a list of



**Fig. 1** Molecular structure of **1a** showing all non-H atoms. Ellipsoids are shown at the 50% probability level and key atoms are labelled.



Fig. 2 Molecular structure of the cationic part of 3a showing all non-H atoms. Ellipsoids are shown at the 50% probability level and key atoms are labelled.

selected bond lengths and angles for both complexes appear in Table 4.

The molecular structure of these complexes are strikingly similar. Both feature a nickel atom bonded to a  $\eta^{5}$ -Cp\* group, a IPr moiety, and a chloride (1a) or an acetonitrile (3a) ligand

Compound	1a	3a	
Compound Empirical formula $M_r$ Crystal system Space group a/Å b/Å b/Å c/Å $\beta/^\circ$ $V/Å^3$ Z $D_c/Mg m^{-3}$ $\mu/mm^{-1}$ T/K Crystal form, colour Crystal size/mm $h, k, l_{max}$ $T_{min}, T_{max}$ Reflns collected R (reflections)	1a $C_{37}H_{51}ClN_2Ni$ $617.96$ Monoclinic $Cc$ 11.9474(8)         31.263(3)         10.6055(5)         93.510(4)         3953.8(5)         4         1.038         0.581         173(2)         Prism, red         0.30 × 0.10 × 0.05         11, 37, 13	$\begin{array}{c} \textbf{3a} \\ \hline \\ C_{39}H_{54}N_{3}Ni\cdot F_{6}P \\ 768.53 \\ Orthorhombic \\ Pnma \\ 13.7019(5) \\ 18.0171(7) \\ 16.5430(7) \\ 90 \\ 4083.9(3) \\ 4 \\ 1.250 \\ 0.571 \\ 173(2) \\ Block, dark yellow \\ 0.20 \times 0.18 \times 0.15 \\ 17, 23, 21 \\ 0.568, 0.784 \\ 26294 \\ 0.0698 (3025) \\ 0.692 \\ (3025) \end{array}$	
GOF on $F^2$	0.965	1.090	

Table 3 X-Ray crystallographic data and data collection parameters for complexes 1a and 3a

 Table 4
 Selected bond lengths (Å) and angles (°) for 1a and 3a

	1a	3a
Ni–C(1)	1.900(4)	1.911(4)
Ni–L <sup>a</sup>	2.2094(13)	1.881(4)
$Ni-C(Cp^*)$ (av)	2.155	2.143
$Ni-C(Cp^*)$ (min)	2.061(5)	2.063(5)
$Ni-C(Cp^*)$ (max)	2.202(5)	2.166(3)
$C(Cp^*)-C(Cp^*)$ (av)	1.430	1.429
$C(Cp^*)-C(Cp^*)$ (min)	1.399(7)	1.392(5)
$C(Cp^*)-C(Cp^*)$ (max)	1.471(8)	1.466(7)
Ni-N(3)-C(2)	_	170.1(4)
N(3) - C(2) - C(3)		179.4(5)
C(1)–Ni–L	93.85(13)	97.54(17)
C(1)-Ni-Cp* <sub>cent</sub>	143.0	140.0
L-Ni-Cp*	123.1	122.5

in a two-legged piano stool geometry. If one considers the Cp\* group as a single ligand, the nickel atom lies at the centre of a trigonal plane formed by the ring centroid, the carbenoid carbon atom C(1) of the NHC ligand, and the chloride Cl or the nitrogen N(3) of the acetonitrile ligand; the sum of all angles subtended by these atoms is equal to 360° in both structures. However there are significant departures from the idealized 120° angles of a trigonal structure. The carbenoid carbon C(1) and the chloride atom Cl of 1a subtend an angle of 93.8(1)° at the nickel atom, and similarly the carbon C(1) and the nitrogen atom N(3) of **3a** subtend a slightly larger angle of  $97.5(2)^{\circ}$ . These angles are in the range of those observed for the closely related neutral mesityl analogue 1b,<sup>29</sup> for its Cp derivative 2b<sup>16e</sup> and for the Cp derivative of 1a, [Ni(IPr)ClCp] 2a,<sup>17b</sup> for which values of 95.3(1), 98.4(2) and  $93.86(3)^{\circ}$  have been registered, respectively. The Cp complexes 2a and 2b, which show the biggest difference for this angle  $(4.5^{\circ})$ , both do not show an observable rotation barrier about the nickel-carbene carbon bond in solution at ambient temperature. Hence, the difference of 3.6° between the C(1)-Ni-L angle in 1a

(L = Cl) and in **3a** [L = N(3)] does not appear to be correlated to the rotation barrier variation.

The C(1)–Ni–Cp<sup>8</sup><sub>cent</sub> angle spans the range of  $142 \pm 0.5^{\circ}$  for the Cp<sup>\*</sup> species **1a** and **1b**,<sup>29</sup> which show a rotation barrier about the nickel–carbene carbon bond. In contrast, the Cp species **2a**,<sup>17b</sup> **2b**<sup>16e</sup> and [Ni(1,3-dimethylimidazol-2-ylidene)ICp],<sup>29</sup> as well as the Cp<sup>\*</sup> complex, [Ni(1,3-dimethylimidazol-2-ylidene)ICp<sup>\*</sup>], exhibit a smaller angle of 134.2 ± 1.8° and do not show an observable rotation barrier.<sup>29</sup> This angle seems thus to be correlated to the presence or absence of a rotation barrier about the nickel– carbene carbon bond. However, despite the C(1)–Ni–Cp\*<sub>cent</sub> angle of 140.0° (Table 4) measured in the cationic derivative **3a**, a greatly reduced rotational barrier is observed in this complex, but as discussed earlier, this behaviour is probably due to acetonitrile ligand dissociation.

The nickel–carbene carbon bond lengths are not significantly different from each other [Ni–C(1) = 1.900(4) Å (1a); 1.911(4) (3a)]. These value are comparable to those reported for the closely related neutral mesityl analogue 1b [1.906(3) Å]<sup>29</sup> and for its Cp derivative 2b [1.917(9) Å],<sup>16e</sup> but are somewhat longer than that reported for 2a [1.8748(11) Å].<sup>17b</sup> The Ni–Cl distance of 2.2094(13) Å in 1a is close to the Ni–Cl distance observed in 1b, where a value of 2.1962(9) has been registered,<sup>29</sup> but is slightly longer than those reported for the neutral Cp derivatives 2a and 2b, where values of 2.1876(3)<sup>17b</sup> and 2.185(2) Å<sup>16e</sup> have been observed, respectively. The acetonitrile ligand of 3a is linear [N(3)–C(2)–C(3) = 179.4(5)°] but the Ni–N(3) bond is nevertheless not perfectly co-linear with this axis [Ni–N(3)–C(2) = 170.1(4)°].

The plane that contains the imidazol-2-ylidene ring is almost orthogonal to the Cl–Ni–Cp\*<sub>cent</sub> plane and makes an angle of 86.3° with it in the neutral complex **1a**. The two halves of the molecule are thus not related by a mirror plane, bur are not too far off from mirror symmetry, and the two aryl groups approximately eclipse each other. In contrast a crystallographically imposed mirror plane bisects the cation of **3a** and the  $PF_6^-$  anion, so this angle is precisely 90° in **3a**.

Both aryl rings in **1a** are close to perpendicular to the imidazolylidene ring (the plane of all aromatic carbon atoms in each aryl ring makes angles of 83.1 and  $86.3^{\circ}$  with the carbone plane). The corresponding angle in **3a** is  $85.7^{\circ}$ .

In both complexes, the Cp\* ring exhibits structural distortions, as there are significant variations in the Ni–Cp\* carbon distances, which range from 2.061(5) to 2.202(5) Å in **1a** and from 2.063(5) to 2.166(3) Å in **3a**, as well as fluctuations in the aromatic C–C distances, which extend from 1.3991(7) to 1.471(8) Å in **1a** and from 1.392(5) to 1.466(7) Å in **3a**. Such variations arise from "allyl–ene" distortions in the Cp\* ligand and have been previously observed in other Cp\*Ni systems.<sup>32</sup>

There are no abnormally short non-bonded contacts or unusual packing features in molecule **1a**. However, all the acetonitrile methyl protons in **3a** interact with fluorine atoms of the  $PF_6^-$  anion: the hydrogen atom on the mirror plane undergoes two C– $H \cdots F$  interactions of 2.441 Å, while the two other protons each interact with one fluorine atom of another  $PF_6^-$  group (each C– $H \cdots F = 2.571$  Å).

In conclusion, there appear to be no significant structural differences between **1a** and **3a** that might explain the low rotation barrier in **3a**. This behaviour is thus more likely due to the labile nature of the acetonitrile ligand in solution (*vide supra*).

Table 5Optimization of reaction conditions for the Suzuki–Miyauracross-coupling of 4'-bromoacetophenone with phenylboronic acid cat-<br/>alyzed by  $3b^{\alpha}$ 

B(OH)<sub>2</sub> 3b (3 mol%) 5 K<sub>3</sub>PO<sub>4</sub> solvent / T 6 PhB(OH)<sub>2</sub> K<sub>3</sub>PO<sub>4</sub> Conv.<sup>b</sup> Select.<sup>b</sup> *t*/min (5/6)Entry Solvent (equiv.)  $T/^{\circ}C$ (equiv.) (%) 2.2 DME 1.1 25 60 22 100/0DME 2.2 82 120 82 100/02 1.1 82 90 3 DME 2.6 120 100'/01.3 32 4 CH<sub>3</sub>CN 1.3 2.6 85 120 100/05 Toluene 1.3 2.6 90 120 100 96/490 96/4 6 1.3 2.6 40 100 Toluene

<sup>*a*</sup> Reaction conditions: 4'-bromoacetophenone (1 mmol), phenylboronic acid (1.1–1.3 mmol),  $K_3PO_4$  (2.2–2.6 mmol) as base, **3b** (3 mol%), solvent (3 mL). <sup>*b*</sup> According to NMR.

#### Catalytic Suzuki-Miyaura coupling reactions

Initial studies focussed on the reaction of 4'-bromoacetophenone with various amounts of phenylboronic acid and  $K_3PO_4$  in the presence of the cationic Cp\* complex **3b** (3 mol%) under various solvent and temperature conditions to optimize the reaction conditions (Table 5). All reactions were run *without* any additive such as PPh<sub>3</sub> as is often the case.<sup>20c-f,i,23a,c</sup>

The first runs were conducted in DME. Low conversion to the coupling product **5** was observed with 1.1 equiv. of PhB(OH)<sub>2</sub> and 2.2 equiv. of  $K_3PO_4$  at room temperature (Table 5, entry 1). Increasing the temperature to 82 °C greatly improved the yield (entry 2), and increasing the PhB(OH)<sub>2</sub> and  $K_3PO_4$  loadings to 1.3 and 2.6 equiv., respectively, led to an even better conversion of 90% after 2 h (entry 3). Under these conditions, acetonitrile was not effective (entry 4), whereas toluene proved to be the best solvent. Full conversion was indeed observed in this solvent, though with a slightly decreased selectivity, as small amounts of the homocoupling product 4,4'-acetylbiphenyl **6** were detected (entry 5). In the latter solvent, it even proved to be possible to decrease the reaction time to only 40 min to reach full conversion (entry 6).

The catalytic activities of the various half-sandwich NHCnickel(II) complexes **1–4** were next examined under the standard conditions established with complex **3b**, *i.e.*: with 1.3 equiv. of PhB(OH)<sub>2</sub> and 2.6 equiv. of K<sub>3</sub>PO<sub>4</sub> in toluene at 90 °C (Table 6). All complexes are catalytically active and give the desired product **5** in moderate to excellent yield in *15 min*, which is a very fast reaction time for nickel-catalyzed Suzuki couplings. Typical reactions times, indeed, usually range under similar conditions from 1–2 h at best to 12–24 h at worst.<sup>20,23</sup>

Surprisingly, the neutral or cationic nature of the complexes had almost no influence on the reaction yields and rates (Table 6, entries 1, 4, 8 and 9 vs. 3, 5, 10 and 11, respectively). A marked difference is observed between the Cp-complexes 2a and 2b (entries 6–9), which may be explained by the better steric protection of the active site by the more bulky IPr ligand. Although still present, this influence is less prominent with the more bulky,

 
 Table 6
 Suzuki–Miyaura cross-coupling of 4'-bromoacetophenone with phenylboronic acid catalyzed by 1a–4b<sup>a</sup>



<sup>*a*</sup> Reaction conditions: 4'-bromoacetophenone (1 mmol), phenylboronic acid (1.3 mmol),  $K_3PO_4$  (2.6 mmol) as base, **1a–4b** (1–3 mol%), toluene (3 mL), 90 °C. <sup>*b*</sup> According to NMR. <sup>*c*</sup> Run at 110 °C.

electron-rich Cp\* complexes 1 and 3. These latter species gave much better results overall in terms of rates and conversions, but with a slightly decreased selectivity, as the Cp species did not produce the homocoupling product 6 (entries 1-5 vs. 6-11). Conversions up to 95% were obtained in the case of 2a after only 10 min, and 98% after 15 min, leading to turnover frequencies (TOF) of 190 and 131 h<sup>-1</sup> (entries 2 and 3). These are among the best TOFs observed so far in Suzuki–Miyaura cross-coupling catalyzed by a Ni(II) complex in the *absence* of reductant and co-catalyst.<sup>20,23</sup> We are indeed aware of only one example where a higher TOF of 261 h<sup>-1</sup> has been observed (with a pincer-type bis-NHC-nickel(II) catalyst), for the coupling of 4-bromobenzonitrile with phenylboronic acid.<sup>20a,33</sup>

Longer reaction times with the Cp species **2** and **4** afforded only slightly improved conversions (entries 7, 9 and 11). Attempts to decrease the catalyst loadings of the Cp\* species **1b** and **3a** to 1 mol% led to only 63 and 61% conversion, respectively, after 1 h at 110 °C (entries 12 and 13). These results indicate fast catalyst deactivation.

The precise reaction mechanism remains to be elucidated. Nevertheless, a few comments can be made. The absence of significant reactivity difference between the cationic and the neutral complexes suggest that the necessary creation of a vacant site might arise through Cp or Cp\* ring slippage rather than acetonitrile or chloride dissociation. We have indeed observed many cases of Cp\* ring slippage in NiCp\* complexes,<sup>34</sup> and our recent work with CpNi–NHC complexes has also shown that Cp ligands are much more labile than expected in such systems.<sup>6a</sup> In addition, it is noteworthy that traces of biphenyl were observed in all cases. This suggests initial reduction of the Ni(II) precursor to a Ni(0) active species by the homocoupling of phenylboronic acid *via* a mechanism previously postulated for related Pd(II) species<sup>24</sup> and

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for other nickel based systems.<sup>23</sup> Initial reduction to an unstable Ni(0) species is further corroborated by the very high air sensitivity of the active species, and the fast colour change of the reaction medium (after only 1-2 min at 90 °C).

To get some further insight into the roles played by the different reactive species present in the medium and in particular by the phenylboronic acid, we conducted a series of control experiments. The first one was carried out in the absence of the phenylboronic acid but in otherwise unchanged conditions. No reaction was observed, nor was there any colour change of the reaction medium. The 4'-bromoacetophenone and the catalyst precursor were found to be unchanged by <sup>1</sup>H NMR analysis of the crude mixture. A second control experiment was run in the absence of 4'-bromoacetophenone. In this case, the colour of the reaction medium changed in a couple of minutes as observed during the typical catalytic runs. Unfortunately <sup>1</sup>H NMR analysis of the medium gave a complicated spectrum that could not be interpreted. Finally a last control experiment was run in the absence of base. A rapid colour change was observed, and signals of the catalyst precursor were not observable any more by <sup>1</sup>H NMR; nevertheless no coupling had occurred. These control experiments demonstrate the crucial role played by phenylboronic acid in the generation of the catalytically active species (presumably a Ni(0) species as discussed above), as well as the necessary presence of K<sub>3</sub>PO<sub>4</sub> for this nickel complex to achieve the cross-coupling reaction.

The better results observed with complexes 1 and 3 bearing the bulky Cp\* ligand, as compared to the Cp species 2 and 4, may be explained by a better stabilization of the coordinatively unsaturated sites through steric protection and electronic donation and/or by a faster or more efficient reduction of the initial Ni(II) species by the electron-rich ligand.

As the cationic Cp\* species 3a presents the best results in terms of rate (Table 6, entries 2 and 3) and the neutral Cp\* species **1b**, the best results in terms of rate *vs.* selectivity (entry 4), the reaction scopes of these two complexes have been examined with a short series of aryl bromides and chlorides bearing electron-withdrawing and electron-donating substituents. Results are presented in Table 7.

Excellent yields of 4-acetylbiphenyl were obtained from 4'chloroacetophenone with both catalysts (Table 7, entries 1 and 2). In addition, a remarkable increase of selectivity was observed with **1b** compared to the result obtained with 4'-bromoacetophenone (Table 6, entry 4 vs. Table 7, entry 2). It is noteworthy that excellent selectivity was also observed with 4-bromotoluene (entries 7 and 8). Electron-donating substrates were however converted to the desired coupling products in lower yields (entries 3–8) and, excepting 4-bromoanisole, which was converted to 4-methoxybiphenyl in 70% by **3a** and only 21% by **1b**, the neutral catalyst precursor was slightly more active with these substrates.

#### Conclusions

In summary, cationic Ni(II)-NHC complexes of formula  $[Ni(NHC)(NCCH_3)Cp^{\$}](PF_6)$  ( $Cp^{\$} = Cp^*$ , NHC = IPr **3a**;  $Cp^{\$} = Cp^*$ , NHC = IMes **3b**;  $Cp^{\$} = Cp$ , NHC = IMes **4b**) were isolated in high yields from the reaction of their neutral counterparts  $[Ni(NHC)ClCp^{\$}]$  **1a**, **1b** and **2b** with KPF<sub>6</sub> in

Table 7Suzuki–Miyaura cross-coupling of aryl bromides and chlorideswith phenylboronic acid catalyzed by 1b and  $3a^{a}$ 

✓ x-	B(OH) <sub>2</sub> +	1b or 3a ( K <sub>3</sub> P toluene	(3 mol%) 0 <sub>4</sub> / 90°C	- + R-⟨_)- 8	R R
Entry	Cat.	R	Х	Conv. <sup>b</sup> (%)	Select. <sup>b</sup> (7/8)
1 2 3 4 5 6 7 8	3a 1b 3a 1b 3a 1b 3a	COMe COMe OMe OMe OMe Me Me	Cl Cl Br Br Cl Cl Br Br	92 91 70 21 0 12 <sup>e</sup> 31 <sup>d</sup> .e	93/7 100/0 90/10 88/12  92/8 100/0 100/0

<sup>*a*</sup> *Reaction conditions*: aryl halide (1 mmol), phenylboronic acid (1.3 mmol), K<sub>3</sub>PO<sub>4</sub> (2.6 mmol) as base, **1b** or **3a** (3 mol%), toluene (3 mL), 90 °C, 1 h. <sup>*b*</sup> According to NMR. <sup>*c*</sup> Isolated yield. <sup>*d*</sup> Run at 110 °C. <sup>*e*</sup> GC yield.

acetonitrile. Single-crystal X-ray diffraction studies established the molecular geometries of the neutral and cationic analogues **1a** and **3a**. No remarkable structural differences were observed. Nevertheless, solution NMR spectroscopy established that in contrast to the sterically congested neutral Cp\* species **1a** and **1b**, the corresponding cationic complexes **3a** and **3b** show a greatly reduced barrier to the nickel–carbene bond rotation at ambient temperature. In addition, NMR spectroscopy also established that the acetonitrile ligand of the cationic species is labile in solution. Hence, the absence of a rotation barrier in **3a** and **3b** is most probably due to the labile nature of the acetonitrile ligand in solution rather than to the smaller size of acetonitrile as compared to the chloride.

The neutral and the cationic complexes  $[Ni^{II}(NHC)LCp^{\$}]$  (L = Cl<sup>-</sup> or NCMe, PF<sub>6</sub><sup>-</sup>) 1-4 catalyse the Suzuki-Miyaura crosscouplings of aryl halides and phenylboronic acid in the presence of K<sub>3</sub>PO<sub>4</sub> as the sole additive. The bulky electron-rich Cp\* species are much more efficient than the Cp complexes, and one of the highest rates for nickel(II)-based catalysts in the absence of a co-catalyst or reductant was observed for the coupling of phenylboronic acid and 4'-bromoacetophenone with 3a. Although the novel cationic species possess a labile acetonitrile ligand, no substantial benefit was observed during the catalytic reactions. The necessary creation of a vacant site might arise through Cp or Cp\* ring slippage rather than acetonitrile or chloride dissociation. The high rates observed with the Cp\* complexes is believed to be derived at least partially from the presence of the bulky electron-rich Cp\* ligand, which may both facilitate the probable initial reduction to Ni(0) by phenylboronic acid and stabilize the coordinatively unsaturated sites through steric protection and electronic donation. Mechanistic studies are currently under way to try to confirm these hypotheses. Catalytic studies with other half-sandwich Ni-NHC complexes that bear a weakly coordinating dangling arm that may stabilize the coordinatively unsaturated active site (and hence allow for a better catalyst stability) are also underway.

## Experimental

#### General

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 a FT-Bruker Ultra Shield 300 spectrometer operating at 300.13 MHz for <sup>1</sup>H, and at 75.47 MHz for <sup>13</sup>C {<sup>1</sup>H}. DEPT <sup>13</sup>C spectra were recorded for all complexes to help in the 13C signal assignments. The chemical shifts are referenced to the residual deuterated solvent peaks. Chemical shifts ( $\delta$ ) and coupling constants (J) are expressed in ppm and Hz respectively. IR spectra of complexes 3a, 3b and 4b were recorded on a FT-IR Nicolet 380 spectrometer with KBr pellets. Vibrational frequencies are expressed in cm<sup>-1</sup>. 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. Commercial compounds were used as received. Complexes [Ni(IPr)ClCp\*] 1a,<sup>29</sup> [Ni(IMes)ClCp\*] 1b,<sup>29</sup> [Ni(IPr)ClCp] 2a<sup>17b</sup> and [Ni(IMes)ClCp] 2b<sup>16e,30</sup> were prepared according to published methods.

#### Synthesis of [Ni(IPr)(NCMe)Cp\*](PF<sub>6</sub>) (3a)

KPF<sub>6</sub> (94 mg, 0.511 mmol) was added to a suspension of **1a** (316 mg, 0.511 mmol) in acetonitrile (5 mL). The mixture was stirred for 1 h at room temperature. During the first 15 min, the colour changed from violet to dark yellow. The reaction medium was filtered through Celite, concentrated to *ca*. 1 mL, and treated with diethyl ether (3 mL) to yield an orange–brown solid after standing at -28 °C for 1 h. The mother-liquor was removed by syringe, and the solid washed with diethyl ether (3 × 1 mL), and dried under vacuum to give **3a** (280 mg, 0.364 mmol, 71%). Anal. Calc. for C<sub>39</sub>H<sub>54</sub>F<sub>6</sub>N<sub>3</sub>NiP: C, 60.95; H, 7.08; N, 5.47. Found: C, 61.37; H, 7.22; N, 5.41%. <sup>1</sup>H NMR (CD<sub>3</sub>CN, 300.13 MHz): see Table 1. <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>3</sub>CN, 75.47 MHz): see Table 2. FT-IR:  $\nu$ (CN) 2281 (w),  $\nu$ (P–F) 838 (s).

#### Synthesis of [Ni(IMes)(NCMe)Cp\*](PF<sub>6</sub>) (3b)

Complex **3b** was prepared from [Ni(IMes)ClCp\*] **1b** by a procedure similar to that used for **3a**, and was isolated as an analytically pure yellow–brown solid in 79% yield. Anal. Calc. for  $C_{33}H_{42}F_6N_3NiP$ : C, 57.92; H, 6.19; N, 6.14. Found: C, 57.80; H, 6.19; N, 6.02%. <sup>1</sup>H NMR (CD<sub>3</sub>CN, 300.13 MHz): see Table 1. <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>3</sub>CN, 75.47 MHz): see Table 2. FT-IR: *v*(CN) 2294 (w); *v*(P–F) 839 (s).

#### Synthesis of [Ni(IMes)(NCMe)Cp](PF<sub>6</sub>) (4b)

Complex **4b** was prepared from [Ni(IMes)ClCp] **2b** by a procedure similar to that used for **3a**, and was isolated as an analytically pure green solid in 84% yield. Anal. Calc. for  $C_{28}H_{32}F_6N_3NiP$ : C, 54.75; H, 5.25; N, 6.84. Found: C, 54.67; H, 5.03; N, 6.70%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300.13 MHz): see Table 1. <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>3</sub>CN, 75.47 MHz): see Table 2. FT-IR: v(CN) 2299 (w); v(P–F) 842 (s).

#### General procedure for the Suzuki coupling reactions

A Schlenk tube equipped with a septum was charged with aryl halide (1.0 mmol), phenylboronic acid (1.3 mmol), K<sub>3</sub>PO<sub>4</sub> (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 vigorous stirring by putting the Schlenk tube in an oil-bath at 90 °C. After 10-60 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 internal standard. NMR yields were determined by removing a sample with a syringe, drying it under high vacuum, extracting the residue with CDCl<sub>3</sub> and filtering the solution in the NMR tube. In a standard work up, the solvent was removed completely 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 Na<sub>2</sub>SO<sub>4</sub>. 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 value of at least two runs.

#### X-Ray diffraction studies. Structure determination and refinement

Single crystals of 1a and 3a suitable for X-ray diffractions studies were selected from batches of crystals obtained at -28 °C from toluene (1a) and acetonitrile-toluene (3a) solutions. Diffraction data for all crystals were collected at 173(2) K on a Nonius Kappa-CCD area detector diffractometer using graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  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 ten frames  $(1.0^{\circ} \text{ steps in phi angle})$ , each at 20 s exposure. All structures were solved using direct methods with SHELXS-97 and refined against  $F^2$  for all reflections using the SHELXL-97 software.35 Multiscan absorption corrections (MULscanABS in PLATON) were applied.<sup>36</sup> 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.

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