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Cyclopentadienyl nickel(II) *N*,*C*-chelating benzothiazolyl NHC complexes: synthesis, characterization and application in catalytic C–C bond formation reactions†

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Cyclopentadienyl (Cp) Ni(II) complexes [CpNiL][PF$_6$] containing hybrid *N*,*C* chelating benzothiazolyl NHC ligands (**L$_1$** = 1-(2-benzothiazolyl)-3-methylimidazol-2-ylidene, **3a**; **L$_2$** = 1-(2-benzothiazolyl)-3-allylimidazol-2-ylidene, **3b**; **L$_3$** = 1-(2-benzothiazolyl)-3-benzylimidazol-2-ylidene, **3c**) have been synthesized and fully characterized. The catalytic activity of **3a–3c** in some C–C bond formation reactions has been examined. They are efficient catalysts for the homo-coupling of benzyl bromide in the presence of MeMgCl at r.t. with good functional group tolerance. Complex **3a** is active in the catalytic oxidative homo-coupling of Grignard reagents with 1,2-dichloroethane as an oxidant at r.t.

Introduction

Strong σ-electron donating properties, high modularity and ease of handling render N-heterocyclic carbene (NHC) a type of widely used ligand to support transition metal based catalyst systems.[1] Nickel complexes containing NHC ligands have been proved to be catalytically active for many organic transformations.[2] Due to their ease in synthesis and high thermal stability, a variety of CpNi(II)–NHC complexes have been synthesized[3–5] and recently significant interest has been drawn on their catalytic application in different organic reactions.[2a–c,4,5] Among them, the use of CpNi(II) complexes containing mono-dentate NHC ligands as pre-catalysts in C–C formation reactions,[4i,5] especially Suzuki–Miyaura coupling[5b–g] has been studied intensively. NHC ligands containing other donor functions can offer metal complexes with enhanced stability and catalytic activity.[1g,h] Ni complexes with hybrid NHC ligands (with C,N,C, N,C, or P,C coordination mode) are known to be generally good catalysts for C–C bond formation reactions.[2a] However, CpNi complexes with hybrid NHC ligands are rare in the literature[3c,l] and their catalytic efficiency is still unknown. Inspired by these recent advances in CpNi–NHC chemistry,[2–5] and as part of our continuous interest in hybrid NHC ligand supported catalysis[6] and the use of Ni in Grignard reagents involved C–C bond formation reactions,[7] we herein report the synthesis and catalytic potential of a series of Ni(II) complexes, [CpNiL][PF$_6$] containing hybrid *N*,*C* chelating benzothiazolyl NHC ligands **L$_1$**–**L$_3$** (1-(2-benzothiazolyl)-3-methylimidazol-2-ylidene, **L$_1$**; 1-(2-benzothiazolyl)-3-allylimidazol-2-ylidene, **L$_2$**; 1-(2-benzothiazolyl)-3-benzylimidazol-2-ylidene, **L$_3$**).

Results and discussion

Synthesis and characterization of benzothiazolyl imidazolium salts and Ni complexes 3a–3c

The synthesis of the benzothiazolyl-imidazolium chloride salts **1a–1c** was accomplished by a previously described procedure.[6c] Through an anionic exchange reaction with NH$_4$PF$_6$, **1a–1c** were converted to the corresponding hexafluorophosphates **2a–2c** (Scheme 1) in 70–84% yield. The ^{1}H- and ^{13}C-NMR spectra of **2a–2c** in CD$_3$CN show the resonances of the NC*H*N protons at *δ* 9.32, 9.35, and 9.43 ppm and of the N*C*HN carbon at *ca.* *δ* 150.60 ppm, respectively. Their ^{31}P-NMR spectra give a septet signal centered at −143.8 ppm. Complexes **3a–3c** with the general formula [CpNiL][PF$_6$] (L = **L$_1$**, **3a**; L = **L$_2$**, **3b**; L = **L$_3$**, **3c**) were prepared through the direct reaction between nickelocene and the corresponding imidazolium salts **2a–2c** (Scheme 1).

Reactions of nickelocene with **1a–1c** resulted in unstable green solid products which turned yellow upon exposure to air

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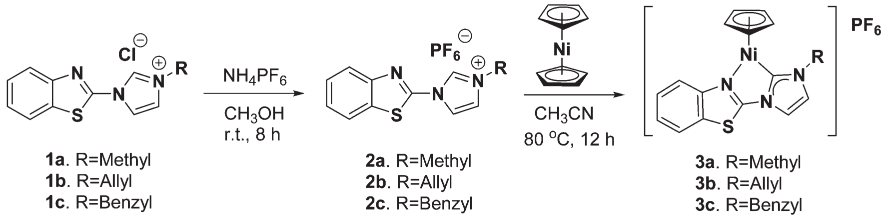
† Electronic supplementary information (ESI) available: For the NMR spectra of compounds **2a–2c** and **3a–3c**, the catalytic reaction results, the characterization data and the NMR spectra of the bibenzyl products, the crystallographic data of **3a–3c**, and the crystal data. CCDC 1441071 (**3b**), 1441072 (**3c**) and 1441073 (**3a**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c6dt00252h



Scheme 1 Synthesis of **2a–2c** and Ni complexes **3a–3c**.

and were not characterized in this work. In contrast, use of the PF_6^- salts resulted in air-stable green solids of complexes **3a–3c** in good yield. Their structures were characterized by ^{1}H-, ^{13}C- and ^{31}P-NMR, ESI-MS and single-crystal X-ray diffraction. Their purity was confirmed by elemental analysis. The disappearance of the ^{1}H-NMR signals of NC*H*C, and the downfield ^{13}C-NMR signals of the NCN carbene carbon at *ca.* 159 ppm in the ^{1}H- and ^{13}C-NMR spectra of **3a–3c** are indicative of Ni–$C_{carbene}$ bond formation. The ^{31}P-NMR spectra of **3a–3c** give a septet peak with a very similar chemical shift as for **2a–2c**, indicating the presence of a non-coordinating $[PF_6]^-$ ion in **3a–3c**. The ESI-MS spectra show the characteristic peaks of the $[CpNiL]^+$ cation at $m/z = 338.1$ (for **3a**), 364.1 (for **3b**) and 414.1 (for **3c**) (+ve mode) and the $[PF_6]^-$ anion at m/z 145 (−ve mode), supporting the formation of the ionic Ni(II)–NHC complexes. The carbene carbon signals of **3a–3c** are located in the range of those observed in the closely related ionic CpNi(II)–NHC complexes where the Ni center is bound to one monodentate NHC and one solvate,[3g–i] such as [CpNi(IMes)($NCCH_3$)][PF_6] (IMes = 1,3-bis-(2,4,6-trimethylphenyl)imidazol-2-ylidene)[3g] or two mono-dentate NHC ligands, [CpNi(IMes)(IMe)][PF_6] (IMe = 1,3-dimethylimidazol-2-ylidene),[5c] and the CpNi complexes containing the NHC ligand with allylic *N*-substitution, [CpNi(η^2-IAll)][BF_4][3c] (IAll = 1-methyl-3-allylimidazolin-2-ylidene or 1,3-diallylimidazolin-2-ylidene) in which one allylic double bond is nickel-coordinated. The singlet ^{1}H-NMR signals of the Cp ligand in **3a–3c** at δ 5.97, 5.89 and 5.78 ppm, respectively, locate at the lower field in comparison with those observed in other CpNi(II)–NHC complexes.[3–5] Only [CpNi(η^2-IAll)][BF_4] showed the comparable downfield signals of the Cp ligand (δ 5.8–5.9 ppm in CD_2Cl_2).[3c] The ^{13}C-NMR signal of the Cp ligand of **3a–3c** is in the range of those observed in other CpNi(II)–NHC complexes (δ 91–96 ppm).[3–5] Similar to those in the CpNi(II) complexes with NHC bearing allylic *N*-substitution,[3c,l,4i] the protons of the terminal CH_2 groups of the allyl group in **3b** give rise to two signals at δ 5.38 ppm (*cis*) and δ 5.15 ppm (*trans*).

Molecular structures of 3a–3c determined by single-crystal X-ray diffraction

The green single crystals of **3a–3c**, suitable for X-ray diffraction, were obtained by cooling their saturated CH_3CN solution at −19 °C. The X-ray diffraction structural analysis confirms **3a–3c** are ionic complexes. In the $[CpNiL]^+$ cation, the benzothiazolyl imidazol-2-ylidene ligand coordinates to the Ni(II) center in a bidentate *N*,*C* chelating mode, forming a five-membered ring as shown in Fig. 1–3. The allyl donor in **3b** is dangling. The key bond lengths and angles of **3a–3c** are given in Table 1.

The Ni center adopts a distorted pseudo-trigonal geometry. The sum of the angles with Ni as the vertex is 360° in all complexes with the $C_{carbene}$Ni–$N_{benzothiazole}$ angle of *ca.* 84° being significantly smaller than the idealized angle. In the other neutral and ionic CpNi(II)–NHC complexes, the $C_{carbene}$–Ni–X or $C_{carbene}$–Ni–L angles (X = halides or SR^-; L = a neutral donor) are in the range of 92°–98°.[3–5] The smaller bite angle observed in **3a–3c** can be attributed to the chelating effect. The Ni–$C_{carbene}$ bond lengths of **3a–3c** (1.866–1.874 Å) are at the short end of the range (1.85–1.92 Å) of the Ni–$C_{carbene}$ distance

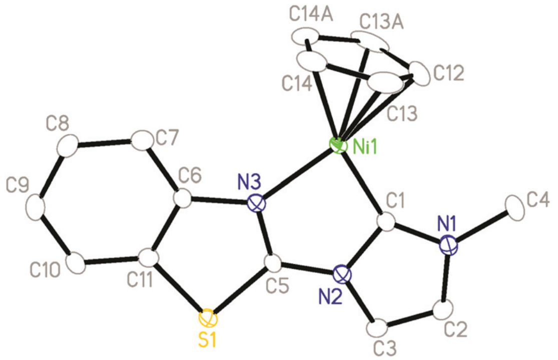


Fig. 1 ORTEP diagram of the $[CpNiL_1]^+$ cation of **3a** (50% probability ellipsoids). Hydrogen atoms are omitted.

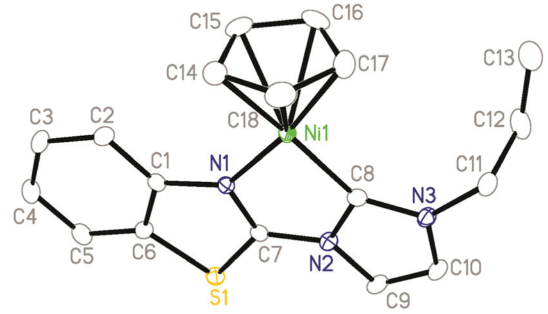


Fig. 2 ORTEP diagram of the $[CpNiL_2]^+$ cation of **3b** (50% probability ellipsoids). Hydrogen atoms are omitted.

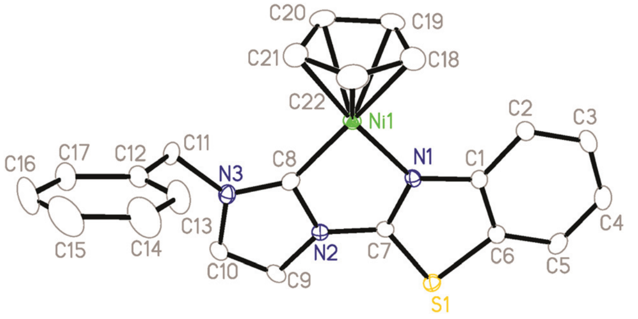


Fig. 3 ORTEP diagram of the $[CpNiL_3]^+$ cation of **3c** (50% probability ellipsoids). Hydrogen atoms are omitted.

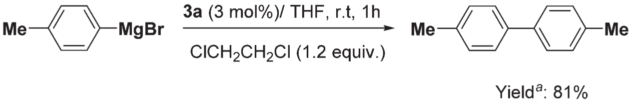
Table 1 Selected bond length (Å) and angles (°) of complexes **3a–3c**

Bond length (Å) or angle (deg)	3a	3b	3c
$Ni–Cp_{cent}$	1.740	1.738	1.730
$Ni–C_{carbene}$	1.868(2)	1.874(2)	1.866(3)
$Ni–N_{benzothiazole}$	1.929(18)	1.9274(19)	1.925(2)
$C_{carbene}–Ni–Cp_{cent}$	138.04	139.89	138.87
$C_{carbene}–Ni–N_{benzothiazole}$	83.83(9)	83.82(9)	83.92(10)
$Cp_{cent}–Ni–N_{benzothiazole}$	138.12	136.23	137.16

found in CpNi(II)–NHC complexes[3–5] due to the chelating effect. Similar shortening of the M–$C_{carbene}$ bond has also been found in their CpMo analogues.[6c]

Catalytic application of 3a–3c in C–C bond formation reactions

A preliminary survey of the catalytic activity of 3a in Kumada–Tamao–Corriu cross-coupling reactions and related reactions. Complex CpNi(IMes)Cl has been reported to be an efficient pre-catalyst for the cross-coupling of aryl *O*-sulfamates with arylmagnesium bromides under mild conditions.[5a] Due to the high activity and easy availability of Grignard reagents,[8] and our recent success in the Ni catalysed cross-coupling of Grignard reagents with organic halides,[7a,b] we employed similar conditions to examine the catalytic activity of **3a** towards Kumada–Tamao–Corriu cross-coupling reactions (Scheme 2 and Table S1 in the ESI†). After 1 h, **3a** (1 mol%) gave only 22% and 40% yield of the cross-coupling product of 4-bromoanisole with phenylmagnesium bromide or with *p*-tolylmagnesium bromide at r.t., respectively. However, a significant amount of the homo-coupling product of Grignard reagents has been observed.

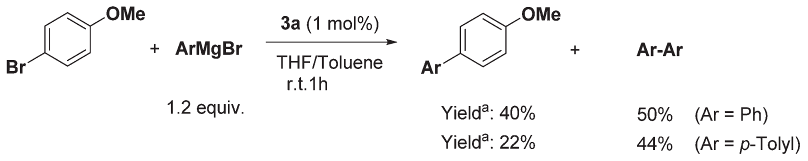


Scheme 3 Oxidative homo-coupling of aryl Grignard reagents catalysed by **3a**. ^{a} Isolated yield.

In transition metal catalysed cross-coupling reactions, the homo-coupling products of the organometallic reagents are unwanted by-products. However, the selective oxidative homo-coupling of aryl metal reagents has been receiving significant attention because this type of reaction provides a straightforward protocol to symmetrical biaryls and polyaromatic conjugated compounds.[9] The oxidative coupling reactions of aryl Grignard reagents have been actively investigated using different transition metal based catalyst systems,[10] such as Fe,[10a–f] Cu,[10g,h] Mn,[10d,i] Co[10f,j,k] and Ru.[10l] The use of Ni catalysts is less common in comparison with their use in other types of C–C bond formation reactions.[10m] The results shown in Scheme 2 prompted us to explore the activity of **3a** in the oxidative homo-coupling product of the aryl Grignard reagent. A preliminary condition screening (Table S2 in ESI†) showed **3a** (3 mol%) gave 81% yield of the homo-coupling product of *p*-tolylmagnesium bromide at r.t. after 1 h in the presence of 1,2-dichloroethane as an oxidant (Scheme 3), suggesting that CpNi(II)–NHC complexes can be used as catalysts for this type of reaction. The results also indicate that the oxidative addition of organo halide to the reduced Ni center could occur during the reaction.

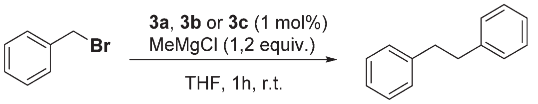
Catalytic application of 3a–3c in the homo-coupling of benzylic halides

Bibenzyl compounds and their derivatives can be found in a wide array of naturally occurring products and pharmaceuticals.[11] It is, thus, important to have a facile entry to symmetrical bibenzyl derivatives through the catalytic homo-coupling of benzylic halides.[12] Some Ni-based catalyst systems supported by different ligands are known to be active for this type of reaction.[12d–h] For example, POCOP-nickel(II) pincer complexes could catalyse the homo-coupling reactions of benzyl halides in the presence of Zn, giving the coupled products in high yields at 115 °C after 15 h.[12g] $NiCl_2(PPh_3)_2$ catalysed the reaction with moderate to good activity in the presence of Mg, Mn or Zn at r.t. for 18 h.[12h] As shown in Table 2, under conditions similar to the Kumada–Tamao–Corriu cross-coupling reactions shown in Scheme 2, **3a–3c** (1 mol%) could catalyse the reaction between benzylic bromide and MeMgCl at r.t. affording bibenzyl in 70–80% yield after 1 h with 100% conversion of benzylic



Scheme 2 Kumada–Tamao–Corriu reactions catalysed by **3a**. ^{a} Isolated yield.

Table 2 Homo-coupling of benzyl bromide catalysed by **3a–3c**[a]



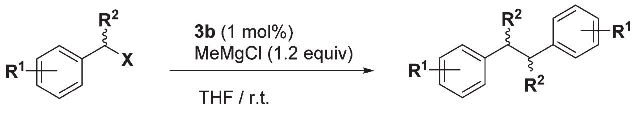
Entry	Catalyst	Yield of bibenzyl[b] (%)	Recovered benzyl bromide[b] (%)
1	**3a**	71 (71)	0
2	**3b**	81 (78)	0
3	**3c**	76 (74)	0
4	—	n.d.[c]	100
5[d]	**3b**	n.d.	86
6	CpNi(IMes)Cl	51	37

[a] Reaction conditions: benzyl bromide (0.5 mmol), MeMgCl (0.6 mmol, 1.0 M in THF), catalyst (1 mol%) in THF (2 mL), r.t. 1 h. [b] Isolated yields and NMR yields. The isolated yields are given in parentheses. [c] n.d. = not detected. [d] 0.1 mmol of MeMgCl used.

bromide (entries 1–3). The reduction product and the cross-coupling product were observed in GC-MS as side products. No reaction occurred in the absence of a catalyst (entry 4). A stoichiometric amount of Grignard reagents was required for the reaction. No bibenzyl was detected when only 0.2 equivalent of MeMgCl was used (entry 5). When the complex CpNi(IMes)Cl was used as the catalyst (entry 6), the yield of bibenzyl was significantly lower and the reaction was incomplete.

The scope of the benzylic halide substrates was studied using **3b** as a catalyst and the results are summarized in Table 3. The electron-donating groups (entries 1 and 2) and electron withdrawing groups (entries 3–5) on the *para*-position did not influence the activity of the catalyst **3b** giving similar high yields of bibenzyl products. It is peculiar that the reaction was tolerant to the nitrile and ester functional groups (entries 4 and 5). The homo-coupling reaction also proceeded selectively on the sp^3 halide instead of the sp^2 halide (entries 6 and 7). The homo-coupling of (1-bromoethyl)benzene led to a parallel amount of diastereomeric products (entry 8) with 77% yield. The reaction of a sterically hindered substrate (entry 9) required an additional hour of reaction to reach full conversion and gave a yield comparable to the less sterically hindered substrates. When the less reactive chlorinated substrates were used (entries 10–13), the reactions required 24 h to achieve full conversion and the yield of bibenzyl products was generally low as expected.

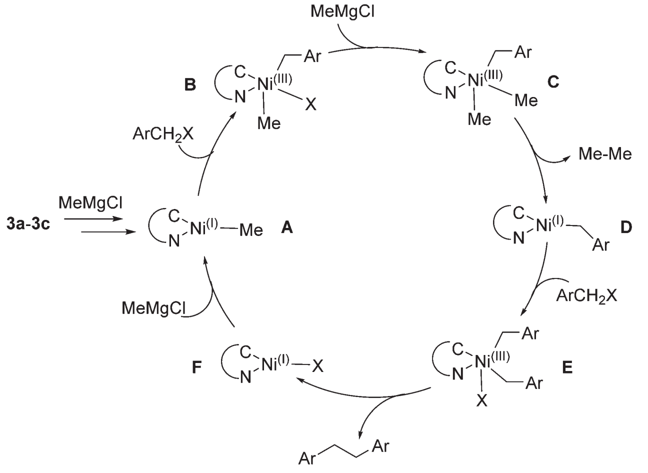
Table 3 Homo-coupling of benzyl halides catalysed by **3b**[a]



Entry	R^1	R^2	X	Time (h)	Yield[b] (%)
1	4-^{i}Pr	H	Br	1	83
2	4-^{t}Bu	H	Br	1	88
3	4-CF$_3$	H	Br	1	77
4	4-CN	H	Br	1	85[c]
5	4-COOMe	H	Br	1	70[c]
6	4-Br	H	Br	1	81
7	2-Br	H	Br	1	83
8	H	Me	Br	1	77[c] [1 : 1][d]
9	2-Me	H	Br	2	87[e]
10[f]	H	H	Cl	24	44
11[f]	2-Me	H	Cl	24	65
12[f]	4-Me	H	Cl	24	24
13[f]	4-CF$_3$	H	Cl	24	16

[a] Reaction conditions: benzylic halide (0.5 mmol), MeMgCl (0.6 mmol, 1.0 M in THF), **3b** (1 mol%), THF (2 mL) at r.t. for 1 h. [b] Isolated yields; complete conversion for all reactions. [c] NMR yield. [d] Diastereomeric ratio [*meso* : *dl*] based on NMR. [e] 87% conversion after 1 h. [f] 3 equiv. of MeMgCl was used.

In CpNi(II)–NHC complex catalysed Buchwald–Hartwig arylaminations and Suzuki–Miyaura coupling reactions, low valent Ni(0) and Ni(I) species stabilized by the NHC ligand have been proposed to be the active species or intermediates.[4a,b,5c] Although neither Ni(0)–NHC nor Ni(I)–NHC species have been isolated by using CpNi(II)–NHC complexes as precursors, they could have been obtained through other synthetic routes and their application in C–C bond formation reactions has been studied.[13] It has been reported recently that CpNi(I)–NHC complexes, CpNi(IPr) and CpNi(SIPr) (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene; SIPr = 1,3-bis(2,6-diisopropylphenyl)imidazolidin-2-ylidene), isolated from the reaction between NaCp and [(μ-Cl)Ni(IPr)]$_2$ or [(μ-Cl)Ni(SIPr)]$_2$, could be used as pre-catalysts for Suzuki–Miyaura cross-coupling reactions.[13h] T-shaped three-coordinate nickel(I) halide bearing two bulky NHC ligands, Ni(IPr)$_2$Cl, has been proved to be a reaction intermediate in Ni(IPr)$_2$Cl$_2$ catalysed Kumada–Tamao–Corriu cross-coupling reactions.[13i] The analogous complex Ni(IMes)$_2$Br has been found to be active for both Kumada–Tamao–Corriu and Suzuki–Miyaura cross-coupling reactions.[13j] For both reactions, Ni(I)(IMes)$_n$Ar formed through transmetalation was proposed to be the active species capable of reacting with aryl halide to form a Ni(III) diaryl halide.[13j] Reaction of [(μ-Cl)Ni(IPr)]$_2$ with {CH(SiMe$_3$)$_2$}MgCl could afford a two coordinate nickel(I) alkyl complex (IPr)Ni{CH(SiMe$_3$)$_2$}.[13k] The use of sterically encumbered Grignard reagents prevents the formation of the Ni(0) dimer. (IPr)Ni{CH(SiMe$_3$)$_2$} could react with benzyl bromide to give Ni(II) alkyl halide, bibenzyl and 1,1-bis(trimethylsilyl)-2-phenylethane through a radical oxidative addition mechanism and a Ni(III) dialkyl bromide complex has been proposed to be the intermediate.[13k] Although the catalytic reaction mechanism has not been investigated in this work, on the basis of the mechanistic studies for Ni-catalysed homo- and cross-coupling reactions of organic halides involving Ni(I) and Ni(III) species[14] and the results mentioned above,[13] a tentative reaction mechanism for the homo-coupling of benzylic halides catalysed by **3a–3c** has been proposed (Scheme 4). Before the beginning of the catalytic cycle, Ni(I) methyl species **A** supported by the bidentate hybrid NHC ligand could be generated from the reactions between **3a–3c** with MeMgCl. Oxidative addition of benzyl halide onto **A** gives the Ni(III) species **B**. Subsequently



Scheme 4 Tentative reaction mechanism of **3a–3c** catalysed sp^3–sp^3 homo-coupling of benzylic halides.

reacting with MeMgCl, **B** is converted to another Ni(III) species **C**. The elimination of ethane from **C** gives a Ni(I)-benzyl intermediate **D**. Through another oxidation addition process of the benzyl halide, **D** is converted to a Ni(III) bisbenzyl species **E**. **E** undergoes reductive elimination to give the bibenzyl product and a Ni(I) halide **F**. **F** reacts further with MeMgCl to regenerate **A**. The higher efficiency of **3a–3c** compared with CpNi(IMes)Cl indicates the beneficial effect of the chelating ligand on catalyst performance which has been observed in many Ni–NHC catalysed C–C formation reactions.[2a] In this system, the bidentate hybrid NHC ligand could stabilize the highly reactive Ni(I) and Ni(III) species more efficiently. Furthermore, the presence of N donors in the hybrid NHC ligand could result in a more facile oxidation addition, while the steric pressure caused by the bidentate ligand could favour the reduction elimination process. When PhMgBr was used to replace MeMgCl, a mixture containing bibenzyl, the cross-coupling product, and the homo-coupling product of PhMgBr could be observed in GC-MS after 1 h using **3a** as a catalyst. The proposed catalytic cycle is also consistent with this observation.

Conclusions

A series of air-stable CpNi(II) complexes **3a–3c** with bidentate hybrid NHC ligands have been synthesized and fully characterized. A preliminary survey of their application in C–C bond formation reactions shows **3a** is active for the catalytic oxidative homo-coupling of Grignard reagents. In the presence of a Grignard reagent, complexes **3a–3c** are efficient catalysts for the homo-coupling of benzyl bromides under facile conditions (r.t., 1 h and 1 mol% of catalyst loading) and with good functional groups tolerance. Further exploration of the catalytic applications of CpNi–NHC complexes towards C–C bond formation reactions is currently underway.

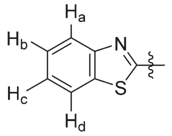
Experimental

Materials and physical measurements

All commercial chemicals were used as purchased. All preparations and manipulations were performed using standard Schlenk techniques under an argon atmosphere. Solvents were dried by standard procedures. Nickelocene,[3d] CpNiCl(IMes)Cl[3d] and benzothiazolyl-imidazolium chloride salts **1a–1c**[6c] were prepared according to the literature methods. Elemental analyses for C, H, and N were performed on a Perkin-Elmer PE 2400 CHNS elemental analyzer and an Elementar vario MICRO Cube. ^{1}H and ^{13}C NMR were recorded at r.t. with Bruker ACF300 300 MHz and AMX500 500 MHz FT NMR spectrometers. Electrospray ionisation mass spectrometric (ESI-MS) analysis was performed on a Finnigan LCQ quadrupole ion trap mass spectrometer and a Bruker amaZon X ion trap mass spectrometer.

General procedure for the synthesis of benzothiazolyl-imidazolium hexafluorophosphates (2a–2c)

To a solution of benzothiazolyl-imidazolium chloride salts **1a–1c** (1.0 mmol) in methanol (40 mL) was added NH$_4$PF$_6$ (173 mg, 1.1 mmol). The solution was stirred at r.t. for 8 h. The precipitate was collected and washed with methanol (2 × 20 mL). The characterization data for **2a–2c** are as follows.



Proton labelling of the benzothiazolyl moiety for NMR signal assignments

For 1-(2-benzothiazolyl)-3-methylimidazolium hexafluorophosphate (**2a**). White solid (yield: 253 mg, 70%). ^{1}H NMR (500 MHz, CD$_3$CN): δ (ppm) = 9.32 (s, 1H, NC*H*N), 8.12 (d, *J* = 8.0 Hz, 1H, H$_a$), 8.08–8.06 (m, 2H, =C*H*N(CH$_3$) and H$_d$), 7.67 (dt, *J* = 8.0 Hz, 1.0 Hz, 1H, H$_c$), 7.62–7.59 (m, 2H, =C*H*N(benzothiazole) and H$_b$), 3.99 (s, 3H, N(C*H*$_3$)). ^{13}C NMR (125.77 MHz, CD$_3$CN): δ (ppm) = 154.91 (N*C*S), 150.60 (N*C*N), 136.90, 134.58, 128.97, 128.23, 126.31, 124.51, 123.77, 121.72, 37.82 (N–*C*H$_3$). ^{31}P NMR (202.44 MHz, CD$_3$CN): δ (ppm) = −143.78 (sep, *P*F$_6$). ESI-MS (in CH$_3$CN: *m/z*): $[\mathrm{L_1H}]^+$ = 216.2, $[\mathrm{PF_6}]^-$ = 145.1. Anal. Calcd for C$_{11}$H$_{10}$F$_6$N$_3$PS: C, 36.57; H 2.79; N, 11.63; S, 8.88. Found: C, 36.16; H, 3.03; N, 11.58; S, 9.10.

For 1-(2-benzothiazolyl)-3-allylimidazolium hexafluorophosphate (**2b**). Off-white solid (yield: 325 mg, 84%). ^{1}H NMR (500 MHz, CD$_3$CN): δ (ppm) = 9.35 (s, 1H, NC*H*N), 8.13–8.12 (m, 2H, =C*H*N(Allyl) and H$_a$), 8.07 (d, *J* = 8.5 Hz, 1H, H$_d$), 7.69–7.64 (m, 2H, =C*H*N(benzothiazole) and H$_c$), 7.61 (dt, *J* = 8.0 Hz, 1.0 Hz, 1H, H$_b$), 6.10 (ddt, *J* = 7.0 Hz, 6.5 Hz, 6.0 Hz, 1H, –CH$_2$C*H*=CH$_2$), 5.54–5.51 (m, 2H, –CH$_2$CH=C*H*$_2$), 4.92 (d, *J* = 6.5 Hz, 2H, –C*H*$_2$CH=CH$_2$). ^{13}C NMR (125.77 MHz, CD$_3$CN): δ (ppm) = 154.91 (N*C*S), 150.59 (N*C*N), 136.39, 134.65, 130.72, 128.99, 128.28, 124.98, 124.54, 123.79, 123.17, 122.14, 53.55. ^{31}P NMR (202.44 MHz, CD_3CN): δ (ppm) = −143.77 (sep, *P*F$_6$). ESI-MS (in CH_3CN: *m*/*z*): $[L_2H]^+$ = 242.2, $[PF_6]^-$ = 145.1. Anal. Calcd for $C_{13}H_{12}F_6N_3PS$: C, 40.31; H, 3.12; N, 10.85; S, 8.28. Found: C, 40.06; H, 3.35; N, 11.02; S, 8.52.

For 1-(2-benzothiazolyl)-3-benzylimidazolium hexafluorophosphate (**2c**). White solid (yield: 354 mg, 81%). ^{1}H NMR (500 MHz, CD_3CN): δ (ppm) = 9.43 (s, 1H, NC*H*N), 8.13–8.10 (m, 2H, ═C*H*N(Bn) and H_a), 8.06 (d, *J* = 8.0 Hz, 1H, H_d), 7.67 (t, *J* = 8.5 Hz, 1H, H_c), 7.63–7.59 (m, 2H, ═C*H*N(benzothiazole) and H_b), 7.52–7.45 (m, 5H, Ph), 5.48 (s, 2H, –C*H*$_2$Ph). ^{13}C NMR (125.77 MHz, CD_3CN): δ (ppm) = 154.91 (N*C*S), 150.56 (N*C*N), 136.39, 134.64, 133.74, 130.61, 130.37, 130.02, 129.00, 128.29, 124.88, 124.53, 123.78, 122.34, 54.87. ^{31}P NMR (202.44 MHz, CD_3CN): δ (ppm) = −143.78 (sep, *P*F$_6$). ESI-MS (in CH_3CN: *m*/*z*): $[L_3H]^+$ = 292.2, $[PF_6]^-$ = 145.1. Anal. Calcd for $C_{17}H_{14}F_6N_3PS$: C, 46.69; H, 3.23; N, 9.61; S, 7.33. Found: C, 46.74; H, 3.40; N, 9.60; S, 7.74.

General procedure for the synthesis of nickel complexes (3a–3c)

A solution of **2a**, **2b** or **2c** (0.1 mmol) in acetonitrile (5 mL) was added to nickelocene (23 mg, 0.12 mmol). The solution was stirred at 80 °C for 12 h. The solution slowly turned from dark green to brownish-green. The solvent was then removed under vacuum. The residue was washed with ethanol (3 × 5 mL) and then redissolved in acetonitrile (10 mL) and filtered. The solvent of the filtrate was evaporated to yield a green solid.

For 3a. Bright green solid (yield: 34 mg, 70%). ^{1}H NMR (500 MHz, CD_3CN): δ (ppm) = 8.07 (d, *J* = 8.0 Hz, 1H, H_a), 7.97 (d, *J* = 2.0 Hz, 1H, ═C*H*N(CH_3)), 7.66 (t, *J* = 7.5 Hz, 1H, H_c), 7.58–7.55 (m, 2H, H_b and H_d), 7.25 (d, *J* = 2.0 Hz, 1H, ═C*H*N (benzothiazole)), 5.97 (s, 5H, Cp), 3.77 (s, 3H, N(C*H*$_3$)). ^{13}C NMR (125.77 MHz, CD_3CN): δ (ppm) = 175.71 (N*C*S), 158.61 (N*C*N), 149.67, 131.19, 129.44, 128.45, 127.66, 125.14, 121.34, 118.97, 93.44 (Cp), 39.04 (N–*C*H$_3$). ^{31}P NMR (202.44 MHz, CD_3CN): δ (ppm) = −143.76 (sep, *P*F$_6$). ESI-MS (in CH_3CN: *m*/*z*): $[CpNiL_1]^+$ = 338.1, $[PF_6]^-$ = 145.1. Anal. Calcd for $C_{16}H_{14}F_6N_3PSNi$: C, 39.70; H, 2.92; N, 8.68; S, 6.62. Found: C, 39.50; H, 3.33; N, 8.66; S, 6.50.

For 3b. Bright green solid (yield: 33 mg, 65%). ^{1}H NMR (500 MHz, CD_3CN): δ (ppm) = 8.08 (d, *J* = 8.0 Hz, 1H, H_a), 8.02 (s, 1H, ═C*H*N(Allyl)), 7.66 (t, *J* = 7.5 Hz, 1H, H_c), 7.58–7.55 (m, 2H, H_b and H_d), 7.27 (s, 1H, ═C*H*N(benzothiazole)), 6.11–6.02 (m, 1H, –CH$_2$C*H*═CH$_2$), 5.89 (s, 5H, Cp), 5.38 (d, *J* = 10.5 Hz, 1H, –CH$_2$CH═C*H*$_2$), 5.15 (d, *J* = 17 Hz, 1H, –CH$_2$CH═C*H*$_2$), 4.66 (s, 2H, –C*H*$_2$CH═CH$_2$). ^{13}C NMR (125.77 MHz, CD_3CN): δ (ppm) = 175.86 (N*C*S), 158.71 (N*C*N), 149.68, 132.89, 131.19, 129.46, 127.69, 127.27, 125.17, 121.32, 119.54, 118.88, 93.76 (Cp), 53.56 (N–*C*–CH═CH$_2$). ^{31}P NMR (202.44 MHz, CD_3CN): δ (ppm) = −143.77 (sep, *P*F$_6$). ESI-MS (in CH_3CN: *m*/*z*): $[CpNiL_2]^+$ = 364.1, $[PF_6]^-$ = 145.1. Anal. Calcd for $C_{18}H_{16}F_6N_3PSNi$: C, 42.39; H, 3.16; N, 8.24; S, 6.29. Found: C, 42.50; H, 3.28; N, 8.11; S, 6.12.

For 3c. Dark green solid (yield: 40 mg, 71%). ^{1}H NMR (500 MHz, CD_3CN): δ (ppm) = 8.09 (d, *J* = 8.0 Hz, 1H, H_a), 8.05 (s, 1H, ═C*H*N(Bn)), 7.66 (t, *J* = 7.5 Hz, 1H, H_c), 7.60–7.51 (m, 2H, H_b and H_d), 7.46–7.26 (m, 6H, ═C*H*N(benzothiazole) and Ph), 5.78 (s, 5H, Cp), 5.29 (s, 2H, –C*H*$_2$Ph). ^{13}C NMR (125.77 MHz, CD_3CN): δ (ppm) = 176.34 (N*C*S), 158.77 (N*C*N), 149.71, 136.15, 131.21, 130.15, 129.47, 127.82, 127.72, 127.54, 125.19, 121.33 119.80, 93.79 (Cp), 54.87 (N–*C*-Ph). ^{31}P NMR (202.44 MHz, CD_3CN): δ (ppm) = −143.77 (sep, *P*F$_6$). ESI-MS (in CH_3CN: *m*/*z*): $[CpNiL_3]^+$ = 414.1, $[L_3H]^+$ = 292.1, $[PF_6]^-$ = 145.1. Anal. Calcd for $C_{22}H_{18}F_6N_3PSNi$: C, 47.17; H, 3.24; N, 7.50; S, 5.72. Found: C, 47.26; H, 3.48; N, 7.19; S, 5.45.

General procedure for the catalytic cross-coupling of 4-bromoanisole with aryl Grignard reagents

A Schlenk tube, placed under an argon atmosphere, was charged with 4-bromoanisole (0.5 mmol), **3a** (0.005 mmol, 1 mol%), and toluene (1 mL) at r.t. under stirring. An aryl Grignard reagent (0.6 mmol, 1.0 M in THF) was added dropwise within 30 min and the resulting reaction mixture was stirred at r.t. for another 30 min. The reaction was quenched with a drop of HCl (aq., 2 M) and the solvent removed under reduced pressure. The product was isolated by flash chromatography on silica gel with hexane as the eluent.

General procedure for catalytic homo-coupling of aryl Grignard reagents

A Schlenk tube, placed under an argon atmosphere, was charged with **3a** (0.005 mmol, 1 mol%), 1,2-dichloroethane (0.62 mmol) and THF (2 mL) at r.t. under stirring. An aryl Grignard reagent (0.5 mmol, 1.0 M in THF) was added and the resulting reaction mixture was stirred at r.t. for 1 h. The reaction was quenched with a drop of HCl (aq., 2 M) and the solvent removed under reduced pressure. The product was isolated by flash chromatography on silica gel with hexane as the eluent.

General procedure for catalytic homo-coupling of benzyl halides

In a typical example, after standard cycles of evacuation and back-fill with pure argon, complex **3b** (2.5 mg, 0.005 mmol) was introduced into a 25 mL-Schlenk tube equipped with a magnetic stir bar. To the catalyst were added THF (2 mL), internal standard 1,3,5-trimethoxybenzene (42 mg, 0.25 mmol) and benzyl bromide (59.5 μL, 0.5 mmol) at r.t. under stirring. A methylmagnesium chloride solution (3.0 M in THF, 0.2 mL, 0.6 mmol) was added and the resulted reaction mixture was stirred at r.t. for 1 h. The reaction was quenched with a drop of HCl (aq., 2 M) and the solvent removed under reduced pressure. The product was isolated by flash chromatography on silica gel with hexane as the eluent. NMR yields were calculated using 1,3,5-trimethoxybenzene as the internal standard.

X-ray crystallography

Diffraction measurements were conducted at 100 K on a Bruker D8 Venture X-Ray diffractometer by using Mo Kα radiation (λ = 0.71073 Å) and a Photon 100 detector. The data were corrected for Lorentz and polarization effects with the Apex 2 suite of programs and for absorption effects with SADABS.[15]

Structure solutions and refinements were performed by using the program Bruker Apex 2. The structures were solved by direct methods to locate the heavy atoms, followed by difference maps for the light non-hydrogen atoms. Anisotropic thermal parameters were refined for the rest of the non-hydrogen atoms. Hydrogen atoms were placed geometrically and refined isotropically. Crystal data and structure refinement for complexes **3a**–**3c** are given in Table S3 in the ESI.†

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