Formation and crystallographic elucidation of stable [4 + 2]-coordinate nickel(II) *N,S*-heterocyclic carbene (NSHC) complexes†

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A series of square-planar *N,S*-heterocyclic carbene (NSHC) complexes *trans*-[NiX$_2$(*N*-RBzTh)$_2$] (BzTh = benzothiazolin-2-ylidene) (R/X = Bz/Br; Me/I; Et/I; Pr^i/I; Bu^i/I) have been synthesized and characterized by X-ray single-crystal diffraction analysis. These are the first crystallographically established NSHC complexes of nickel in the literature. The *N,S*-heterocyclic carbene (NSHC) rings invariably twist away from co-planarity with the metal coordination plane such that the *N*-substituent moves on top and below the metal to facilitate electrostatic γ-hydride interaction, thus giving an essentially [4 + 2] coordination at the Ni(II) center. These compounds are active toward reductive Ullmann-type coupling reactions in Bu$_4$NBr showing higher activities towards bromoanisole or bromotoluene than bromobenzene. The complex *trans*-[NiI$_2$(*N*-Pr^{i}BzTh)$_2$] with the shortest Ni$\cdots$H anagostic separation and a near-ideal orthogonal orientation between the carbene and metal planes gives the highest yields.
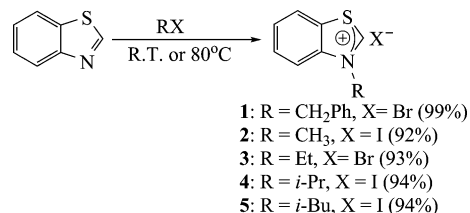
Introduction

Encouraged by the isolation of the first stable *N*-heterocyclic carbene (NHC) by Arduengo in 1991,[1] many research teams have embarked on the synthesis of NHC complexes and a broad range of their catalytic applications.[2] A myriad of purpose-specific catalysts can be accessed through different chemical modifications of heterocyclic skeletons, *N*-substituents, metal atoms and their oxidation states, ancillary ligands and a mix of these permutations. An increasingly popular trend is the design of carbenes with other heteroatoms such as *P*-, *N,O*- and *N,S*-heterocyclic carbenes (PHCs, NOHCs and NSHCs, respectively). Some carbene ligands such as PHCs[3] are stable enough to be isolated but the majority of others such as NOHC and NSHC are usually isolated in their complexed state as the free ligands are unstable and undergo a facile proton-catalyzed chemical equilibrium with their dimers.[4] Accordingly, there are emerging examples of NSHCs among metals such as Cu(I),[5a] Au(I),[5b] Au(III),[5b,5c] Pd(II),[5d,6] Ir(I),[5e] Ru(II)[5f] that are prepared from direct or indirect metallation methods. Among the neglected metals is nickel, which is surprising considering that it exhibits a rich structural chemistry[7] and a host of catalytic functions.[8] Within our knowledge, there is no general method reported for Ni(II) NSHC (*N,S*-heterocyclic carbene) complexes, nor is there any crystallographic structural report of such in the literature. We are hence interested to extend the current commonly used synthetic method for Pd(II)[6] to its congeneric and isoelectronic d^8 Ni(II) benzothiazole carbene complexes and study their structural characteristics. We herein also demonstrate their catalytic potential by their activity in Ullmann coupling reactions.

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Results and discussion

Synthesis of benzothiazolium salts

Benzothiazolium bromide/iodide salts [(C$_6$H$_4$)SCHNR]X (R and X = Bz and Br (**1**); Me and I (**2**); Et and Br (**3**); Pr^i and I (**4**); Bu^i and I (**5**)) with different nitrogen substituents could be obtained as off-white or light yellow powders in good yields (>90%) by treatment of the freshly distilled benzothiazole and appropriate alkyl halide at r.t. (**1**) or 80 °C (**2–5**) using a solvent-free method (Scheme 1).[6] Their ^{1}H NMR spectra invariably show downfield resonances for the SCHN protons in the range of 11.38–12.25 ppm.

1: R = CH$_2$Ph, X= Br (99%)
2: R = CH$_3$, X = I (92%)
3: R = Et, X= Br (93%)
4: R = *i*-Pr, X = I (94%)
5: R = *i*-Bu, X = I (94%)

Scheme 1 Synthesis of benzothiazolium salts **1–5**.

Synthesis and characterization of Ni(II) complexes

The benzothiazolium salts are convenient synthetic precursors to carbene. This is exemplified by a general and one-step condensation reaction with anhydrous Ni(OAc)$_2$ in dry THF, which gives the corresponding neutral benzothiazolin-2-ylidene (BzTh) Ni(II)–NSHC complexes *trans*-[NiX$_2$(*N*-RBzTh)$_2$] (R/X = Bz/Br (**6**); Me/I (**7**); Et/I (**8**); Pr^i/I(**9**); Bu^i/I(**10**)) in 66–84% yields (Scheme 2). Ni(II)–NSHC complexes are generally absent in the literature with a notable early example of a cationic mono-carbene complex prepared from oxidative addition of chloro-1,3-thiazole with Ni(0).[9] In the preparation of **8**, NaI is added to assist the crystallization of good quality single crystals. Complexes **6–10**

are stable in dry air but are moisture sensitive. They are very soluble in solvents of high dielectric constants such as DMF and DMSO. Complex **6** is highly soluble in MeCN, CH_2Cl_2, THF and toluene, whereas **7–10** are moderately soluble in CH_3CN, CH_2Cl_2 and THF, but insoluble in toluene. Their elemental analysis data are consistent with their chemical formulae. The NCHS protons in **1–5** (^1H NMR) are absent in **6–10** upon complex formation. The ^{13}C NMR signals of the carbenoid carbon of **6**, **9** and **10** occur at 220.7–223.5 ppm, but are not observed in **7** and **8**.
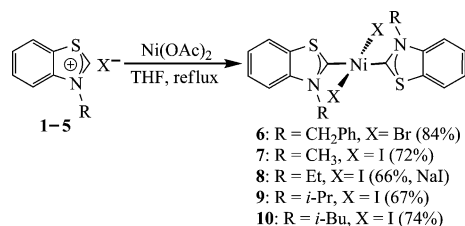
Scheme 2 Synthesis of Ni(II) bis(benzothiazolin-2-ylidene) complexes **6–10**.

Molecular structures of 6–10

The ^1H NMR spectra, except that of complex **6**, show two sets of signals for the aliphatic protons, suggesting the coexistence of *trans-anti* and *trans-syn* rotamers in solutions. X-ray single-crystal crystallographic analysis of **6–10** revealed an essentially square-planar geometry for Ni(II) (*cis* X–Ni–C 89.38(7)°–90.9(3)° and *trans* 179.3(4)°–180°) with two NSHC ligands mutually *trans* to each other, and similar for the two halides X (Fig. 1 and Table 1). These complexes invariably show the *trans-anti* conformers in the crystalline state, which are in good agreement with their analogous Ni–NHC complexes, such as *trans*-NiCl$_2$(Cy$_2$Im)$_2$ (Cy$_2$Im = 1,3-dicyclohexylimidazolin-2-ylidene),[7a] *trans*-NiCl$_2$(Mes$_2$Im)$_2$ (Mes$_2$Im = 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene),[10] and *trans*-NiI$_2$($^iPr_2$Im)$_2$ ($^iPr_2$Im = 1,3-diisopropylimidazolin-2-ylidene).[8b] No *cis*- form of these complexes was isolated or observed. The C$_3$NS heterocyclic planes invariably twist out and nearly perpendicular to the coordination plane (dihedral angle δ >81.1°). The Ni–C bonds (1.890(11)–1.910(9) Å) are similar to those in related Ni–NHC complexes, such as *trans*-NiI$_2$(MePrIm)$_2$ (MePrIm = 3-methyl-1-propylimidazolin-2-ylidene) (1.899(11) Å),[8b] NiBr(η^3-C$_3$H$_5$)(Me$_4$Im) (Me$_4$Im = 1,3,4,5-tetramethylimidazol-2-ylidene) (1.907(2) Å)[11] and NiI$_2$(Me$_2$CH$_2$Im$_2$)$_2$ (Me$_2$CH$_2$Im$_2$ = 1,1'-dimethyl-3,3'-methylenediimidazoline-2,2'-diylidene) (1.909(2) Å).[12] The Ni–Br bond length in **6** (2.3138(3) Å) and Ni–I in **7–10** (2.4757(14)–2.4959(7) Å) are comparable to those reported in related Ni–NHC carbene complexes, such as *trans*-NiBr$_2$(Cy$_2$Im)$_2$ (Cy$_2$Im = 1,3-dicyclohexylimidazol-2-ylidene) (2.3113(4) Å),[7a] *trans*-NiI$_2$(MePrIm)$_2$ (MePrIm = 3-methyl-1-propylimidazolin-2-ylidene) (2.4952(8) Å)[8b] and *trans*-NiI$_2$(PrMeIm)$_2$ (PrMeIm = 1-propyl-3-methylbenzimidazolin-2-ylidene) (2.4906(4) Å).[13]

An additional incentive for the NSHC ring to twist out of the coordination plane is to allow the γ-H on the *N*-substituent to move above and below the Ni center. This promotes weak anagostic M ··· H–C interactions, which are typically associated with d^8 systems and believed to have considerable relevance to many catalytic processes.[14] The Ni ··· H–C distances thus observed
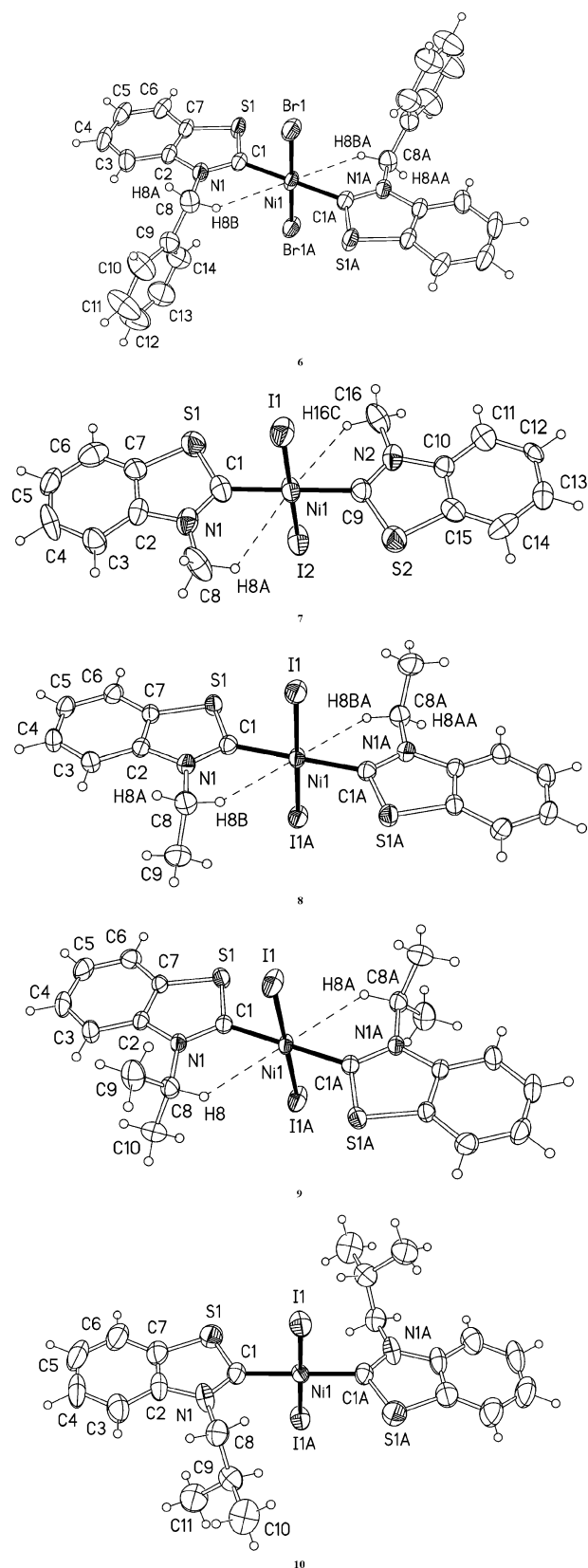

Fig. 1 ORTEP diagrams of **6–10** with 50% probability ellipsoids and labelling scheme, showing the Ni ··· H–C anagostic interactions in complexes **6–9**. A: −x + 1, −y, −z (**6**); −x + 1, −y + 1, −z (**8**); −x + 2, −y + 2, −z (**9**); −x + 0.5, −y + 1.5, −z (**10**).

Table 1 Selected bond lengths (Å) and angles (°) for **6–10**

	6·toluene	**7**	**8**	**9**	**10**
Ni(1)–X(1)^a	2.3139(3)	2.490(1)	2.4883(2)	2.4916(2)	2.4959(7)
Ni(1)–X(2)	—	2.476(1)	—	—	—
Ni(1)–C(1)	1.893(2)	1.910(9)	1.895(2)	1.896(2)	1.89(1)
Ni(1)–C(9)	—	1.893(8)	—	—	—
C(1)–S(1)	1.714(2)	1.73(1)	1.726(2)	1.717(3)	1.74(1)
C(9)–S(2)	—	1.754(9)	—	—	—
C(1)–N(1)	1.329(3)	1.31(1)	1.330(3)	1.333(3)	1.32(2)
C(9)–N(2)	—	1.33(1)	—	—	—
C(1)–Ni(1)–X(1)^a	90.62(7)	90.9(3)	89.61(7)	90.17(7)	89.7(3)
C(9)–Ni(1)–X2	—	89.3(3)	—	—	—
S(1)–C(1)–Ni(1)	119.7(1)	122.8(5)	120.7(1)	121.5(1)	118.1(7)
S(2)–C(9)–Ni(1)	—	22.0(5)	—	—	—
N(1)–C(1)–Ni(1)	130.6(2)	126.9(7)	129.5(2)	128.4(2)	131.8(9)
N(2)–C(9)–Ni(1)	—	128.0(7)	—	—	—
S(1)–C(1)–N(1)	109.7(2)	110.3(7)	109.8(2)	110.1(2)	110.1(9)
S(2)–C(9)–N(2)	—	110.0(6)	—	—	—
Dihedral angle^b	85.7	93.2/93.5	85.3	88.8	81.1

^{a} X = Br for **6**·toluene; X = I for **7–10**. ^{b} Dihedral angle between the [NiC$_2$X$_2$] and N,S-heterocyclic carbene planes.

Table 2 Comparison of selected structural and spectroscopic data for γ-hydride interactions in **6–10**

Complex	$\delta_H{}^a$ $(\Delta\delta_H)^b$ (ppm)	$d(H\cdots M)$/Å	$\theta(C-H\cdots M)/°$
6·2toluene	6.79 (0.36)	2.80	117
7	4.82(0.11)/4.76(0.05)^c	2.77/2.69	112/117
8	5.54(0.38)/5.44(0.28)^c	2.83	113
9	7.12(1.58)/6.99(1.45)^c	2.63	122
10	5.06(0.12)/4.94(0.00)	2.98	103

^{a} Measured in CDCl$_3$. ^{b} $\Delta\delta_H = \delta_H$ (complex) $- \delta_H$ (corresponding ligand precursor). ^{c} Two resonances from *trans-anti* and *trans-syn* rotamers.

(2.63–2.83 Å) are similar or shorter (except in **10**) than the sum of van der Waals radii of 2.83 Å for Ni and H (Table 2). This is consistently found in different substituents, covering benzyl (**6**), methyl (**7**), ethyl (**8**) and isopropyl (**9**), thus resulting in [4 + 2] coordination and tetragonally distorted octahedral-like structures of Ni(II) in the solid state. Similar interactions are found in some Ni(II)–NHC complexes[8j] but not apparent in the others.[7] The interaction would be most effective when the carbene ring plane is near-perpendicular to the coordination plane as it would place the γ-H above or below the metal, giving pseudo-double-chelates. This is exemplified in **9**, which has the shortest Ni···H–C separation (2.63 Å) when the two planes are nearly orthogonal (88.8°), whereas in **10**, the longest separation (2.98 Å) is associated with the smallest dihedral angle (81.1°) (Table 2). These electrostatic interactions are persistent in the solutions of **6–9** as witnessed in the downfield shift of $\Delta\delta_H = 0.05$–1.58 ppm for the deshielding N–CH protons compared to their counterpart in the ligand precursor.

Ullmann-type coupling

The complexes **6–10** are catalytically active towards the reductive Ullmann coupling reactions[15] of aryl bromides under standard conditions of 1 mol% catalyst and 75 mol% of reducing zinc[16] in an ionic liquid Bu$_4$NBr medium (Table 3). Electron donating 4-bromotoluene and 4-bromoanisole, unexpectedly, give better coupling yields (26–92%) than bromobenzene (14–69%). This

Table 3 Ullmann coupling reaction of aryl bromides catalyzed by complexes **6–10**

R—⟨benzene⟩—Br →[1 mol% [Ni] / 75 mol% Zn / [Bu$_4$N]Br / 115°C, 24 h] R—⟨biphenyl⟩—R

R = H, CH$_3$, OCH$_3$

Run	Catalyst	Aryl halide	Yield (%)
1	**6**	Bromobenzene	57
2	**7**	Bromobenzene	19
3	**8**	Bromobenzene	14
4	**9**	Bromobenzene	35
5	**10**	Bromobenzene	69
6	**6**	4-Bromotoluene	48
7	**7**	4-Bromotoluene	37
8	**8**	4-Bromotoluene	26
9	**9**	4-Bromotoluene	92
10	**10**	4-Bromotoluene	82
11	**6**	4-Bromoanisole	43
12	**7**	4-Bromoanisole	44
13	**8**	4-Bromoanisole	46
14	**9**	4-Bromoanisole	75
15	**10**	4-Bromoanisole	70
16	Ni(OAc)$_2$/**4**	4-Bromoanisole	43
17	Ni(OAc)$_2$/**5**	4-Bromoanisole	46

is at odds with other recent reports in which Pd(OAc)$_2$ or Ni–NHC catalysts are used.[8j,17] It is also surprising that electron-withdrawing 4-bromobenzaldehyde gives no significant product in all cases. The use of DMF as solvent also gives no significant product. For bromotoluene or bromoanisole, complexes **9** and **10** (70–92%) generally show better activities than **6–8** (26–48%). Complex **9** in particular, which shows the strongest H···Ni interaction, registers the highest yields of 92% (entry 9) and 75% (entry 14). When the ligand precursor of **9** and **10** *viz.* **4** or **5** (2%) are used with Ni(OAc)$_2$ (1%) in an attempt to generate an *in situ* catalytic mixture, the yields are significantly lower (43% (run 16) and 46% (run 17)). The catalytic yields of the current system are generally comparable to those in the literature.[17] For example, similar coupling of 4-bromoanisole using the more expensive Pd/C in water and liquid CO$_2$ in high pressure (6 MPa) gives

a yield of 53%.[17b] Homocoupling of 4-bromoanisole with 4 mol% Pd(OAc)$_2$ with As(o-tol)$_3$ at 100 °C affords a yield of 54%.[17c]

Conclusion

There are emerging examples of Ni(II)–NHC complexes in the literature.[7c,8,10–13,19] This introduction of the NSHC series with a softer and substituent-less sulfur atom on the heterocyclic ring would provide a simple mechanism to modify the electronic and steric effect imparted by the carbene ligand. At present, there is no evidence of sulfur coordination to metal. Any chemical stability or catalytic activity gained from the use of benzothiazolin-2-ylidene ligand is probably attributed to the π-donation effect of sulfur that could stabilize the M–C coordinative unit. We are currently exploring other metal systems that could benefit from the presence of the thiazol-2-ylidene moiety.

Experimental

General procedures

All manipulations were carried out under a dry nitrogen atmosphere using standard Schlenk techniques. Ligand N-benzylbenzothiazolium bromide (1) was prepared according to the literature method.[6a] Ni(OAc)$_2$·4H$_2$O was dried under vacuum at 130 °C to remove the hydrate. Other commercially available chemicals were purchased from Sigma-Aldrich. All solvents were freshly distilled from standard drying agents. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker ACF 300 spectrometer, and chemical shifts (δ) for ^{1}H and ^{13}C spectra were recorded in ppm relative to the residual proton of CDCl$_3$ (^{1}H: 7.26 ppm; ^{13}C: 75.48 ppm). Elemental analyses were performed on a Perkin-Elmer PE 2400 elemental analyzer. ESI mass spectra were obtained using a Finnigan LCQ. The yields of C–C coupling products were determined by using Hewlett Packard Series 6890 GC (Santa Clara, CA, USA) coupled to a Hewlett Packard 5973 MS detector.

N-methylbenzothiazolium iodide (2)

A mixture of benzothiazole (2.71 g, 20.0 mmol) and iodomethane (3.00 g, 21.2 mmol) was stirred at r.t. for about 24 h to yield an off-white solid, which was collected by filtration and washed successively with CH$_2$Cl$_2$ and Et$_2$O, and dried under vacuum. Yield: 5.12 g (18.5 mmol, 92%). ^{1}H NMR (300.1 MHz, CDCl$_3$): δ 11.96 (s, 1H, NCH), 8.26 (d, 1H, ^3JHH = 8.10 Hz, Ar–H), 8.06 (d, 1H, ^3JHH = 8.70 Hz, Ar–H), 7.95 (t, 1H, Ar–H), 7.88 (t, 1H, Ar–H), 4.71 (s, 3H, CH$_3$). ^{13}C NMR (75.48 MHz, CDCl$_3$): δ 165.4 (NCS), 131.2, 130.2, 125.3, 116.9 (Ar–C), 41.0 (CH$_3$). MS (ESI, positive mode) m/z (%): 150.1 (100) [M – I]$^+$. Anal. calcd for C$_8$H$_8$INS: C 34.67, H 2.91, N 5.05. Found: C 34.82, H 2.99, N 5.01.

N-ethylbenzothiazolium bromide (3)

A mixture of benzothiazole (2.71 g, 20.0 mmol) and bromoethane (2.50 g, 22.9 mmol) was stirred at 80 °C overnight to yield a large amount of light yellow crude product, which was collected and washed with diethyl ether. The solid was then washed with dichloromethane to afford a white solid, and dried under vacuum.

Yield: 3.86 g (18.6 mmol, 93%). ^{1}H NMR (300.1 MHz, CDCl$_3$): δ 11.87 (s, 1H, NCH), 8.45 (d, 1H, ^3JHH = 8.10 Hz, Ar–H), 8.16 (d, 1H, ^3JHH = 8.40 Hz, Ar–H), 7.86 (t, 1H, Ar–H), 7.76 (t, 1H, Ar–H), 5.16 (m, 2H, CH$_2$), 1.73 (t, 3H, CH$_3$). ^{13}C NMR (75.48 MHz, CDCl$_3$): δ 165.1 (NCS), 140.6, 132.1, 130.8, 129.7, 126.0, 117.2 (Ar–C), 49.6 (CH$_2$CH$_3$), 15.6 (CH$_2$CH$_3$). MS (ESI, positive mode) m/z (%): 164.1 (100) [M – Br]$^+$. Anal. calcd for C$_9$H$_{10}$BrNS: C 44.27, H 4.13, N 5.74. Found: C 44.34, H 4.11, N 5.68.

N-isopropylbenzothiazolium iodide (4)

Compound 4 was prepared and purified in a similar way to that used for 3, using benzothiazole (2.71 g, 20.0 mmol) and 2-iodo-propane (3.65 g, 21.5 mmol) as starting materials. The product was precipitated as a light yellow solid. Yield: 5.74 g (18.8 mmol, 94%). ^{1}H NMR (300.1 MHz, CDCl$_3$): δ 11.38 (s, 1H, NCH), 8.54 (d, 1H, ^3JHH = 7.80 Hz, Ar–H), 8.28 (d, 1H, ^3JHH = 8.70 Hz, Ar–H), 7.88 (t, 1H, Ar–H), 7.78 (t, 1H, Ar–H), 5.54 (m, 1H, CH), 1.91 (d, 3H, CH$_3$), 1.88 (d, 3H, CH$_3$). ^{13}C NMR (75.48 MHz, CDCl$_3$): δ 161.6 (NCS), 139.6, 130.9, 130.1, 128.9, 125.4, 117.3 (Ar–C), 57.0 (CH(CH$_3$)$_2$), 22.2 (CH(CH$_3$)$_2$). MS (ESI, positive mode) m/z (%): 178.0 (100) [M – I]$^+$. Anal. calcd for C$_{10}$H$_{12}$INS: C 39.36, H 3.96, N 4.59. Found: C 39.31, H 3.97, N 4.52.

N-isobutylbenzothiazolium iodide (5)

Compound 5 was prepared and purified similarly as 3, using benzothiazole (2.71 g, 20.0 mmol) and 1-iodo-2-methyl-propane (3.72 g, 20.2 mmol) as starting materials. The product was precipitated as light yellow solid. Yield: 6.02 g (18.8 mmol, 94%). ^{1}H NMR (300.1 MHz, CDCl$_3$): δ 11.56 (s, 1H, NCH), 8.51 (d, 1H, ^3JHH = 8.70 Hz, Ar–H), 8.18 (d, 1H, ^3JHH = 8.40 Hz, Ar–H), 7.89 (t, 1H, Ar–H), 7.80 (t, 1H, Ar–H), 4.94 (d, 2H, JHH = 7.80 Hz, CH$_2$), 2.47 (m, 1H, CH), 1.07 (d, 3H, CH$_3$), 1.04 (d, 3H, CH$_3$). ^{13}C NMR (75.48 MHz, CDCl$_3$): δ 163.9 (NCS), 141.0, 131.3, 130.9, 129.7, 126.2, 117.7 (Ar–C), 60.3 (CH$_2$CH(CH$_3$)$_2$), 29.6 (CH$_2$CH(CH$_3$)$_2$), 20.3 (CH$_2$CH(CH$_3$)$_2$). MS (ESI, positive mode) m/z (%): 192.1 (100) [M – I]$^+$. Anal. calcd for C$_{11}$H$_{14}$INS: C 41.39, H 4.42, N 4.39. Found: C 41.39, H 4.39, N 4.33.

Dibromobis(N-benzylbenzothiazolin-2-ylidene)nickel(II) (6)

A mixture of Ni(OAc)$_2$ (0.088 g, 0.5 mmol) and 1 (0.306 g, 1 mmol) was stirred under vacuum at 50 °C for 1 h. THF (20 mL) was then added and the suspension refluxed overnight. After cooling, the solvent was removed under vacuum, leaving a red residue. The solid was washed with hexane (20 mL) and extracted with toluene (20 mL). Red crystals were formed when the solution extract was cooled to −20 °C for several days. Yield: 0.28 g (0.42 mmol, 84%). ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.74 (b, 1H, Ar–H), 7.53 (b, 3H, Ar–H), 7.33 (b, 4H, Ar–H), 7.38 (b, 1H, Ar–H), 6.79 (s, 2H, CH$_2$). ^{13}C NMR (75.48 MHz, CDCl$_3$): δ 220.7 (NCHS), 162.2, 154.3, 144.3, 138.0, 134.9, 129.7, 128.9, 128.4, 127.2, 124.8, 122.6, 115.1 (Ar–C), 59.9 (CH$_2$). Anal. calcd for C$_{28}$H$_{22}$Br$_2$N$_2$NiS$_2$ (6·0.2C$_6$H$_5$CH$_3$): C 50.26, H 3.31, N 4.19. Found: C 51.15, H 3.54, N 4.13.

General procedures for the preparation of *trans*-diiodobis(benzothiazolin-2-ylidene)nickel(II) complexes (7–10)

A mixture of $Ni(OAc)_2$ (0.088 g, 0.5 mmol) and ligand **2–5** (1 mmol) was stirred under vacuum at 50 °C for 1 h (for ligand **3**, NaI (0.30 g, 2 mmol) was added). THF was then added and the suspension refluxed overnight. After cooling, the solvent was removed under vacuum, leaving a red residue, which was re-dissolved in 20 mL of CH_2Cl_2 and was filtered. The solution was mixed with Et_2O (5 mL) and cooled to −20 °C to yield red crystals of **7–10** in one week.

Diiodobis(*N*-methylbenzothiazolin-2-ylidene)nickel(II) (7)

Yield: 0.22 g (0.36 mmol, 72%). ^1H NMR (300 MHz, $CDCl_3$): δ 7.75 (d, 1H, ^3JHH = 7.80 Hz, Ar–H), 7.60 (d, 1H, ^3JHH = 8.10 Hz, Ar–H), 7.75 (t, 1H, Ar–H), 7.35 (t, 1H, Ar–H), 4.82 (m, CH_3), 4.76 (m, CH_3). ^{13}C NMR (75.48 MHz, $CDCl_3$): δ 144.7, 126.2, 124.2, 121.6, 112.6 (Ar–C), 42.1 (CH_3). Anal. calcd for $C_{16}H_{14}I_2N_2NiS_2$: C 31.46, H 2.31, N 4.59. Found: C 31.27, H 2.36, N 4.49.

Diiodobis(*N*-ethylbenzothiazolin-2-ylidene)nickel(II) (8)

Yield: 0.21 g (0.33 mmol, 66%). ^1H NMR (300 MHz, $CDCl_3$): δ 7.79 (d, 1H, ^3JHH = 8.10 Hz, Ar–H), 7.62 (d, 1H, ^3JHH = 7.20 Hz, Ar–H), 7.44 (t, 1H, Ar–H), 7.33 (t, 1H, Ar–H), 5.54 (m, CH_2), 5.44 (m, CH_2), 1.95 (t, 3H, CH_3). ^{13}C NMR (75.48 MHz, $CDCl_3$): δ 126.0, 124.1, 121.8, 113.1, 112.9 (Ar–C), 50.8 (CH_2CH_3), 12.9

(CH_2CH_3). Anal. calcd for $C_{18}H_{18}I_2N_2NiS_2$: C 33.83, H 2.84, N 4.38. Found: C 33.68, H 2.84, N 4.28.

Diiodobis(*N*-isopropylbenzothiazolin-2-ylidene)nickel(II) (9)

Yield: 0.28 g (0.28 mmol, 67%). ^1H NMR (300 MHz, $CDCl_3$): δ 7.79 (d, 1H, ^3JHH = 8.10 Hz, Ar–H), 7.70 (d, 1H, ^3JHH = 7.80 Hz, Ar–H), 7.38 (t, 1H, Ar–H), 7.28 (t, 1H, Ar–H), 7.12 (m, CH), 6,99 (m, CH), 2.09 (d, CH_3), 1.99 (d, CH_3). ^{13}C NMR (75.48 MHz, $CDCl_3$): δ 221.8 (NCHS), 142.7, 139.2, 125.5, 123.9, 122.0, 115.2 (Ar–C), 62.2 ($CH(CH_3)_2$), 19.9 ($CH(CH_3)_2$). Anal. calcd for $C_{20}H_{22}I_2N_2NiS_2$: C 36.01, H 3.32, N 4.20. Found: C 35.75, H 3.38, N 4.09.

Diiodobis(*N*-isobutylbenzothiazolin-2-ylidene)nickel(II) (10)

Yield: 0.31 g (0.33 mmol, 74%). ^1H NMR (300 MHz, $CDCl_3$): δ 7.74 (d, 1H, Ar–H), 7.60 (d, 1H, Ar–H), 7.42 (t, 1H, Ar–H), 7.32 (t, 1H, Ar–H), 5.05 (d, CH_2), 4.94 (d, CH_2), 3.85 (m, CH_2), 3.42 (m, CH_2), 1.27 (d, CH_3), 1.21 (d, CH_3). ^{13}C NMR (75.48 MHz, $CDCl_3$): δ 223.5 (NCHS), 145.2, 137.3, 125.7, 124.0, 121.6, 113.5 (Ar–C), 62.0 ($CH_2CH(CH_3)_2$), 28.3 ($CH_2CH(CH_3)_2$), 21.0 ($CH_2CH(CH_3)_2$). Anal. calcd for $C_{22}H_{26}I_2N_2NiS_2$: C 38.01, H 3.77, N 4.03. Found: C 37.98, H 3.76, N 3.96.

General procedure for the Ullmann coupling reaction

A mixture of zinc powder (0.049 g, 0.75 mmol) and [Bu_4N]Br (1 g, excess) was dried in vacuum at 80 °C for 2 h. The corresponding nickel(II) carbene complex catalyst (0.01 mmol) was added, followed by the injection of liquid aryl halides (1 mmol).

Table 4 Summary of crystallographic parameters and refinement results for complexes **6–10**

	$6\cdot2C_6H_5CH_3$	7	8	9	10
Formula	$C_{42}H_{38}Br_2N_2NiS_2$	$C_{16}H_{14}I_2N_2NiS_2$	$C_{18}H_{18}I_2N_2NiS_2$	$C_{20}H_{22}I_2N_2NiS_2$	$C_{22}H_{26}I_2N_2NiS_2$
FW	853.39	610.92	638.97	667.03	695.08
Crystal system	Triclinic	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$Pna2_1$	$P2_1/n$	$P2_1/n$	$C2/c$
a/Å	8.3327(5)	15.503(2)	9.0231(5)	8.4018(5)	17.355(2)
b/Å	8.7543(5)	10.986(2)	10.4549(5)	12.2872(7)	9.9210(9)
c/Å	14.4928(9)	11.369(2)	11.1487(6)	11.0743(6)	14.951 (1)
α/°	98.214(1)				
β/°	104.950(1)	93.817(1)	90.503(1)	93.931(2)	
γ/°	102.293(1)				
V/Å^3	975.9(1)	1936.2(5)	1049.4(1)	1143.2 (1)	2568.2(4)
Z	1	4	2	2	4
D_{calcd}/g cm^{-3}	1.452	2.096	2.022	1.938	1.798
μ/mm^{-1}	2.683	4.406	4.069	3.740	3.333
$F(000)$	434	1160	612	644	1352
No. of reflections collected	12 903	13 192	7234	14 493	7236
No. of unique reflections	4481	4084	2404	2612	2264
R_{int}	0.0262	0.0453	0.0208	0.0284	0.0318
No. of observed reflections	3640	3547	2270	2522	2126
Parameters	265	211	116	126	135
T/K	293(2)	223(2)	223(2)	293(2)	223(2)
$R_1{}^a$ (all data)	0.0475	0.0564	0.0232	0.0277	0.0820
$wR_2{}^b$ (all data)	0.0956	0.1128	0.0543	0.0581	0.2055
GOF^c	1.043	1.025	1.043	1.103	1.264
$\Delta\rho_{max}$/e Å^{-3}	0.689	1.015	0.670	0.870	3.792
$\Delta\rho_{min}$/e Å^{-3}	−0.264	−0.415	−0.884	−0.428	−0.904

^{a} $R_1 = \sum\|F_o| - |F_c\|/\sum|F_o|$. ^{b} $wR_2 = \{w\sum(|F_o| - |F_c|)^2/\sum w|F_o|^2\}\}^{1/2}$. ^{c} $GOF = \{\sum w(|F_o| - |F_c|)^2/(n-p)\}^{1/2}$, where n is the number of reflections and p is total number of parameters refined.

The mixture was stirred at 115 °C for 24 h. The reaction was quenched with deionized water and the biaryl product extracted with Et$_2$O and dried with MgSO$_4$. The volatiles were removed under vacuum to give a crude product which was analyzed by GC-mass chromatography.

X-Ray diffraction studies

Suitable crystals were mounted on quartz fibers and X-ray data were collected on a Bruker AXS APEX diffractometer equipped with a CCD detector, using graphite-monochromated MoKα radiation ($\lambda = 0.71073$ Å). The data were corrected for Lorentz and polarization effects with the SMART program suite and for absorption effects with SADABS. The crystal structures were solved by direct methods and refined by full-matrix least squares on F^2 using the SHELXTL program package.[18] For **6**·2C$_6$H$_5$CH$_3$, the toluene solvate shows two-fold disorder and was refined with a disorder model. The occupancy factors for the two disordered parts were refined with 0.52 : 0.48. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were calculated in ideal geometries and refined isotropically. Selected crystal data for complexes **6–10** are summarized in Table 4.

Acknowledgements

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