Dalton
Transactions

PAPER

View Article Online
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Cite this: DOI: 10.1039/c4dt03786c

Novel imidazolium and imidazolinium salts containing the 9-nickelafluorenyl anion – synthesis, structures and reactivity†

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Received 10th December 2014,
Accepted 3rd March 2015

DOI: 10.1039/c4dt03786c

www.rsc.org/dalton

Investigation of the properties of carbene complexes is one of the most important fields of modern coordination chemistry. In this paper, we propose the convenient synthesis of NHC–nickel compounds. The 9-nickelafluorenyllithium complex reacts with imidazolium or imidazolinium salts to afford 9-nickelafluorenyl–NHC salts *via* ionic metathesis with very good yields (66–92%). These compounds can be isomerised at elevated temperatures to give Ni–NHC complexes with excellent yields (88–91%), probably *via* nickel mediated hydrogen transfer to the biphenyl moiety. In this reaction, the nickelacyclic ring itself serves as a base in the deprotonation of the carbene precursor. DFT calculations show the thermodynamic instability of the synthesized salts, with Gibbs free energy differences for **1** of −84 kJ mol^{-1} at 298 K and −167 kJ mol^{-1} at 374 K. The obtained salts and carbene complexes are relatively air and moisture stable in the solid state.

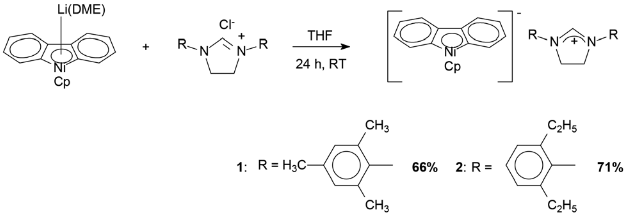
Introduction

The first syntheses of carbenes in the 19th century[1] and the dramatic increase in scientific interest in these compounds in the 20th century have resulted in a huge class of ligands and one of the most important subjects of research in coordination chemistry.[2] The convenient synthesis by Arduengo and co-workers[3] of stable carbenes based on 1,3-imidazole moieties with bulky N-substituents was a breakthrough in carbene chemistry.[2] Carbene complexes can be obtained by various methods, for example *via* reactions with isolated free carbenes or *in situ* generated carbenes.[4] The only disadvantage of the Arduengo method was the use of strong bases for deprotonation of the carbene precursors. Several alternative pathways have been proposed in order to omit this obstacle.[2,5] Recently, Nolan and co-workers reported a method of synthesizing copper–NHC complexes under mild conditions.[6] In this paper, we propose a novel synthetic pathway to nickel–NHC complexes under base-free conditions *via* ionic metathesis and nickel mediated hydrogen transfer.

Results and discussion

Reactions between 9-nickelafluorenyllithium and imidazolium or imidazolinium salts were carried out in THF at room temperature.

Salt metathesis occurred in all cases (Schemes 1 and 2). Compounds containing the 9-nickelafluorenyl anion and imidazolium or imidazolinium cations were formed. They were relatively air and moisture stable in the solid state. Salts **1–4** were characterized by ^{1}H and ^{13}C NMR spectra, ESI MS spectra and single-crystal X-ray analysis. In the ^{1}H NMR spectra of complexes **1–4**, the most characteristic signals are a singlet at 8–8.5 ppm corresponding to the hydrogen atoms bonded to



Scheme 1 Synthesis of **1** and **2**.

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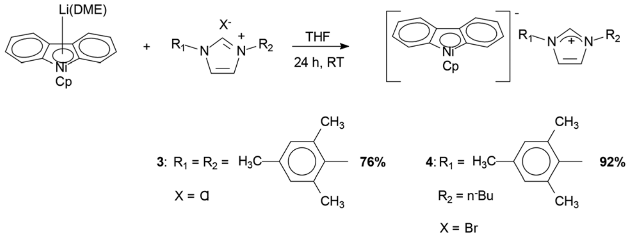
† Electronic supplementary information (ESI) available: CIF files providing X-ray crystallographic data for the structure determinations of **1**, **2**, **3**, **4**, **5** and **7**. Table of crystal data and structure refinement (Table S1). Exact results and graphics for DFT calculations. CCDC 1038668–1038673. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4dt03786c



Scheme 2 Synthesis of **3** and **4**.

the imidazole or imidazoline carbon atom, and the Cp singlet at 4.8–5.1 ppm. Compounds **1–4** exhibit characteristic ^{13}C NMR shifts at approximately 175 ppm, corresponding to the carbene carbon atom.

Crystals of compounds **1–4** appropriate for X-ray diffraction studies were grown from THF–hexane solutions. The molecular structures of **1–4** are presented in Fig. 1–4. Crystal data, data collection parameters and refinement parameters are provided in Table S1.† Compound **1** crystallises in an orthorhombic crystal system, while compounds **2–4** crystallize in a monoclinic crystal system. All compounds form separated ion pairs: the 9-nickelafluorenyl group acts as an anion and the imidazolium or imidazolinium group acts as a cation. The average length of the Ni–C (biphenyl) bonds is 1.89 Å, which is within the range of nickel–carbon single bonds and is similar to the distances in other complexes containing the 9-nickelafluorenyl group.[7] The shortest distance between the carbene carbon atom and the nickel atom varies from approximately 3.5 Å in compound **3** to 4.7 Å in compound **2**.

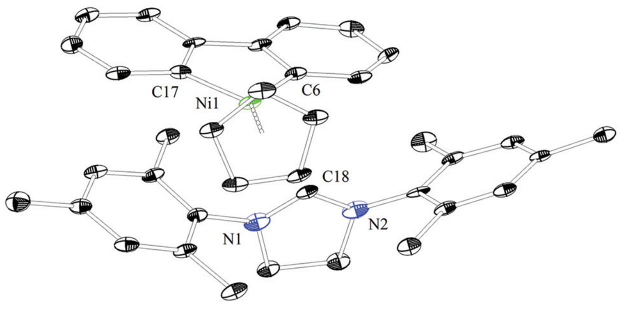


Fig. 1 ORTEP view of the molecular structure of **1**, showing the atom numbering scheme. Thermal ellipsoids are drawn at the 30% probability level. Selected bond lengths [Å] and angles [°]: Ni1–C6 1.882(6), Ni1–C17 1.893(6), N1–C18 1.285(9), N2–C18 1.302(8); C6–Ni1–C17 85.0(3), N1–C18–N2 114.6(6).

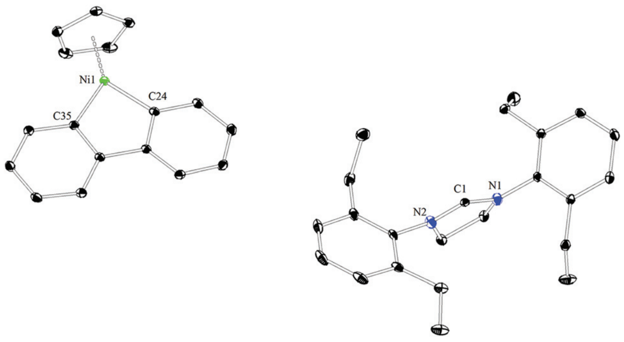


Fig. 2 ORTEP view of the molecular structure of **2**, showing the atom numbering scheme. Thermal ellipsoids are drawn at the 30% probability level. Selected bond lengths [Å] and angles [°]: C24–Ni1 1.885(1), C35–Ni1 1.881(1), C1–N1 1.315(2), C1–N2 1.318(2); C24–Ni1–C35 84.92(5), N1–C1–N2 113.2(1).

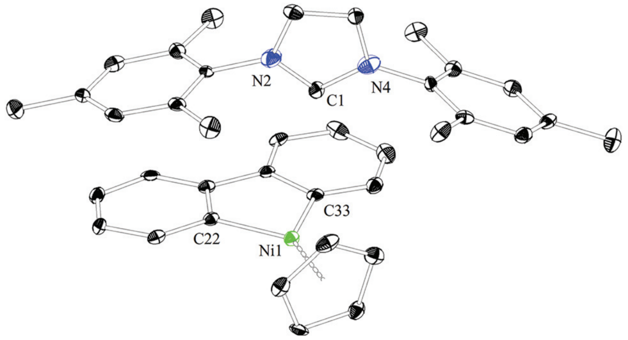


Fig. 3 ORTEP view of the molecular structure of **3**, showing the atom numbering scheme. Thermal ellipsoids are drawn at the 30% probability level. Selected bond lengths [Å] and angles [°]: C1–N2 1.318(6), C1–N4 1.346(6), C22–Ni1 1.893(5), C33–Ni1 1.892(5); N2–C1–N4 107.1(5), C22–Ni1–C33 84.4(2).

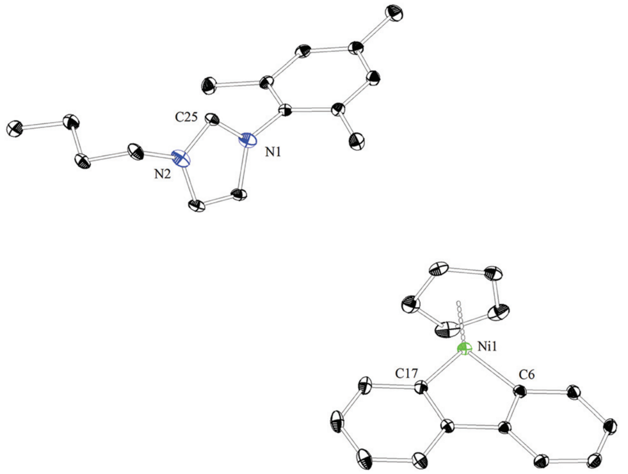
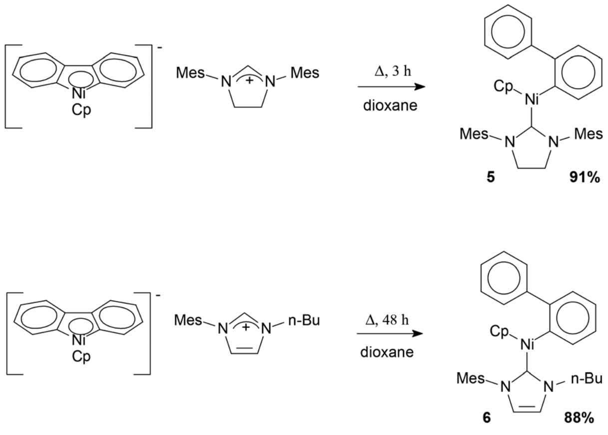


Fig. 4 ORTEP view of the molecular structure of **4**, showing the atom numbering scheme. Thermal ellipsoids are drawn at the 30% probability level. Selected bond lengths [Å] and angles [°]: C6–Ni1 1.8860(9), C17–Ni1 1.8869(9), N1–C25 1.339(1), N2–C25 1.333(1); C6–Ni1–C17 84.76(4), N1–C25–N2 107.99(8).

We conducted DFT calculations on the free nickelacyclic anion and imidazolium cations. As expected, all investigated cations have lowest unoccupied natural bond orbitals (NBOs) with significantly lower energy than the 9-nickelafluorenyl anion's highest occupied NBO. The energy gap is 2.49 eV for



Scheme 3 Synthesis of **5** and **6**.

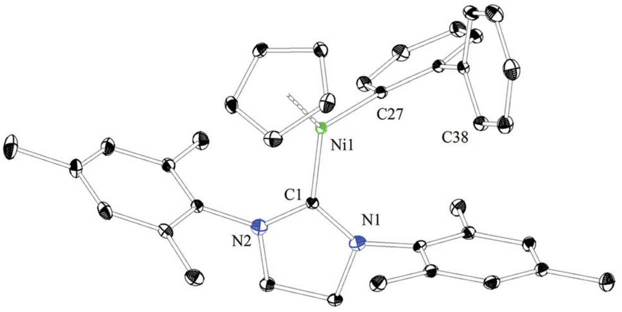


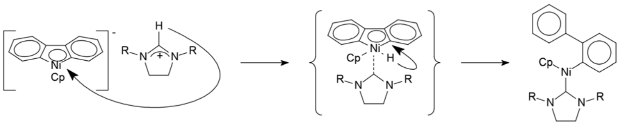
Fig. 5 ORTEP view of the molecular structure of **5**, showing the atom numbering scheme. Thermal ellipsoids are drawn at the 30% probability level. Selected bond lengths [Å] and angles [°]: C1–N1 1.351(1), C1–N2 1.355(1), C1–Ni1 1.882(1), C27–Ni1 1.921(1); N1–C1–N2 106.16(9), C1–Ni1–C27 95.90(4).

compound **1**, 2.62 eV for compound **2**, 0.27 eV for compound **3**, and 0.26 eV for compound **4**. As expected, the lowest unoccupied NBO of the cation is located on the imidazolium ring. Since salts **1–4** can be considered as Lewis pairs, we decided to test their stability in solution at elevated temperatures. First, we heated solutions of **1** and **4** in THF to approximately 60 °C, but no visual changes were observed. We decided to exchange THF for 1,4-dioxane. The reactions were carried out in boiling solvent (Scheme 3). **1** reacted much faster than **4**. The colours of the reaction mixtures changed from orange to olive. **1** completely reacted in 3 hours, while **4** needed almost two days of heating.

The products of the reactions were carbene complexes **5** and **6**, in which the nickel atom is also bonded to the cyclopentadienyl and biphenyl groups. They were characterized by ^{1}H and ^{13}C NMR and EI MS spectra. In the ^{1}H NMR spectra of **5** and **6**, there are very characteristic singlets that correspond to the Cp groups: 4.51 ppm for **5** and 4.93 ppm for **6**. The EI MS spectra of **5** and **6** showed the parent ions at *m*/*z* 582 (**5**) and 518 (**6**) (^{58}Ni calc.) with isotopic patterns that are characteristic of molecules containing one nickel atom.

Crystals of **5** appropriate for X-ray diffraction studies were grown from a hexane–THF solution. The molecular structure of **5** is presented in Fig. 5. Crystal data, data collection parameters and refinement parameters are provided in Table S1.† The compound crystallises in a monoclinic crystal system. The sum of the bond angles around the Ni atom, C1–Ni–C27 (95.9°), C27–Ni–Cg (126.6°) and Cg–Ni–C1 (136.8°) where Cg denotes the centre of gravity of the Cp ring, is 359.3° which indicates planar trigonal coordination of the nickel atom. The C1–Ni1 distance of 1.882 Å is similar to the nickel–carbon bond lengths in other Ni–carbene complexes.[8]

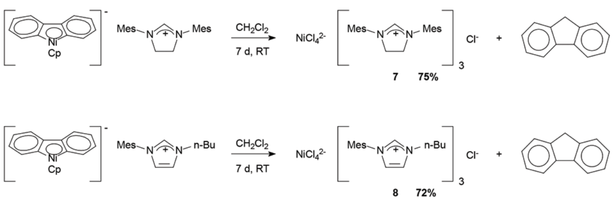
Carbene complexes of nickel are often obtained in the reactions between imidazolium salts and various nickel complexes.[9] In our case, the mechanism of formation of **5** and **6** is most probably based on the nickel mediated hydrogen transfer from the carbene carbon atom to the carbon atom of the biphenyl group (Scheme 4). Such a hydrogen shift is known for nickel compounds,[10] and was studied by our group.[11] To make sure that the hydrogen atom on the biphenyl comes from the carbene and not the solvent, we carried out the thermal rearrangement of a sample of **1** in boiling 1,4-dioxane-d$_8$ for 3 hours. The ^{1}H NMR spectrum of the product was consistent with the spectrum of the product formed in the reaction in non-deuterated solvent.



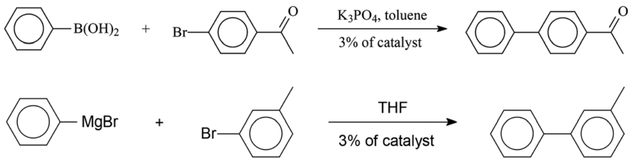
Scheme 4 Hydrogen transfer in **1** and **4**.

The room temperature Gibbs free energy for the isomerisation reaction of salt **1** is −84 kJ mol^{-1}. The isomerisation reaction takes place in refluxing 1,4-dioxane, so we calculated the Gibbs free energy of this reaction at 374 K. The result was −167 kJ mol^{-1}, which is 83 kJ mol^{-1} less than at 298 K. Since the computational results show that the isomerisation reaction is favoured at both room temperature and elevated temperatures, and the experimental results show that products **5** and **6** are stable under the above mentioned conditions, only heat seems to be required to overcome the reaction's kinetic barrier. Unfortunately, we have so far been unable to locate the transition state for this reaction.

We tested the reactivity of salts **1** and **4** towards dichloromethane (Scheme 5).



Scheme 5 Reactions of **1** and **4** with CH_2Cl_2.



Scheme 6 Suzuki and Kumada cross-coupling reactions.

Table 1 Yields of the Kumada and Suzuki coupling reactions

Compound	1	2	3	4	5
Kumada coupling yield (%)	96	94	96	54	92
Suzuki coupling yield (%)	93	92	98	71	98

It is well known[10a] that metallacyclic compounds react with dichloromethane to form carbocyclic rings. Salts **1** and **4** were dissolved in dichloromethane and stirred for 7 days at room temperature. They underwent decomposition to form fluorene as the main organic product (yield over 70%). Nickel–carbon bonds were destroyed to form **7** and **8**, containing the $NiCl_4^{2-}$ complex and carbene cations.

Complexes similar to **5** and **6** were recently thoroughly examined. They are known to be catalysts in the formation of carbon–carbon bonds.[12] Therefore, we decided to test the catalytic activity of the new salts **1–4**, as well as compound **5**, in the Suzuki and Kumada cross-coupling reactions (Scheme 6).

The Suzuki reaction between 4-bromoacetophenone and phenylboronic acid was carried out for 3 hours at 90 °C. Potassium phosphate was used as a base. The Kumada reaction between phenylmagnesium bromide and 3-bromotoluene was carried out for 21 hours at room temperature. The results of the catalytic reactions are summarized in Table 1.

Complexes **1**, **2**, **3** and **5** provided high yields (over 90%) of the expected cross-coupling products. Although in our case the times of the Suzuki reactions were prolonged (from 1 to 3 hours), the results are comparable with the previously reported ones.[9h,12b,c] Salt **4** gave moderate yields for the Suzuki and Kumada reactions. This complex is the only one that has an alkyl chain bonded to the imidazolium ligand. Previous research showed that nickel complexes with more bulky ligands gave better yields in the Suzuki cross-coupling.[9h,12b]

Conclusions

In summary, we have synthesized the new relatively air and moisture stable salts **1–4**, containing the 9-nickelafluorenyl anion and imidazolium or imidazolinium cations, in very good yields. They were transformed into nickel–carbene complexes **5** and **6** by nickel mediated hydrogen transfer. Compounds **1**, **2**, **3** and **5** proved to be very good catalysts in the Suzuki and Kumada cross-coupling reactions.

Experimental section

All reactions were carried out in an atmosphere of dry argon or nitrogen using Schlenk tube techniques. Solvents were dried by conventional methods. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Mercury 400 MHz instrument. Mass spectra were recorded on an AMD-604 spectrometer. Electrospray mass spectra were recorded on an Applied Biosystems 4000 QTRAP spectrometer.

Imidazolium salts[3,13] and the 9-nickelafluorenyllithium complex[7c] were synthesized according to the published procedures.

Synthesis of 1

430 mg (1.2 mmol) of 9-nickelafluorenyllithium dimethoxyethane complex and 60 mL of THF were placed in a Schlenk flask, and 400 mg (1.2 mmol) of 1,3-bis(2,4,6-trimethylphenyl)-imidazolinium chloride was added at room temperature. The reaction was carried out for 24 hours. A red solution and a dark-orange precipitate were obtained. The solvent was removed under vacuum. The orange solid was washed with hexane and deoxygenated water, and dried under vacuum. Compound **1** was obtained as an orange solid. Yield: 460 mg (0.79 mmol, 66%). **^{1}H NMR** (acetonitrile-d_3) (20 °C) δ (ppm): 7.98 (s, 1H, imidazole), 7.25 (d, ^3J = 7.2 Hz, 2H, Ph), 7.05 (s, 4H, Ph), 7.00 (d, ^3J = 7.2 Hz, 2H, Ph), 6.62 (t, ^3J = 7.2 Hz, 2H, Ph), 6.36 (t, ^3J = 7.2 Hz, 2H, Ph), 5.14 (s, 5H, Cp), 4.35 (s, 4H, imidazole), 2.33 (s, 12H, CH_3), 2.19 (s, 6H, CH_3). **^{13}C NMR** (acetonitrile-d_3) (20 °C) δ (ppm): 174.21, 160.66, 156.37, 143.45, 141.66, 136.68, 131.59, 130.85, 122.31, 120.30, 118.73, 90.43, 52.50, 21.51, 18.31. **Electrospray MS** (acetone) *m/z*: 307 ($C_{21}H_{27}N_2^+$). **Anal.** calcd for $C_{38}H_{40}N_2Ni$: C, 78.23; H, 6.91. Found: C, 78.67; H, 6.60.

Synthesis of 2

617 mg (1.65 mmol) of 9-nickelafluorenyllithium dimethoxyethane complex and 50 mL of THF were placed in a Schlenk flask, and 614 mg (1.65 mmol) of 1,3-bis(2,6-diethylphenyl)-imidazolinium chloride was added at room temperature. The reaction was carried out for 24 hours. A red solution was obtained. The solvent was removed under vacuum. The orange solid was washed with hexane and deoxygenated water, and dried under vacuum. Compound **2** was obtained as an orange solid. Yield: 719 mg (1.18 mmol, 71%). **^{1}H NMR** (acetonitrile-d_3) (20 °C) δ (ppm): 8.08 (s, 1H, imidazole), 7.49 (t, ^3J = 8.0 Hz, 2H, Ph), 7.35 (d, ^3J = 8.0 Hz, 4H, Ph), 7.26 (d, ^3J = 7.2 Hz, 2H, Ph), 7.03 (d, ^3J = 7.2 Hz, 2H, Ph), 6.63 (t, ^3J = 7.2 Hz, 2H, Ph), 6.37 (t, ^3J = 7.2 Hz, 2H, Ph), 5.14 (s, 5H, Cp), 4.38 (s, 4H, imidazole), 2.71 (q, ^3J = 7.6 Hz, 8H, CH_2), 1.30 (t, ^3J = 7.6 Hz, 12H, CH_3). **^{13}C NMR** (acetonitrile-d_3) (20 °C) δ (ppm): 174.35, 160.23, 156.40, 143.52, 142.76, 132.53, 132.08, 128.45, 122.31, 120.32, 118.73, 90.43, 54.00, 25.11, 15.88. **Electrospray MS** (acetone) *m/z*: 335 ($C_{23}H_{31}N_2^+$). **Anal.** calcd for $C_{40}H_{44}N_2Ni$: C, 78.57; H, 7.25. Found: C, 78.24; H, 7.44.

Synthesis of 3

360 mg (0.97 mmol) of 9-nickelafluorenyllithium dimethoxyethane complex and 40 mL of THF were placed in a Schlenk flask, and 329 mg (0.97 mmol) of 1,3-bis(2,4,6-trimethylphenyl)imidazolium chloride was added at room temperature. The reaction was carried out for 24 hours. The solvent was removed under vacuum. The orange solid was washed with hexane and deoxygenated water, and dried under vacuum. Compound **3** was obtained as an orange solid. Yield: 432 mg (0.74 mmol, 76%). **^{1}H NMR** (acetonitrile-d_3) (20 °C) δ (ppm): 8.54 (s, 1H, imidazole), 7.66 (s, 2H, =CH), 7.24 (d, ^3J = 7.2 Hz, 2H, Ph), 7.16 (s, 4H, Ph), 6.99 (d, ^3J = 7.2 Hz, 2H, Ph), 6.62 (t, ^3J = 7.2 Hz, 2H, Ph), 6.35 (t, ^3J = 7.2 Hz, 2H, Ph), 5.14 (s, 5H, Cp), 2.39 (s, 6H, CH_3), 2.09 (s, 12H, CH_3). **^{13}C NMR** (acetonitrile-d_3) (20 °C) δ (ppm): 174.33, 156.38, 143.51, 142.63, 135.70, 130.71, 130.13, 125.96, 122.33, 120.33, 118.76, 90.45, 21.61, 17.95. **Electrospray MS** (acetone) *m*/*z*: 305 ($C_{21}H_{25}N_2^+$). **Anal.** calcd for $C_{38}H_{38}N_2Ni$: C, 78.50; H, 6.59. Found: C, 78.87; H, 6.71.

Synthesis of 4

365 mg (0.98 mmol) of 9-nickelafluorenyllithium dimethoxyethane complex and 30 mL of THF were placed in a Schlenk flask, and 316 mg (0.98 mmol) of 1-(2,4,6-trimethylphenyl)-3-(*n*-butyl)-imidazolium bromide was added at room temperature. The reaction was carried out for 24 hours. The solvent was removed under vacuum. The dark-orange solid was washed with hexane and deoxygenated water, and dried under vacuum. Compound **4** was obtained as an orange solid. Yield: 466 mg (0.90 mmol, 92%). **^{1}H NMR** (THF-d_8) (20 °C) δ (ppm): 8.33 (s, 1H, imidazole), 7.24 (s, 1H, =CH), 7.03 (d, ^3J = 7.2 Hz, 2H, Ph), 6.97 (s, 1H, =CH), 6.91 (s, 2H, Ph), 6.80 (d, ^3J = 7.2 Hz, 2H, Ph), 6.36 (t, ^3J = 7.2 Hz, 2H, Ph), 6.05 (t, ^3J = 7.2 Hz, 2H, Ph), 4.84 (s, 5H, Cp), 3.50 (2H, CH_2), 2.30 (s, 9H, CH_3), 1.22 (m, 2H, CH_2), 0.84 (m, 2H, CH_2), 0.70 (t, ^3J = 7.2 Hz, 3H, CH_3). **^{1}H NMR** (acetonitrile-d_3) (20 °C) δ (ppm): 8.48 (s, 1H, imidazole), 7.56 (s, 1H, =CH), 7.37 (s, 1H, =CH), 7.25 (d, ^3J = 7.2 Hz, 2H, Ph), 7.12 (s, 2H, Ph), 7.05 (d, ^3J = 7.2 Hz, 2H, Ph), 6.61 (t, ^3J = 7.2 Hz, 2H, Ph), 6.36 (t, ^3J = 7.2 Hz, 2H, Ph), 5.12 (s, 5H, Cp), 4.13 (t, ^3J = 7.2 Hz, 2H, CH_2), 2.38 (s, 3H, CH_3), 1.98 (s, 6H, CH_3), 1.81 (m, 2H, CH_2), 1.28 (m, 2H, CH_2), 0.95 (t, ^3J = 7.2 Hz, 3H, CH_3). **^{13}C NMR** (THF-d_8) (20 °C) δ (ppm): 174.60, 156.30, 144.00, 141.57, 138.48, 135.88, 132.79, 130.58, 124.76, 124.18, 122.73, 120.68, 119.33, 90.53, 50.40, 33.75, 21.66, 20.33, 17.92, 14.60. **Electrospray MS** (acetone) *m*/*z*: 243 ($C_{16}H_{23}N_2^+$). **Anal.** calcd for $C_{33}H_{36}N_2Ni$: C, 76.32; H, 6.99. Found: C, 76.08; H, 7.25.

Synthesis of 5

520 mg (0.89 mmol) of **1** and 20 mL of dioxane were placed in a Schlenk flask. The reaction was refluxed for three hours. The orange solid was dissolved, and the colour of the solution changed to olive. After the reaction was completed, the solvent was removed under vacuum. The olive solid was washed with hexane and dried under vacuum. 470 mg (0.81 mmol, 91%) of **5** was isolated. **^{1}H NMR** (benzene-d_6) (55 °C) δ (ppm): 6.77–8.06 (m, 13H, Ph), 4.51 (s, 5H, Cp), 3.15 (s, 4H, CH_2), 2.07 (broad s, 18H, CH_3). **^{13}C NMR** (benzene-d_6) (20 °C) δ (ppm): 214.5, 184.2, 155.4, 149.2, 144.7, 139.7, 138.8, 138.0, 137.0, 130.3, 129.9, 126.9, 125.3, 122.6, 122.1, 92.2, 51.5, 20.9. **EI MS** (70 eV) *m*/*z* (rel. int.) (^{58}Ni): 582 (M^+, 18%), 429 ($C_{26}H_{31}N_2Ni^+$, 21%), 304 ($C_{21}H_{24}N_2^+$, 100%), 218 ($C_{15}H_{10}N_2^+$, 18%), 154 ($C_{12}H_{10}^+$, 50%). **Anal.** calcd for $C_{38}H_{40}N_2Ni$: C, 78.23; H, 6.91. Found: C, 77.94; H, 6.63

Reaction of 1 in 1,4-dioxane-d_8

20 mg of **1** and 2 mL of 1,4-dioxane-d_8 were placed in a Schlenk flask. The reaction was refluxed for three hours. The orange solid was dissolved, and the colour of the solution changed to olive. After the reaction was completed, the solvent was removed under vacuum. The olive solid was dissolved in 0.6 mL of benzene-d_6. **^{1}H NMR** (benzene-d_6) (55 °C) δ (ppm): 6.77–8.06 (m, 13H, Ph), 4.51 (s, 5H, Cp), 3.15 (s, 4H, CH_2), 2.07 (broad s, 18H, CH_3).

Synthesis of 6

486 mg (0.94 mmol) of **4** and 20 mL of dioxane were placed in a Schlenk flask. The reaction was refluxed for 48 hours. The orange solid was dissolved and the colour of the solution changed to olive. After the reaction was completed, the solvent was removed under vacuum. The olive solid was washed with hexane and dried under vacuum. The dark solid was extracted with two portions (2 × 25 mL) of toluene. The combined extracts were dried under vacuum. 430 mg (0.83 mmol, 88%) of **6** was isolated. **^{1}H NMR** (acetonitrile-d_3) (20 °C) δ (ppm): 6.62–7.31 (m, 11H, Ph), 6.58 (m, 1H, =CH), 6.36 (m, 1H, =CH), 4.93 (s, 5H, Cp), 3.89 (m, 2H, CH_2), 2.37 (s, 3H, CH_3), 1.55 (m, 2H, CH_2), 1.43 (s, 6H, CH_3), 1.40 (m, 2H, CH_2), 1.02 (t, ^3J = 7.2 Hz, 3H, CH_3). **^{13}C NMR** (acetonitrile-d_3) (20 °C) δ (ppm): 176.6, 154.7, 150.9, 146.3, 143.2, 139.5, 137.9, 131.1, 129.9, 128.5, 127.7, 126.7, 125.0, 123.8, 122.4, 121.9, 92.3, 51.1, 34.0, 21.6, 21.4, 18.0, 14.7. **EI MS** (70 eV) *m*/*z* (rel. int.) (^{58}Ni): 518 (M^+, 17%), 306 ($C_{21}H_{26}N_2^+$, 33%), 243 ($C_{16}H_{23}N_2^+$, 100%), 154 ($C_{12}H_{10}^+$, 82%). **Anal.** calcd for $C_{33}H_{36}N_2Ni$: C, 76.32; H, 6.99. Found: C, 76.89; H, 7.17.

Reaction of 1 with dichloromethane

210 mg (0.36 mmol) of **1** and 40 mL of CH_2Cl_2 were placed in a Schlenk flask. The reaction was carried out for 7 days at room temperature. The green–brown solution was filtered and concentrated to approximately 10 mL. 20 mL of hexane was added, and a green oil precipitated from the solution. The red solution was separated, and the green oil was dried under vacuum. The resulting green solid was washed with toluene and dried under vacuum. Compound **7** was obtained as a green solid. Yield: 98 mg (0.09 mmol, 75%). **^{1}H NMR** (dichloromethane-d_2) (20 °C) δ (ppm): 7.14 (broad s, 4H, Ph), 6.66 (broad s, 1H, N–CH), 5.81 (broad s, 4H, CH_2), 2.52 (broad s, 12H, CH_3), 2.43 (broad s, 6H, CH_3). **^{13}C NMR** (dichloromethane-d_2) (20 °C) δ (ppm): 158.2; 140.0, 134.9, 129.9, 46.1, 26.4, 20.5. Crystals were grown from the CH_2Cl_2–hexane system. We are unable to provide elemental analysis for **7**

because we could not remove dichloromethane from the solid and obtain repeatable results. The red solution was exposed to air for 24 hours (to separate the organic products from traces of organometallic products), filtered and dried under vacuum. 110 mg of solid was obtained. GC/MS analysis revealed that it was a mixture of organic compounds, and that the main product was fluorene (71%).

Reaction of 4 with dichloromethane

330 mg (0.63 mmol) of **4** and 30 mL of CH_2Cl_2 were placed in a Schlenk flask. The reaction was carried out for 7 days at room temperature. The green–brown solution was filtered and concentrated to approximately 10 mL. 20 mL of hexane was added, and a green oil precipitated from the solution. The red solution was separated, and the green oil was dried under vacuum. The resulting green solid was washed with toluene and dried under vacuum. Compound **8** was obtained as a green solid. Yield: 154 mg (0.15 mmol, 72%). **^{1}H NMR** (dichloromethane-d_2) (20 °C) δ (ppm): 7.44 (broad s, 1H, N–CH), 7.10 (broad s, 2H, Ph), 6.89 (broad s, 1H, =CH), 4.73 (broad s, 1H, =CH), 4.56 (m, 2H, CH_2), 2.46 (s, 3H, CH_3), 2.43 (m, 2H, CH_2), 2.13 (m, 2H, CH_2), 2.10 (s, 6H, CH_3), 1.62 (t, ^3J = 7.0 Hz, 3H, CH_3). **^{13}C NMR** (dichloromethane-d_2) (20 °C) δ (ppm): 140.3, 133.8, 129.6, 123.2, 122.2, 45.1, 34.3, 26.6, 22.8, 20.6, 15.4. We are unable to provide elemental analysis for **8** because we could not remove dichloromethane from the solid and obtain repeatable results. The red solution was exposed to air for 24 hours (to separate the organic products from traces of organometallic products), filtered and dried under vacuum. 170 mg of solid was obtained. GC/MS analysis revealed that it was a mixture of organic compounds, and that the main product was fluorene (76%).

General procedure for Kumada coupling

100 mg of *m*-bromotoluene (1.0 eq.), 1.2 mL of phenylmagnesium bromide solution (c = 0.73 M) (1.5 eq.), 3% catalyst and 2 mL of THF were placed in a round-bottom flask. The flask was sealed with a serum cap. Reactions were carried out for 21 hours at room temperature. The reaction mixtures were tested by GC.

General procedure for Suzuki coupling

91 mg of phenylboronic acid (1.5 eq.), 99 mg of *p*-bromoacetophenone (1.0 eq.), 318 mg of K_3PO_4 and 3% catalyst were placed in a round-bottom flask. Afterwards, 3 mL of toluene was added and the flask was sealed with a serum cap. Reactions were carried out for 3 hours at 90 °C. The reaction mixtures were tested by GC.

X-ray structure determination for 1, 2, 4 and 5

Selected crystallographic data and further details of the data collection and refinement are summarized in Table S1.† X-ray diffraction data were collected at 100 K on an Agilent SuperNova diffractometer equipped with a Mo-Kα micro-focus X-ray source. Experimental temperatures were regulated using an Oxford Cryosystems open-flow nitrogen cryostat. The raw data were treated with the CrysAlisPro[14] (version 1.171.35.15) crystallographic package. Structures were solved by direct methods with SHELXS-97[15] and refined against F^2 with full-matrix least-squares using SHELXL-97.[16] All non-H atoms were refined with anisotropic atomic displacement parameters, while the hydrogen atoms were placed in geometrically calculated positions and refined using a riding model.

X-ray structure determination for 3 and 7

Selected crystallographic data and further details of the data collection and refinement are summarized in Table S1.† X-ray data were collected on a Nonius KappaCCD diffractometer using graphite-monochromated Mo-Kα radiation and the Collect[17] diffractometer control program. Unit cell parameters were obtained and data reduction was carried out using Denzo and Scalepak.[18] The structures were solved by direct methods using SHELXS-97[15] and refined on F^2 by full-matrix least-squares using SHELXL-97.[16] All the hydrogen atoms were placed in calculated positions and refined using a riding model.

Crystallographic data for the structural analysis of **1**, **2**, **3**, **4**, **5** and **7** have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 1038668–1038673.

Computational details

Geometry optimizations were accomplished using the Minnesota functional M06-L[19] with the 6-31+G(d,p)[20] basis set as implemented in Gaussian for carbon, nitrogen and hydrogen atoms, and def2-TZVPD[21] for nickel atoms. The redefined TZVPD basis set was suggested for the 3d elements by Truhlar and co-workers.[22] Diffusion functions were included because of the anionic character of the investigated nickelacyclic substrate. The def2-TZVPD basis set was obtained using the EMSL basis set exchange database.[23] A restricted approach was applied for all systems. The conductor-like polarizable continuum model[24] with THF and 1,4-dioxane as solvents was applied for self-consistent reaction field calculations. NBO analyses were carried out using Gaussian NBO version 3.1, as implemented in the Gaussian 09 package. Molecular geometries were optimized to the minimum, which was confirmed by frequency calculations in which no imaginary frequencies were found. Exact energies are listed in the ESI.† All DFT calculations were carried out using the Gaussian 09 suite of programs.[25] Chemcraft[26] was used for visualizations of the natural bond orbitals.

Acknowledgements

The authors thank the National Science Centre for financial support of this work (grant DEC-2011/01/B/ST5/06297). Calculations were carried out at the Interdisciplinary Centre for Mathematical and Computational Modelling (grant no. G53-27).

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