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Nickel(II) complexes with bifunctional phosphine–imidazolium ligands and their catalytic activity in the Kumada–Corriu coupling reaction

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Abstract

Zwitterionic Ni(II) complexes of type $NiX_3(NCN^+)$, (NCN^+ = 1-(2-diphenylphosphinoethyl)-3-(2,4,6-trimethylphenyl)imidazolium and X = Cl, **6**; Br, **7**), have been prepared by addition of NCN^+ bromide (**1a**) or tetrafluoroborate (**1b**) to NiX_2L, and characterised by X-ray crystallography. They have been used as catalytic precursors in the Kumada–Corriu coupling reaction between phenylmagnesium chloride and 4-chloroanisole, yielding high catalytic activities. Stoechiometric deprotonation investigations did not provide clear evidence for the formation of coordinated carbene species.

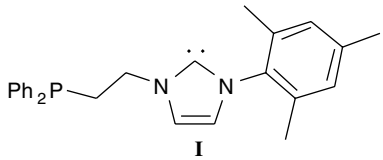
Keywords: Nickel(II); Phosphine; Imidazolium; Bifunctional ligands; Kumada–Corriu reaction

1. Introduction

The preparation of transition metal complexes of imidazolin-2-ylidenes has received an ever growing attention over the past 10 years [1–3]. Many transition metals have been used for this purpose, particularly palladium, nickel, rhodium and iridium [4–30]. The main interest of these *N*-heterocyclic carbene complexes, in comparison to phosphine complexes, resides in producing robust catalysts which will not undergo decomposition or deactivation. On the other hand, the incorporation of a weaker coordinating unit on the same ligand should ensure a good activity for catalytic applications.

The synthesis of complexes bearing a chelating phosphine/*N*-heterocyclic carbene (P-NCN) ligand has been recently described [4,9,23,31,32]. They are catalytically active, although no thorough study has been published yet concerning their potential in this domain.

In this paper, we describe the preparation of nickel(II) complexes bearing a chelating P-NCN ligand **I**. The synthesis of the phosphine–imidazolium precursor of this ligand, previously described by Nolan et al. [4] and Tsoureas et al. [9], has been improved. We also report the preparation and characterisation of two nickel(II) complexes containing the phosphine–imidazolium ligand and our attempts to characterise the species obtained by subsequent deprotonation of the imidazolium moiety. Finally, preliminary results on C–C coupling-catalysed reactions are given.



I

2. Results and discussion

2.1. Ligand synthesis

The synthesis of salts of the previously reported phosphine–imidazolium cation, 1-(2-diphenylphosphinoethyl)-

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3-mesityl-imidazolium (**1**), has been improved. Indeed, the first method, described by Nolan et al. [4], gives the desired compound in only 21% overall yield (starting from *N*-mesitylimidazole) (Scheme 1a).

The alternative procedure, developed by Tsoureas et al. [9], involves a phosphine oxide intermediate which is reduced under harsh conditions, and was hardly reproducible in our hands (Scheme 1b). Moreover, the latter method yields the imidazolium ligand as a mixture of chloride and bromide salts, which can prove problematic for the synthesis of metal complexes.

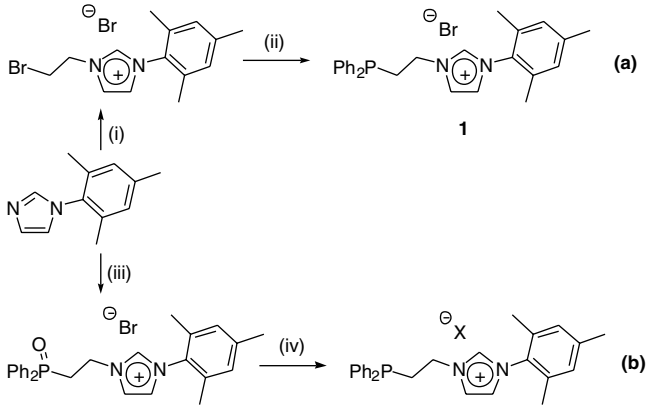
Our synthetic method is based on the quaternisation of *N*-mesitylimidazole (**2**) with 1-bromoethanol, to give (1-hydroxyethylene-3-mesityl) imidazolium bromide (**3a**) (90%). We then developed two different routes to obtain the title compound. The first one involves mesylation of alcohol **3a** (Scheme 2).

In a first attempt, mesylate **4** was obtained in only 13% yield. However, the presence of a bromide anion made the imidazolium salt quite soluble in water, and most of the product was lost in the aqueous phase during work-up. We thus proceeded to exchange the anion with tetrafluoroborate, leading to the salt **3b** in 96% yield. Mesylation using **3b** gave us compound **4** in 88% yield, then nucleophilic substitution with $KPPh_2$ [4] produced ligand **1b** in 76% yield. However, a drawback of this procedure is the fact that the tetrafluoroborate anion is partially replaced by mesylate. A second route was thus developed to avoid this problem: the imidazolium salt was obtained via bromination of alcohol **3a** with PBr_3 and subsequent nucleophilic substitution with $KPPh_2$ (67% overall yield, starting from *N*-mesitylimidazole) (Scheme 3).

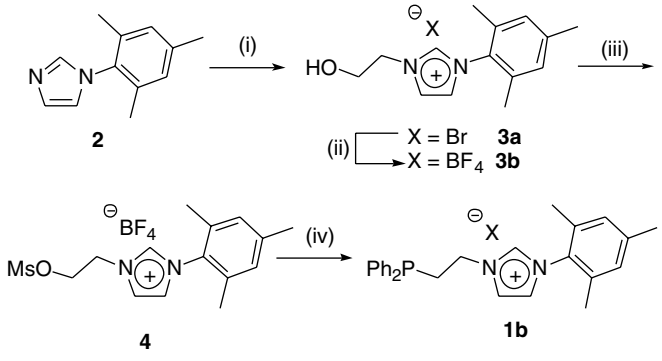
The successful introduction of PPh_2 on the brominated intermediate allowed us to avoid the phosphine protection/deprotection sequence described in Scheme 1(iv), and to obtain the salt with Br^- as the only anion.

Although compound **1a** could be used directly for coordination studies, pure compound **1b** (without mesylate contamination) was also needed in order to prepare Ni(II) complexes bearing only chloride ligands, vide infra. It was obtained in good yields from **1a** (83%), following an anion exchange reaction with $NaBF_4$.

Single crystals of compounds **1a** and **1b** were investigated by X-ray crystallography. Molecule **1a** (see Fig. 1, left) shows a hydrogen bonding interaction between the bromide anion and the acidic imidazolium proton [C(1)···Br = 3.506(5) Å, H(1)···Br=2.561(1) Å]. Selected bond distances and angles are listed in Table 1. Such hydrogen bonding is well known from other imidazolium structures [33,34].



Scheme 1. *Reagents and conditions:* (i) 1,2-dibromoethane (4.4 equiv.), THF, r.t., 2 d (23%); (ii) $HPPh_2$ (1.1 equiv.), *t*-BuOK (1.05 equiv.), DMSO, r.t., 1 h (91%). (iii) $Ph_2P(=O)(CH_2)_2Br$, 150–160 °C, 4–5 d (83%); (iv) $HSiCl_3$, chlorobenzene, 120 °C, 3 h (75%).



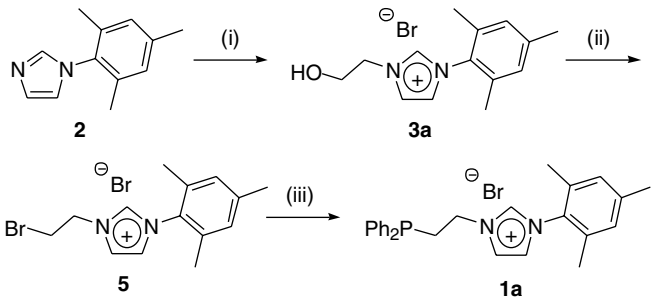
Scheme 2. *Reagents and conditions*: (i) 1-bromoethanol, toluene, 120 °C, 18 h (90%); (ii) $NaBF_4$, H_2O/CH_2Cl_2, r.t., 3 d (96%); (iii) MsCl, NEt_3, CH_2Cl_2, 0 °C, 3 h (88%); (iv) $HPPh_2$, *t*-BuOK, DMSO, r.t., 1 h (76%).$HSiCl_3$, chlorobenzene, 120 °C, 3 h (75%).

2.2. Nickel(II) complexes preparation and characterisation

Heating a sample of $NiCl_2$ with **1b** and NaCl, or $NiBr_2$(DME) with **1a**, in refluxing THF led, respectively, to the air stable complexes **6** (blue crystalline solid, 63% yield) and **7** (green crystalline solid, 95% yield) (Scheme 4).

Both complexes gave X-ray quality crystals from slow evaporation of acetone solutions (see Fig. 2). The metal is bonded to three halide ligands and to the phosphorus atom of the phosphine–imidazolium ligand, to give an overall neutral, zwitterionic structure. Selected bond distances and angles are listed in Table 2.

The coordination geometry is distorted tetrahedral. For both structures, the X(2)–Ni–X(3) angle is significantly



Scheme 3. *Reagents and conditions*: (i) 1-bromoethanol, toluene, 120 °C, 18 h (90%); (ii) PBr_3, CH_2Cl_2, 0 °C, 15 h (78%); (iii) $HPPh_2$, *t*-BuOK, DMSO, r.t., 1 h (95%).

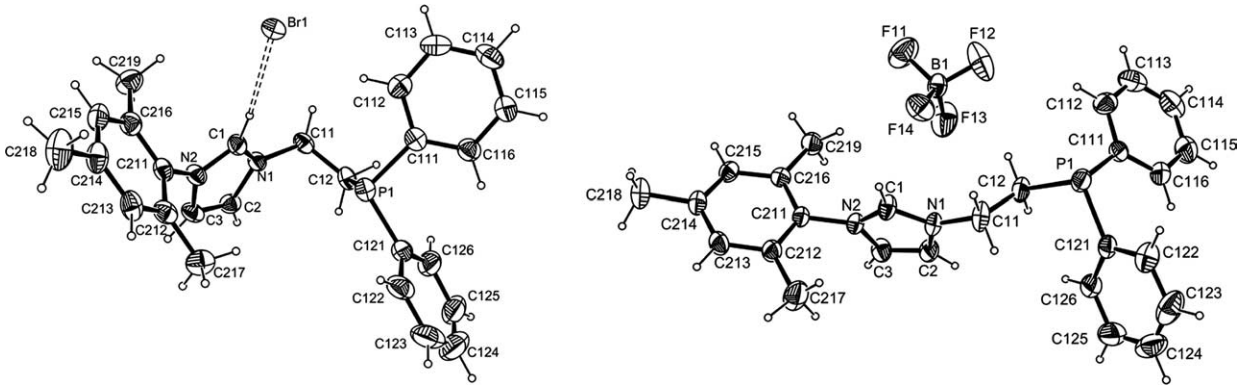
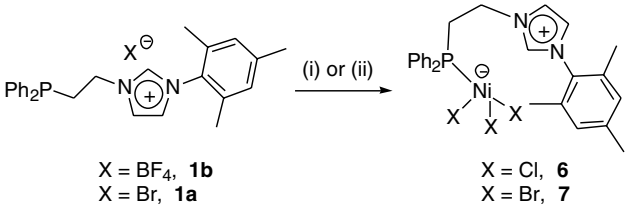


Fig. 1. An ORTEP view of compounds **1a** (left) and **1b** (right). Ellipsoids are drawn at the 50% probability level. For **1a**, C–H···Br bonding interaction is shown as dashed line.

Table 1
Selected bond distances (Å) and angles (°) for compounds **1a** and **1b**

	1a	1b
(a) Distances (Å)		
P(1)–C(111)	1.825(4)	1.833(2)
P(1)–C(121)	1.827(5)	1.832(2)
P(1)–C(12)	1.857(4)	1.856(2)
N(1)–C(1)	1.315(5)	1.331(2)
N(1)–C(2)	1.389(5)	1.374(2)
N(1)–C(11)	1.479(5)	1.477(2)
N(2)–C(1)	1.337(5)	1.321(2)
N(2)–C(3)	1.388(5)	1.378(2)
N(2)–C(211)	1.448(5)	1.460(2)
C(2)–C(3)	1.330(6)	1.340(3)
C(11)–C(12)	1.505(6)	1.515(3)
(b) Angles (°)		
C(111)–P(1)–C(121)	103.7(2)	102.60(9)
C(111)–P(1)–C(12)	101.46(19)	99.20(10)
C(121)–P(1)–C(12)	101.6(2)	102.48(10)
C(1)–N(1)–C(2)	109.0(3)	108.31(17)
C(1)–N(1)–C(11)	125.4(3)	125.37(17)
C(2)–N(1)–C(11)	125.0(4)	126.26(16)
C(1)–N(2)–C(3)	107.9(4)	108.25(16)
C(1)–N(2)–C(211)	124.1(3)	124.79(16)
C(3)–N(2)–C(211)	127.9(4)	126.72(16)
N(1)–C(1)–N(2)	108.6(4)	108.89(17)
C(3)–C(2)–N(1)	106.9(4)	107.14(17)
C(2)–C(3)–N(2)	107.6(4)	107.40(18)
N(1)–C(11)–C(12)	112.1(3)	112.78(17)
C(11)–C(12)–P(1)	113.5(3)	110.15(15)



Scheme 4. *Reagents and conditions*: (i) $NiCl_2$, NaCl, THF, 60 °C, 18 h; (ii) $NiBr_2$(DME), THF, 75 °C, 1 h.

wider [122.56(4)° and 123.29(4)° for X = Cl and Br, respectively], than the other two X–Ni–X angles. This could be attributed to the conformation adopted by the C(12) phenyl ring, which is parallel to the X(2)–Ni–X(3) wedge plane, or to the establishment of a hydrogen bonding interaction between the C(1) hydrogen atom and the halogen atom X(3). The latter is suggested by the slightly longer Ni–X(3) distance relative to Ni–X(1) and Ni–X(2) for both structures. Indeed, the X(3)–H(1) distances are 2.678 Å (X = Cl) and 2.826 Å (X = Br), which, although longer than in the free ligand **1a** (vide supra), are shorter than the sum of the van der Waals radii of H and X. This does not exclude, however, the possibility of an intermolecular stacking interaction. It is important to underline that the other crystallographically characterized $[NiX_3L]^-$ with X = Cl and Br show a much smaller dispersion for the Ni–X distances and X–Ni–X angles. In particular, these are symmetry imposed (C_3) for $[NiCl_3(PPh_3)]^-$ [Ni–Cl = 2.233(2) Å; Cl–Ni–Cl = 114.61(6)] in the Et_4N^+ salt [35]. For the corresponding Cy_3PH^+ salt they are in the ranges Ni–Cl = 2.231–2.239 Å; Cl–Ni–Cl = 111.2–117.7° [36]. Crystallographically characterized phosphine tribromide anions are $Ph_4As^+[NiBr_3(PPh_3)]^-$ [Ni–Br = 2.365–2.382 Å; Br–Ni–Br = 110.6–116.8°] [37] and $tBu_3PH^+[NiBr_3(PtBu_3)]$ [Ni–Br = 2.368–2.391 Å; Br–Ni–Br = 107.3–110.3°] [38,39]. The Ni–P distances for **6** and **7** [2.2811(11) and 2.2865(17) Å, respectively], are substantially shorter than those found in the above mentioned $[NiX_3L]^-$ structures, a factor which may be related to the presence of the hydrogen bonding and the lengthening of the Ni–X(3) distance.

As expected for tetrahedral Ni(II) complexes, compounds **6** and **7** are paramagnetic: no signal is observed by ^{31}P NMR, while the ^1H NMR spectra show broad signals between 30 and −22 ppm. A variable temperature ^1H NMR study in acetone-d_6 shows a linear dependence of the chemical shifts with 1/T (e.g., see Fig. 3 for compound **6**), which indicates Curie–Weiss behaviour for both complexes. Therefore, the compounds are typical tetrahedral complexes of Ni(II), for which a spin triplet ground state is expected [40].

Rather surprisingly, these complexes give relatively sharp ^1H NMR and ^{31}P resonances in MeOD, indicating diamagnetism. It would seem, therefore, that the methanol solvent has replaced the phosphine ligand in the metal

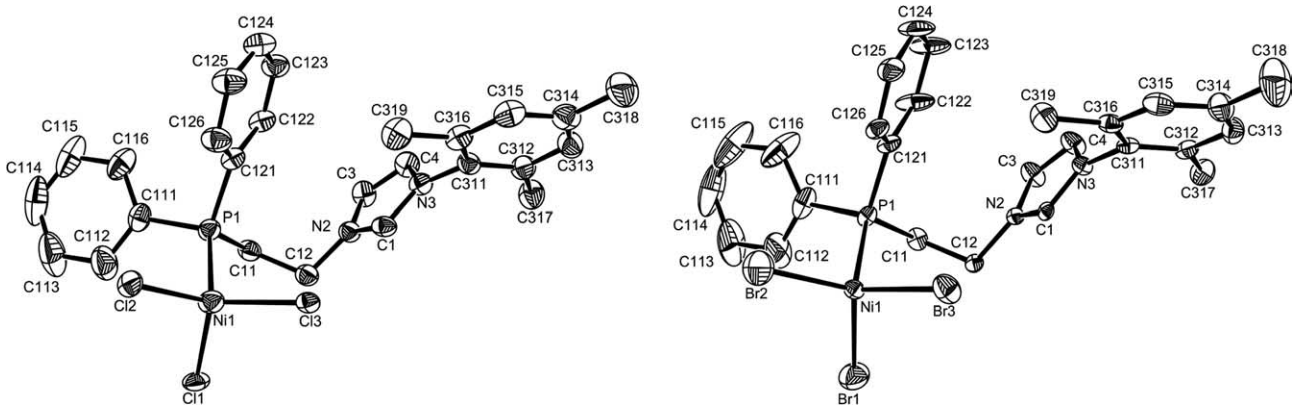


Fig. 2. An ORTEP view of compounds **6** (left) and **7** (right). Ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity.

Table 2
Selected bond distances (Å) and angles (°) for compounds **6** and **7**

	6	**7**
(a) Distances (Å)		
Ni(1)–X(1)	2.2644(11)	2.3376(11)
Ni(1)–X(2)	2.2197(11)	2.3072(11)
Ni(1)–X(3)	2.2959(11)	2.3679(10)
Ni(1)–P(1)	2.2811(11)	2.2865(17)
N(2)–C(1)	1.317(5)	1.310(7)
N(2)–C(3)	1.382(4)	1.386(8)
N(2)–C(12)	1.470(5)	1.485(7)
N(3)–C(1)	1.339(5)	1.323(7)
N(3)–C(4)	1.370(5)	1.391(8)
N(3)–C(311)	1.446(5)	1.455(7)
P(1)–C(121)	1.805(4)	1.807(6)
P(1)–C(111)	1.817(4)	1.809(7)
P(1)–C(11)	1.840(4)	1.839(6)
C(3)–C(4)	1.346(5)	1.330(9)
C(11)–C(12)	1.524(5)	1.527(8)
(b) Angles (°)		
X(2)–Ni(1)–X(1)	110.34(4)	112.65(4)
X(2)–Ni(1)–P(1)	104.29(4)	103.80(5)
X(1)–Ni(1)–P(1)	101.68(4)	103.00(5)
X(2)–Ni(1)–X(3)	122.56(4)	123.29(4)
X(1)–Ni(1)–X(3)	109.96(4)	107.36(4)
P(1)–Ni(1)–X(3)	105.66(4)	104.45(5)
C(1)–N(2)–C(3)	109.1(3)	108.5(5)
C(1)–N(2)–C(12)	125.6(3)	125.1(5)
C(3)–N(2)–C(12)	124.9(3)	126.1(5)
C(1)–N(3)–C(4)	108.3(3)	108.1(5)
C(1)–N(3)–C(311)	127.0(3)	125.7(5)
C(4)–N(3)–C(311)	124.7(3)	126.0(5)
N(2)–C(1)–N(3)	108.4(3)	109.1(5)
C(4)–C(3)–N(2)	106.4(4)	107.3(6)
C(3)–C(4)–N(3)	107.7(4)	106.9(5)
C(12)–C(11)–P(1)	116.1(3)	116.0(4)
N(2)–C(12)–C(11)	112.5(3)	111.9(5)

coordination sphere and that the signals observed are due to the free ligand. Indeed, the observed ^{1}H and ^{31}P chemical shift(s) correspond to that of compound **1**. This behaviour can be rationalized by the presence of a dynamic coordination/dissociation process, inducing broadening and shifting of the free ligand resonances as a result of the complex paramagnetism. This hypothesis is confirmed by a variable temperature ^{31}P NMR study of solutions

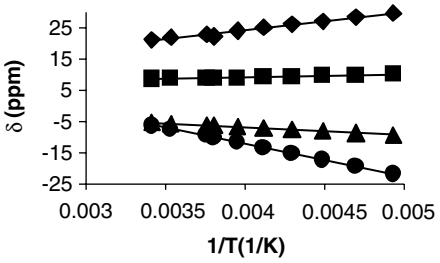


Fig. 3. Temperature dependence of selected ^{1}H NMR resonances of complex **6**.

obtained by dissolving complex **7** in MeOD. At lower temperatures, the signal shifts downfield and becomes sharper and more intense.

In an attempt to dihydrohalogenate complexes **6** and **7** and generate a neutral phosphine-functionalized *N*-heterocyclic carbene complex of nickel(II), which would be related to the recently reported palladium(II) analogue [9], the reaction of **6** and **7** with various base/solvent systems was investigated. In a parallel fashion, we also investigated the deprotonation of compound **1a** under the same conditions. We first settled our choice on strong bases like *n*-BuLi, $LiN(SiMe_3)_2$ or $KN(SiMe_3)_2$. Compounds **1a**, **6** and **7** are all insoluble in THF, but readily dissolve when either one of these bases is added, to afford orange-brown solutions. Our attempts to isolate a nickel complex from these solutions, however, were not successful.

The formation and stability of the putative carbenic species was therefore probed by ^{1}H, ^{13}C and ^{31}P NMR investigations of the reaction of **1a** with $KN(SiMe_3)_2$ in THF-d_8. At −10 °C, the ^{1}H NMR spectrum clearly indicated the absence of the imidazolium proton between 10 and 11 ppm, while the ^{31}P NMR spectrum shows only one signal at −22.2 ppm, and the ^{13}C NMR spectrum shows a large upfield shift of the carbon situated between the two nitrogen atoms, from 141 to 215 ppm.

All these observations agree with the generation of a carbenic species. No degradation of the ligand occurs under these conditions. However, our attempts to crystallise the free carbene were not successful, because decomposition

occurred as shown by a colour change from colourless to red at room temperature. This behaviour is quite different from that of a similar ligand, bearing a (2,6-diisopropyl)phenyl moiety instead of a mesityl, which could be crystallized under the same conditions [41]. This results suggests that the steric protection by the 2,6-isopropyl substituents plays a key role in the stabilization of the *N*-heterocyclic carbene at room temperature.

The ^{1}H and ^{31}P NMR monitoring of the deprotonation product of **1a** in THF-d_8 demonstrates its thermal instability. The two imidazole ring proton signals in the ^{1}H NMR (located at 7.45 and 7.04 ppm at or below −10 °C) noticeably shift upfield to 7.32 and 6.91 ppm, respectively, by the time the temperature reaches 0 °C (Fig. 4(a)). Simultaneously, the ^{31}P NMR spectrum exhibits a sharp, predominant signal at −21.75 ppm and a small, broad signal at ca. −20.5 ppm (probably minor amounts of material that has already decomposed) at −10 °C or below (Fig. 4(b)).

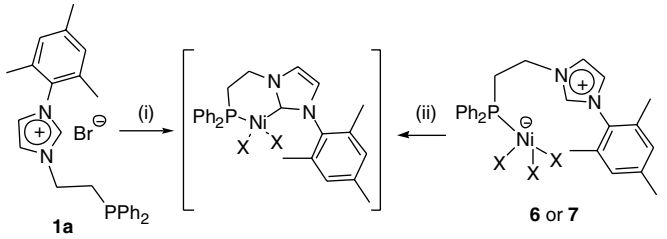
However, when the temperature reached 0 °C, only one sharp signal at −20.55 ppm was left. Furthermore, no carbenic carbon resonance at 215 ppm could be seen in the ^{13}C NMR spectrum after leaving the sample for several days at room temperature, under argon. These results indicate the occurrence of an irreversible structural change that consumes the carbene functionality at or above 0 °C, consistent with the colour change of the carbenic solution. However, decomposition yields complex NMR spectra. The only exploitable data is the absence of signal between 10 and 11 ppm in ^{1}H NMR, that should correspond to the imidazolium proton.

One hypothesis is that the carbene compound dimerizes to yield an alkene derivative, as was shown to occur for analogous systems [42–44]. We have made no further efforts to characterize the decomposition products. Danopoulos et al. [41] isolated the {1-[β-(diphenylphosphino)ethyl]-3-[(2,6-diisopropyl)phenyl]imidazol-2-ylidene} compound and suggested that the presence of bulky groups on both nitrogen atoms of the heterocyclic ring is not necessary for the isolation of stable carbenes. Our results, however, show that the replacement of the (2,6-diisopropyl)phenyl substituent by a mesityl group, whose steric protection is not much smaller, does not allow room temperature stability. However, the formation of the carbene by deprotonation of **1** below 0 °C is indeed confirmed, thus it may be intercepted by the nickel ion to form a stable coordination compound.

In initial studies aimed at obtaining a nickel(II)–carbene complex, ligand **1a** was first deprotonated using Li(N-$SiMe_3)_2$ or $K(NSiMe_3)_2$ in THF at −40 °C and then added to a nickel(II) precursor ($NiBr_2$ or $NiBr_2$(DME)). The disappearance of the imidazolium proton could be observed by ^{1}H NMR monitoring. However, the resulting brown-orange reaction mixture showed a complex ^{31}P NMR spectrum and we could not isolate and characterise the expected complex (see Scheme 5). In subsequent studies, complexes **6** and **7** were deprotonated using similar conditions (Scheme 5). A brown-orange mixture was again formed, but once again a clean product could not be obtained.

2.3. Catalytic studies

Nickel catalysts have been proved highly effective for C–C coupling reactions between a Grignard reagent and an aryl or alkyl halide (Kumada–Corriu reaction), usually more so than their palladium analogues. Since the discovery of the metal-catalysed reaction by Kumada and Corriu



Scheme 5. Reagents and conditions: (i) $KN(SiMe_3)_2$, THF, −40 °C, then $NiBr_2$ or $NiBr_2$(DME). (ii) *n*-BuLi, $LiN(SiMe_3)_2$ or $KN(SiMe_3)_2$, THF, −40 °C.

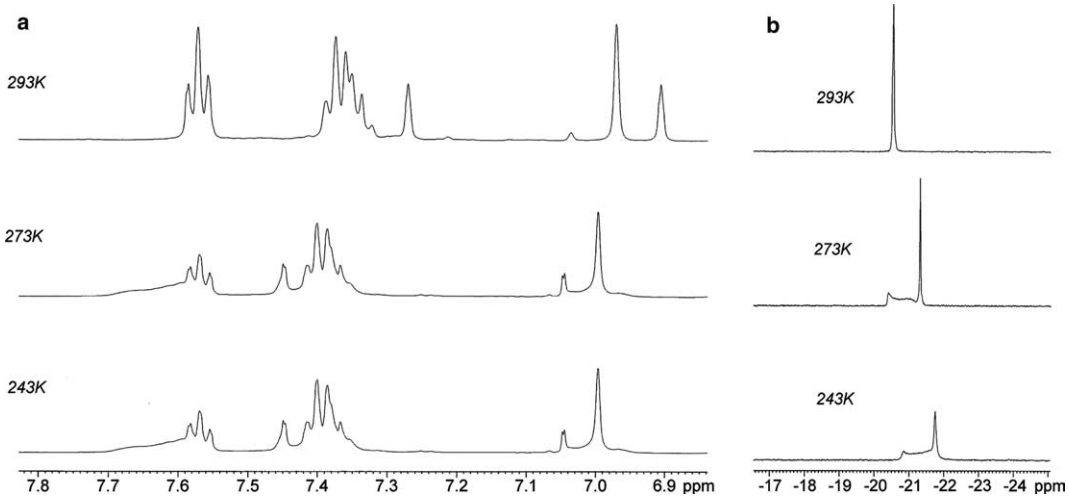
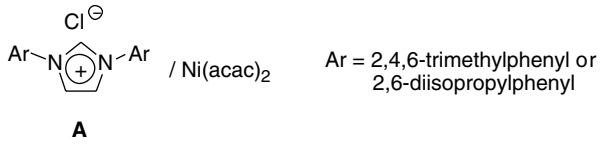


Fig. 4. NMR monitoring of the THF-d_8 solution obtained from **1a** and $KN(SiMe_3)_2$. (a) ^{1}H NMR spectra. (b) ^{31}P spectra.

in the early 1970s [45,46], many ligands have been reported, especially (chelating) diphosphines [47–57], but very few examples of metal-imidazolium salt systems have been reported. Moreover, catalytic systems involving the reaction of unactivated aryl chlorides with aryl Grignard reagents have been described only recently [58,59]. Amongst them is a very efficient Pd-imidazolium chloride precatalyst described by Huang et al. [59], though this system required the use of relatively elevated temperatures. The only known examples involving nickel-*N*-heterocyclic carbene systems are complexes A, reported by Böhm et al. in [21].



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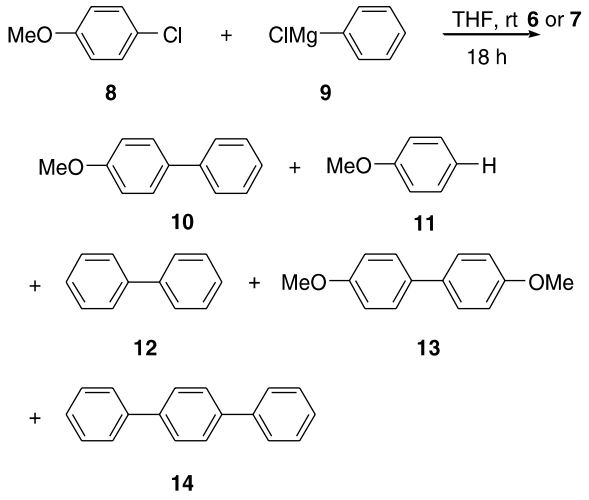
These systems are able to couple aryl chlorides with aryl Grignard reagents at room temperature and in very good yields [21]. To date, no catalyst bearing a bifunctional ligand with a *N*-heterocyclic carbene has been tested in the Kumada–Corriu reaction. However, it is known that a proper choice of ligands can affect both oxidative addition and reductive elimination steps involved in the generally accepted mechanism, by stabilising the metal centre at different stages of the catalytic cycle.



Scheme 6.

For the above reasons, we considered that the nickel carbene-phosphine complex that is expected to form upon dehydrohalogenation of **6** or **7** may exhibit an interesting catalytic activity. Our inability to isolate this complex did not prevent us from testing **6** and **7** themselves, since they may be deprotonated to the neutral carbene complex in situ by the Grignard reagent. A first test was thus carried out with compound **7** for the reaction between phenylmagnesium chloride and iodobenzene in *N*,*N*-dimethylacetamide (the precatalyst being soluble in this solvent). The catalytic activity was poor (80% conversion, 8% yield of biphenyl after 20 h at room temperature), even lower than that of $NiBr_2$ under identical conditions (100% conversion, 56% yield of biphenyl). Much more encouraging results were obtained, on the other hand, for the Kumada coupling of 4-chloroanisole with phenylmagnesium chloride in THF (Scheme 6). The results are summarised in Table 3.

Pleasingly, when the reaction was carried out with a 3 mol% suspension of **6** in THF, without prior deprotonation of the imidazolium moiety (Table 3, entry 3), a 100% conversion and a 80% yield (relative to the limiting 4-chloroanisole reagent) for the expected product **10** were obtained. Under the same conditions, Böhm et al. recovered a non negligeable amount of 4-chloroanisole (entries 1 and 2) and obtained a lower proportion of **10**.

When a base was added to pre-catalyst **6** (entry 4), a total conversion was again observed (only traces of 4-chloroanisole could be detected), but with a lower proportion of **10**, and more biphenyl **12**. This change in selectivity does not seem to be related to the prior addition of a base to the pre-catalyst, since similar results were obtained with **7** (entries 5 and 7), but with an inversion of the selectivity. Slightly better yields, however, were obtained with **7** compared to **6**. In order to evaluate the activity of our complexes, the catalyst ratio (**7**, entry 6) was lowered to 2 mol%. Again, the conversion after 18 h was complete, and the distribution of products was quite similar to that observed with 3 mol% catalyst. However, the amount of homocoupling product **13** raised from 1% to 7%, and the isolated yield was somewhat lower (68%). A small amount

Table 3
Nickel-catalysed ($NiCl_3L$ (**6**) and $NiBr_3L$ (**7**)) Kumada–Corriu reaction of 4-chloroanisole (1 equiv.) with phenylmagnesium chloride (1.5 equiv.) at room temperature in THF (18 h)

Entry	Catalyst (mol%)	Base	Products (%) distribution (GC) **10/8/11/12/13/14**	Isolated yield **10** (%)[c]
1[a]	IMes/$Ni(acac)_2$	–	67/18/2/6/7/0	–
2[a]	IPr/$Ni(acac)_2$	–	71/19/1/16/9/0	–
3[b]	$NiCl_3L$ **6** (3)	–	85/0/0.5/9.5/2/3	80
4[b]	$NiCl_3L$ **6** (3)	$KN(SiMe_3)_2$	75/0.3/0.5/18/4/1.3	80
5[b]	$NiBr_3L$ **7** (3)	–	74/0/4/20/1/tr.	83
6[b]	$NiBr_3L$ **7** (2)	–	66/0/4/22/7/1	68
7[b]	$NiBr_3L$ **7** (3)	*n*-BuLi	87/0/1/10/1.5/0.5	92

[a] Ref. [21].
[b] All reactions were repeated to ensure a good reproducibility of the results. Yields are not optimised.
[c] Relative to 4-chloroanisole. The relatively large amount of biphenyl **12** originates from the excess Grignard reagent.

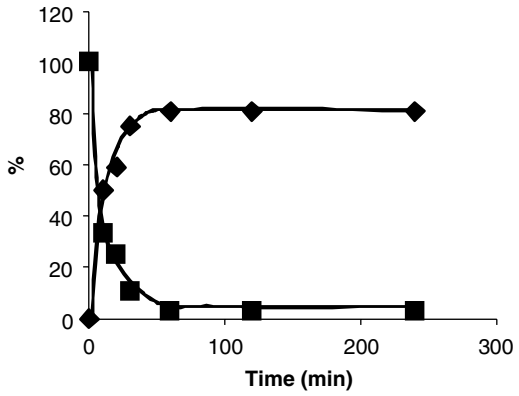


Fig. 5. Percent conversion of 4-chloroanisole **8** (■) vs. time to give coupling product **10** (◆, GC yield). Conditions are as shown in Experimental (method A).

of terphenyl was observed as well, which did not occur with IMes/Ni(acac)$_2$ or IMes/Ni(acac)$_2$ systems [60]. These results are equal or slightly superior to those reported by Böhm et al. for their bis-carbene nickel(II) catalytic system.

As we always observed a total conversion of the starting material after 18 h, we decided to follow the conversion of 4-chloroanisole in time (typical reaction conditions of Table 1, entry 5): aliquots of the reaction mixture were quenched at regular intervals and analysed by gas chromatography: we were pleased to see that the conversion was almost total after only 1 h (96%, see Fig. 5), which suggests that the catalytic species is very active for this system. Indeed, 75% product is formed after only 30 min, and 81% after 1 h. To the best of our knowledge, no analogous monitoring experiments have been previously reported for this reaction with use of related complexes as catalysts. It is therefore impossible to make more precise comparisons of catalytic activity. It seems, however, that this system is much more active than previously appreciated and looks very promising for future catalytic applications.[21] Further studies in our laboratory will be devoted to further optimizing it.

3. Conclusions

In summary, we have presented the synthesis and characterisation of new nickel(II) complexes, where the metal is bonded to a phosphine ligand that contains a pendant imidazolium moiety. The deprotonation of the free ligand generates an unstable imidazolin-2-ylidene (observed at low temperature by NMR). By comparison with the previously reported *N*-2,6-diisopropylphenyl analogue, the N-mesityl group is much poorer for sterically protecting the carbene function. The deprotonation of the coordinated ligand does not lead to isolable neutral carbene complexes. However, these precursors have shown promising results in catalysis for the Kumada–Corriu coupling reaction, with low catalyst loadings and good yields. We are now interested in: (i) studying more thoroughly the reactivity of complexes **6** and **7** in catalysis; (ii) identify the nature of the deprotonation products of **6** and **7** and understand their catalytic role; (iii) develop related systems by ligand modification in order to improve the catalytic activity in this and other C–C coupling reactions.

4. Experimental

All reactions were carried out under a dry argon atmosphere using Schlenk glassware and vacuum line techniques. Solvents for synthesis were dried and degassed by standard methods before use. Elemental analyses were carried out by the "Service d'Analyse du Laboratoire de Chimie de Coordination" in Toulouse. ^{1}H, ^{13}C{^{1}H, ^{31}P}, ^{31}P{^{1}H} and ^{19}F NMR data were recorded on Bruker AM-250 and AV-500 spectrometers for ^{1}H, operating at 250 and 500 MHz, respectively, on Bruker AV-500 for ^{13}C and ^{31}P, operating at 125.8 and 202.5 Hz respectively, and on Bruker AC-200 for ^{19}F, operating at 188 MHz. The spectra were referenced internally using the signal from the residual protiosolvent (^{1}H) or the signals of the solvent (^{13}C). Mass spectra (electrospray ionisation or chemical ionisation) were obtained from acetonitrile or methanol solutions on a Nermag R10-10 instrument. GC chromatograms were recorded on a Fisons 8000 Series GC equipped with a SPB-5 capillary column and the products were identified by comparison with authentic samples. Chromatographic work was performed on Silica gel 60Å. Commercial chemicals were from Acros, Aldrich and Avocado.

*4.1. 1-(2-Hydroxyethyl)-3-(2,4,6-trimethylphenyl)-imidazolium bromide (**3a**)*

2-Bromoethanol (2.1 mL, 29.0 mmol) was added at room temperature to a toluene solution (75 mL) of *N*-(2,4,6-trimethylphenyl) imidazole (**2**) (4.92 g, 26.4 mmol). The mixture was stirred at 120 °C for 18 h. During this time a white solid precipitated in the flask. The suspension was cooled to room temperature, the solid was decanted off and washed with toluene (2 × 15 mL). A white solid was obtained. Yield: 7.4 g, 90%. ^{1}H NMR (250 MHz,$CDCl_3$): $\delta = 2.07$ (s, 6H), 2.33 (s, 3H), 3.54 (br, ^{1}H), 4.03 (t, $^3J = 4.8$ Hz, 2H), 4.85 (t, $^3J = 4.9$ Hz, 2H), 6.99 (s, 2H), 7.16 (t, $^3J = 1.5$ Hz, 1H), 7.97 (t, $^3J = 1.5$ Hz, 1H), 9.64 (s, 1H) (data consistent with those found in the literature).

*4.2. 1-(2-Hydroxyethyl)-3-(2,4,6-trimethylphenyl)-imidazolium tetrafluoroborate (**3b**)*

$NaBF_4$ (7.05 g, 64.26 mmol) was added to a biphasic solution (CH_2Cl_2/H_2O: 1/2, 60 mL) of **3a** (4.0 g, 12.85 mmol). The mixture was stirred for three days at room temperature (10 mL). The two layers were separated, the aqueous phase was extracted with CH_2Cl_2 (5 mL) and the combined organic extracts washed with water (10 mL). The solution was dried ($MgSO_4$), filtered and concentrated in vacuum to give a pale orange wax. Yield: 3.95 g (97%). Mp 81–82 °C. $C_{14}H_{19}BF_4N_2O$ (318.12) Calcd: C, 52.86;

H, 6.02; N, 8.81%. Found: C, 52.82; H, 5.76; N, 8.63%. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 2.03$ (s, 6H), 2.34 (s, 3H), 3.06 (br, ^{1}H), 3.96 (t, $^3J = 4.8$ Hz, 2H), 4.51 (t, $^3J = 4.8$ Hz, 2H), 7.01 (s, 2H), 7.19 (t, $^3J = 1.6$ Hz, 1H), 7.78 (t, $^3J = 1.6$ Hz, 1H), 8.70 (t, $^3J = 1.6$ Hz, 1H); ^{13}C NMR (125.8 MHz, $CDCl_3$): $\delta = 17.15$, 21.09, 52.37, 60.46, 123.28, 123.95, 129.77, 130.68, 134.46, 136.85, 141.24; ^{19}F NMR (188 MHz, $CDCl_3$): $\delta = -74.79$. MS (IS), *m/z* (%): 232, (100) [$M^+ - BF_4$]; 87, (100) [$M^- - C_{14}H_{19}N_2O$].

*4.3. 1-(2-Bromoethyl)-3-(2,4,6-trimethylphenyl)-imidazolium bromide (**5**)*

PBr_3 (0.19 mL, 2 mmol) was slowly added to a cold CH_2Cl_2 solution (10 mL, 0 °C) of **3a** (622 mg, 2 mmol). The mixture was stirred for 15 h at room temperature, diluted with CH_2Cl_2 (30 mL) and added to a cold saturated $NaHCO_3$ solution (20 mL, 0 °C). The organic phase was extracted and washed with cold saturated $NaHCO_3$ solution (1×5 mL, 0 °C). The solution was dried ($MgSO_4$), filtered and concentrated in vacuum. A white solid was obtained. Yield: 580 mg (78%). ^{1}H NMR (250 MHz, $CDCl_3$): $\delta =$ 2.07 (s, 6H), 2.33 (s, 3H), 4.03 (t, $^3J = 5.5$ Hz, 2H), 5.23 (t, $^3J = 5.4$ Hz, 2H), 7.00 (s, 2H), 7.17 (t, $^3J = 1.7$ Hz, 1H), 8.31 (t, $^3J = 1.7$ Hz, 1H), 10.09 (t, $^3J = 1.7$ Hz, 1H) (data consistent with those found in the literature).

*4.4. 1-(2-Ethylmesylate)-3-(2,4,6-trimethylphenyl)-imidazolium tetrafluoroborate (**4**)*

NEt_3 (1 mL, 6.84 mmol) was added to a cold CH_2Cl_2 solution (0 °C, 20 mL) of **3b** (1.45 g, 4.56 mmol). The mixture was stirred at 0 °C for 15 min, then CH_3SO_2Cl (0.53 mL, 6.84 mmol) was slowly added. The temperature was allowed to reach slowly 25 °C over 3 h and the mixture was concentrated (ca. 5 mL). Water (10 mL) was added and the mixture was stirred for 12 h. The two layers were separated, the aqueous phase was extracted with CH_2Cl_2 (5 mL) and the combined organic extracts washed with water (5 mL). The solution was dried ($MgSO_4$), filtered and concentrated in vacuum to give a brown wax. Yield: 1.6 g (89%). Mp 42–44 °C. $C_{15}H_{21}BF_4N_2O_3S$ (396.21) Calcd: C, 45.47; H, 5.34; N, 7.07%. Found: C, 45.36; H, 4.95; N, 6.84%. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 2.06$ (s, 6H), 2.35 (s, 3H), 3.07 (s, 3H), 4.71 (t, $^3J = 4.3$ Hz, 2H), 4.82 (t, $^3J = 4.3$ Hz, 2H), 7.02 (s, 2H), 7.22 (s, 1H), 7.85 (s, 1H), 8.73 (s, 1H);^{13}C NMR (125.8 MHz, $CDCl_3$): $\delta = 17.18$, 21.12, 37.34, 49.45, 68.09, 123.63, 124.17, 129.80, 130.56, 134.56, 137.23, 141.35; ^{19}F NMR (188 MHz, $CDCl_3$): $\delta = -74.22$. MS (IS), *m/z* (%): 309.6, (100) [$M^+ - BF_4$]; 87, (100) [$M^- - C_{15}H_{21}N_2O_3S$].

*4.5. 1-(2-Diphenylphosphinoethyl)-3-(2,4,6-trimethylphenyl)imidazolium bromide (NCN^+Br^-) (**1a**)*

$KPPh_2$, freshly made from *t*-BuOK (140 mg, 1.24 mmol) and $HPPh_2$ (0.24 mL, 1.30 mmol) in DMSO (2 mL), was added to a DMSO solution (2 mL) of **5** (445 mg, 1.13 mmol). The solution was allowed to stir for 1 h at room temperature. The solvent was then removed under vacuum. Methanol (5 mL) was added to quench excess $KPPh_2$, then removed under vacuum. Dichloromethane (10 mL) was added and the mixture was filtered. The filtrate was concentrated (ca. 1.5 mL) and diethyl ether (20 mL) was added. The resulting precipitate was separated and the product was obtained as a white air sensitive solid. Colorless crystals were obtained by slow diffusion of diethyl ether into a CH_2Cl_2 solution. Yield: 540 mg (95%). ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 2.08$ (s, 6H), 2.36 (s, 3H), 2.93 (t, $^3J = 6.9$ Hz, 2H), 4.86 (dt, $^3J = 11.9$ Hz, $^3J = 6.8$ Hz, 2H), 7.02 (s, 2H), 7.10 (t, $^3J = 1.8$ Hz, 1H), 7.36 (m, 6H), 7.46 (m, 4H), 7.66 (t, $^3J = 1.7$ Hz, 1H), 10.41 (t, $^3J = 1.4$ Hz, 1H); ^{31}P NMR (202.5 MHz, $CDCl_3$): $\delta = -23.29$ (s) (data consistent with those found in the literature).

*4.6. 1-(2-Diphenylphosphinoethyl)-3-(2,4,6-trimethylphenyl)imidazolium tetrafluoroborate ($NCN^+BF_4^-$) (**1b**)*

Method A: $KPPh_2$, freshly made from *t*-BuOK (460 mg, 4.1 mmol) and $HPPh_2$ (0.75 mL, 4.3 mmol) in DMSO (5 mL), was added to a DMSO solution (3 mL) of **4** (1.55 g, 3.9 mmol). The solution was allowed to stir for 1 h at room temperature. The solvent was then removed under vacuum. Methanol (15 mL) was added to quench excess $KPPh_2$, then removed under vacuum. CH_2Cl_2 (10 mL) was added and the mixture was filtered. The filtrate was concentrated (ca. 3 mL) and diethyl ether (40 mL) was added. The resulting precipitate was separated and the product was obtained as a white air sensitive solid. Yield: 1.42 g (75%).^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 2.03$ (s, 6H), 2.33 (s, 3H), 2.80 (t, $^3J = 6.9$ Hz, 2H), 4.64 (t, $^3J =$ 6.9 Hz, 2H), 6.99 (s, 2H), 7.10 (s, 1H), 7.35 (m, 6H), 7.46 (m, 4H), 7.57 (s, 1H), 9.34 (s, 1H). ^{19}F NMR (188 MHz, $CDCl_3$): $\delta = -74.70$ (s); ^{31}P NMR (101 MHz, $CDCl_3$): $\delta = -20.08$ (s).^{1}H NMR revealed a mixture of anions ($MeSO_3^-$ [δ 2.61, s]/BF_4^-).

Method B: $NaBF_4$ (530 mg, 4.75 mmol) was added to a biphasic solution (CH_2Cl_2/H_2O, 1/3, 12 mL) of **1a** (460 mg, 0.95 mmol). The mixture was stirred for 24 h at room temperature then the two layers were separated, the aqueous phase was extracted with CH_2Cl_2 (5 mL) and the combined organic extracts washed with water (2 mL). The solution was dried ($MgSO_4$),filtered and concentrated (2 mL). Et_2O (20 mL) was added to give a white precipitate, it was separated and dried in vacuum. Colorless, air sensitive crystals were obtained by slow diffusion of diethyl ether into a CH_2Cl_2 solution. Yield: 410 mg (88%). Mp 109–110 °C. $C_{26}H_{28}BF_4N_2P$ (486.3). Calcd: C, 64.22; H, 5.80; N, 5.76%. Found: C, 63.73; H, 6.28; N, 5.29%. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 2.03$ (s, 6H), 2.35 (s, 3H), 2.77 (t, $^3J = 7.1$ Hz, 2H), 4.55 (dt, $^3J = 10.7$, $^3J = 7.2$ Hz, 2H), 7.01 (s, 2H), 7.15 (t, $^3J = 1.8$ Hz, 1H), 7.36 (m, 6H), 7.44 (m, 4H), 7.61 (t, $^3J = 1.8$ Hz, 1H), 8.82 (t,$^3J =$ 1.8 Hz, 1H); ^{13}C NMR (125.8 MHz, $CDCl_3$): $\delta = 17.31$, 21.13,

29.11, 48.09, 123.43, 123.44, 128.98, 129.44, 129.79, 130.56, 132.77, 134.44, 136.82, 141.37; ^{19}F NMR (188 MHz, $CDCl_3$): $\delta = -74.69$ (s); ^{31}P NMR (202.5 MHz, $CDCl_3$): $\delta = -23.52$ (s). MS (IS), *m/z* (%): 399.6, (100) $[M^+ - BF_4]$; 87, (100) $[M^- - C_{26}H_{28}N_2P]$.

4.7. $[NiCl_3]^-(NCN^+)$ (6)

$NiCl_2$ (18 mg, 0.14 mmol) was added to a THF suspension (3 mL) of **1b** (49 mg, 0.1 mmol) [synthesised by method B]. The mixture was stirred for 18 h at 60 °C to give a red/violet suspension. After filtration, a blue solid was obtained and washed with $CHCl_3$ (3×2 mL), dissolved in acetonitrile (2 mL), filtered and acetonitrile was removed in vacuum to give a blue solid. NaCl (30 mg, 0.5 mmol) was added to the violet solution. The mixture was stirred at 60 °C for 1 h. A blue precipitate appeared and the solution became colorless. The suspension was filtered and washed with THF (2×5 mL). The product was dissolved in acetonitrile, filtered and dried in vacuo to give a blue solid. Global yield: 35 mg (63%). Blue crystals were obtained by slow diffusion of diethyl ether into an acetonitrile solution. Mp 231–233 °C. $C_{26}H_{28}Cl_3N_2NiP$ (564.55) Calcd: C, 55.32; H, 5.00; N, 4.96%. Found: C, 55.00; H, 4.99; N, 4.57%. ^{1}H NMR (500 MHz, d_3-MeOD): $\delta = 1.94$ (s, 6H), 2.23 (s, 3H), 2.71 (t, $^3J = 5.9$ Hz, 2H), 4.35 (t, $^3J = 5.8$ Hz, 2H), 6.99 (s, 2H), 7.26 (m, 6H), 7.35 (m, 4H), 7.59 (t, $^3J = 1.3$ Hz, 1H), 7.84 (t, $^3J = 1.3$ Hz, 1H), 9.14 (s, 1H); ^{31}P NMR (202.5 MHz, d_3-MeOD): $\delta = -23.25$ (br);^{13}C NMR (125.8 MHz, d_3-MeOD): $\delta = 15.94$, 19.62, 28.27, 47–48, 123.06, 124.20, 128.47, 128.97, 129.19, 130.95, 132.43, 134.33, 136.42, 141.06. ^{1}H NMR (500 MHz, d_6-$(Me)_2CO$): $\delta = -2.13$ (br), 0.47 (br), 1.30 (s), 1.42 (br), 1.90 (s), 2.07 (br + acetone), 2.12 (s), 2.90 (br), 3.76 (s), 4.07 (br), 6.16 (s), 6.33 (s), 6.57 (br), 20.80 (br). MS (IS), *m/z* (%): 399, (100) $[M^+ - NiCl_3]$; 35, (100) $[M^- - C_{26}H_{28}N_2PNiCl_2]$. MS (DCI[$NH_3$]), *m/z* (%): 544, (3) $[(M + NH_3)^+ - Cl]$.

4.8. $[NiBr_3]^-(NCN^+)$ (7)

$NiBr_2$(DME) (309 mg, 1.00 mmol) was added to a suspension of **1a** (400 mg, 0.83 mmol) in THF (5 mL). The mixture was stirred at 75 °C for 1 h. The precipitate was filtered, the green solid obtained was washed with THF (2×5 mL) and $CHCl_3$ (2×10 mL). The product was dissolved in acetone (20 mL), filtered on silica and was crystallised from acetone to give green crystals. Yield: 555 mg (95%). Mp 231–233 °C. $C_{26}H_{28}Br_3N_2NiP$ (697.9) Calcd: C, 44.75; H, 4.04; N, 4.01%. Found: C, 43.59; H, 4.06; N, 3.52%. ^{1}H NMR (500 MHz, d_3-MeOD): $\delta = 2.01$ (s, 6H), 2.30 (s, 3H), 2.78 (t, $^3J = 6.0$ Hz, 2H), 4.40 (t, $^3J = 5.9$ Hz, 2H), 7.06 (s, 2H), 7.32 (m, 6H), 7.43 (m, 4H), 7.66 (d, $^3J = 1.3$ Hz, 1H), 7.92 (d, $^3J = 1.3$ Hz, 1H), 9.17 (s, 1H); ^{31}P NMR (202.5 MHz, d_3-MeOD): $\delta = -23.36$ (br).^{13}C NMR (125.8 MHz, d_3-MeOD): $\delta = 16.05$, 19.70, 28.27, 47–48, 123.12, 124.22, 128.53, 129.03, 129.26, 131.02, 132.46, 134.42, 136.47, 141.11. NMR ^{1}H (500 MHz, d_6-$(Me)_2CO$): $\delta = -2.13$ (br), 0.47 (br), 1.30 (s), 1.42 (br), 1.90 (s), 2.07 (br + acetone), 2.12 (s), 2.90 (br), 3.76 (s), 4.07 (br), 6.16 (s), 6.33 (s), 6.57 (br), 20.80 (br). MS (IS), *m/z* (%): 399, (100) $[M^+ - NiBr_3]$; 79–81, (100) $[M^- - C_{26}H_{28}N_2PNiBr_2]$. MS (DCI[$NH_3$]), *m/z* (%): 535, (82) $[(M + NH_3)^+ - Br]$.

4.9. Typical procedures for Kumada–Corriu reactions

Method A: 4-Chloroanisole (0.12 mL, 1.0 mmol) was added to a suspension of **7** (21 mg, 0.03 mmol) in 1 mL THF. Phenylmagnesium chloride (0.75 mL, 1.5 mmol) was then added dropwise, and the reaction mixture was stirred for 18 h at room temperature. H_2O was added, the solution was dried ($MgSO_4$), filtered on a short path of silica gel and rinsed with dichloromethane. The crude mixture was analysed by gas chromatography, and then purified by column chromatography on silica gel (eluent: pentane/dichloromethane 95:5) to give **10** as a white solid (NMR data consistent with those found in the literature). Yield: 153 mg (83%).

Method B: *n*-BuLi (22 μL, 0.036 mmol) was added to a suspension of **7** (21 mg, 0.03 mmol) in 1 mL THF, which dissolved instantaneously to give a brown solution. 4-Chloroanisole (0.12 mL, 1.0 mmol) was added to the solution

Table 4
Crystal data and structure refinement, compounds **1a** and **1b**

Identification code	**1b**	**1a**
Empirical formula	$(C_{26}H_{28}N_2P)(BF_4)$	$(C_{27}H_{30}Cl_2N_2P)Br$, CH_2Cl_2
Formula weight	486.28	564.31
Temperature (K)	180(2)	180(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a (Å)	9.3799(12)	14.352(2)
b (Å)	10.8049(14)	10.7141(18)
c (Å)	14.090(2)	17.644(2)
α (°)	71.863(13).	
β (°)	70.702(13)	90.289(10)
γ (°)	74.799(11)	
Volume (Å^3)	1260.5(3)	2713.1(7)
Z	2	4
D_{calc} (Mg/m^3)	1.281	1.382
Absorption coefficient (mm^{-1})	0.155	1.789
F(000)	508	1160
Crystal size (mm^3)	$0.51 \times 0.14 \times 0.137$	$0.61 \times 0.55 \times 0.056$
θ Range (°)	2.80–26.37	2.84–26.37
Reflections collected	9909	18 657
Independent reflections (R_{int})	5159 (0.0323)	5539 (0.0734)
Completeness (%)	99.7	99.8
Absorption correction	None	Multi-scan
Max. and min. transmission		0.4461 and 0.2067
Refinement method	F^2	F^2
Data/restraints/parameters	5159/0/310	5539/0/301
Goodness-of-fit on F^2	0.890	0.906
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0444$, $wR_2 = 0.0953$	$R_1 = 0.0570$, $wR_2 = 0.1423$
R indices (all data)	$R_1 = 0.0833$, $wR_2 = 0.1073$	$R = 0.0935$, $wR_2 = 0.1685$
Residual density (e Å^{-3})	0.248 and −0.215	1.530 and −1.061

and after stirring for 5 min at room temperature, phenylmagnesium chloride (0.75 mL, 1.5 mmol) was added dropwise. The reaction mixture was stirred for 18 h at room temperature. H_2O was added, the solution was dried ($MgSO_4$), filtered on a short path of silica gel and rinsed with dichloromethane. The crude mixture was analysed by gas chromatography, and then purified by column chromatography on silica gel (eluent: pentane/dichloromethane 95:5) to give **10** as a white solid. Yield: 170 mg (92%) (NMR data consistent with those found in the literature).

4.10. X-ray structure determinations

Single crystal of each compound was mounted under inert perfluoropolyether at the tip of glass fibre and cooled in the cryostream of the Oxford-Diffraction XCALIBUR CCD diffractometer. Data were collected using the monochromatic Mo Kα radiation ($\lambda = 0.71073$). The structures were solved by direct methods (SIR97 [61]) and refined by least-squares procedures on F^2 using SHELXL-97 [62]. All H atoms attached to carbon were introduced in calculation in idealised positions and treated as riding models. The drawing of the molecules was realised with the help of ORTEP32 [63]. Crystal data and refinement parameters are shown in Tables 4 and 5. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 277961–277964. Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; deposit@ccdc.cam.ac.uk).

Table 5
Crystal data and structure refinement, compounds **6** and **7**

Identification code	**6**	**7**
Empirical formula	$C_{27}H_{31}Cl_3N_2Ni$ P, $1/2(C_3H_6O)$	$C_{26}H_{28}Br_3N_2$ Ni P
Formula weight	593.57	697.91
Temperature (K)	180(2)	180(2)
Wavelength (Å)	0.70930	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
a (Å)	12.1663(11)	9.2547(7)
b (Å)	9.1747(8)	13.0627(10)
c (Å)	26.402(2)	23.2366(17)
β (°)	102.537(7)	94.230(6)
Volume (Å^3)	2876.7(4)	2801.5(4)
Z	4	4
D_{calc} (Mg/m^3)	1.371	1.655
Absorption coefficient (mm^{-1})	1.030	5.045
F(000)	1232	1384
Crystal size (mm^3)	$0.32 \times 0.21 \times 0.073$	$0.25 \times 0.2 \times 0.18$
θ Range °	3.01–26.31	2.89–26.37
Reflections collected	18 520	20 049
Independent reflections (R_{int})	5867 (0.0523)	5730 (0.0490)
Completeness (%)	99.8	99.8
Absorption correction	Analytical	Analytical
Max. and min. transmission	0.9303 and 0.7776	0.5762 and 0.4246
Refinement method	F^2	F^2
Data/restraints/parameters	5872/2/317	5730/263/301
Goodness-of-fit on F^2	0.868	0.931
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0458$, $wR_2 = 0.0977$	$R_1 = 0.0529$, $wR_2 = 0.1450$
R indices (all data)	$R_1 = 0.0974$, $wR_2 = 0.1115$	$R_1 = 0.0939$, $wR_2 = 0.1613$
Residual density (e Å^{-3})	0.608 and −0.477	1.530 and −1.061

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