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Aryl Grignard Cross-Coupling of Aryl Chlorides Catalysed by New, Highly Active Phosphine/Imidazolium Nickel(II) Complexes

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Abstract

Two new zwitterionic Nickel(II) complexes, bearing phosphine/imidazolium ligands, have been prepared. Their catalytic activity, and the activity of an analogous Ni(II) complex, previously described by us, has been evaluated with a range of aryl chlorides, an aryl bromide and arylmagnesium halides. The catalytic activity is related to the length of the tether between the carbene and phosphine moieties. Thus the catalysts possessing a 6-membered metallacycle are more active than that having a 7-membered metallacycle. Changing from a mesityl (Mes) to a 2,6-diisopropylphenyl (DIP) on the imidazole ring does not strongly influence the activity. The three complexes show moderate to very good activities with most substrates, and enhanced selectivities compared to previously published Ni(II)/*N*-heterocyclic carbene systems. The low activity observed with 4-chlorobenzotrifluoride seems to be related to the presence of a phosphine on the ligands.

Keywords

Nickel, Phosphine, *N*-heterocyclic carbene, C-C coupling, Grignard

1. Introduction

The development of very active, yet robust catalysts for application to organic synthesis is still a challenge. Complexes bearing *N*-heterocyclic carbenes are actively studied nowadays, because of their high thermal stability, and because metal-NHC bonds have high dissociation energies [1-3]. On the other hand, phosphine complexes of nickel(II) are very active in the C-C coupling reaction between aryl halides and aryl Grignard reagents (Kumada-Corriu reaction), but it is not rare to observe some ligand dissociation [4-11]. Consequently, mixed phosphine/N-heterocyclic carbene nickel complexes should be good candidates as catalysts for C-C coupling reactions [12-17]. To date, only two Ni(II)/*N*-heterocyclic carbene systems have been successfully tested in the reaction of aryl chlorides with aryl Grignard reagents [18].

We have recently described the preparation of two zwitterionic nickel(II) complexes, bearing a phosphine/imidazolium ligand (**1a** and **1d**) [19]. These complexes proved very active as precatalysts for the coupling of phenylmagnesium chloride and 4-chloroanisole, giving an essentially total conversion of the starting aryl chloride after 1 h at room temperature, with only 3 mol% of precatalyst.

Based on these results, we wanted to further explore the field and study the scope and limitations of our systems in the Kumada-Corriu reaction. In the present paper, we describe the preparation and characterisation of two new members of this family of nickel(II) phosphine-imidazolium complexes, and the evaluation of their catalytic activity with a range of aryl chlorides, one aryl bromide and arylmagnesium halides.

2. Experimental

2.1. General comments

All reactions were carried out under a dry argon atmosphere using Schlenk glassware and vacuum line techniques. Solvents for syntheses were dried and degassed by standard methods before use. Elemental analyses were carried out by the analytical service of the Laboratoire de Chimie de Coordination in Toulouse.

^{1}H data were recorded on Bruker AC200, AM-250 and AV-500 spectrometers, operating at 200, 250 and 500 MHz, respectively. ^{13}C{H, P}and ^{31}P{H} NMR data were recorded on the Bruker AV-500 instrument, operating at 125.8 and 202.5 Hz respectively. The spectra were referenced internally using the signal from the residual protiosolvent (^{1}H) or the solvent signals (^{13}C), and externally using 85% H_3PO_4 for ^{31}P. Mass spectra were obtained from acetonitrile or methanol solutions on a TSQ7000 instrument from ThermoElectron (electrospray ionisation or chemical ionisation), and from DMSO or DMF solutions on a Nermag R10-10 instrument (FAB). 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. Commercial chemicals were from Acros, Aldrich, Alfa Aesar, Avocado or Fluka and used as received. *N*-(2,4,6-trimethylphenyl)imidazole **2a** and *N*-(2,6diisopropylphenyl)imidazole **2b** were prepared as described by Arduengo [20] and Johnson [21]. Compound **1a** was synthesised as previously described [19].

2.2. Synthesis of ligands

*1-(2-hydroxyethyl)-3-(2,6-diisopropylphenyl)-imidazolium bromide **3b***

2-Bromoethanol (2.5 mL, 35 mmol) was added to a toluene solution (150 mL) of **2b** (6.2 g, 27.2 mmol). The mixture was stirred at 120°C for 20 h. During this time a yellow-orange oil separated out in the flask. The mixture was cooled to room temperature and the toluene phase was removed. The oil was extracted with CH_2Cl_2 (20 mL), the resulting solution was slowly precipitated in ether (400 mL), and the pale yellow solid which formed was filtered and dried in vacuo. Yield: 6.83 g (72 %). ^{1}H NMR (δ, 500 MHz, $CDCl_3$): 9.50 (s, 1H, N-CH-N), 8.19 (s, 1H, (DIP)N-CH=C), 7.38 (t, J = 7.9 Hz, 1H, p-CH (DIP)), 7.15 (d, J = 7.9 Hz, 2H, *m*-CH (DIP)), 7.09 (s, 1H, AlkN-CH=C), 4.73 (t, J = 4.8 Hz, 2H, N-CH_2), 3.96 (br, 1H, OH), 3.84 (t, J = 4.8 Hz, 2H, CH_2-OH), 2.15 (h, J = 6.8 Hz, 2H, C<u>H</u>-$(CH_3)_2$), 1.01 (d of d, J = 6.8 Hz, 12H, CH-(C<u>H</u>$_3$)$_2$); ^{13}C NMR (δ, 125.8 MHz, $CDCl_3$): 145.35 (*o*-C (DIP)), 137.63 (N-CH-N), 131.75 (*p*-CH (DIP)), 130.00 (N-C (DIP)), 124.50 (*m*-CH (DIP)), 124.31 ((DIP)N-CH=), 123.73 (AlkN-CH=), 60.17 (CH_2-OH), 52.01 (CH_2-N), 28.43 (C<u>H</u>-$(CH_3)_2$), 24.33 (CH-(C<u>H</u>$_3$)$_2$), 24.00 (CH-(C<u>H</u>$_3$)$_2$). Mp 169-170°C. Anal. cal. for $C_{17}H_{25}BrN_2O$; C: 57.79, H: 7.13, N: 7.93%; found: C: 57.54, H: 6.90, N: 7.79%. MS (ESI) m/z, (%): 273.15, (100) [$C_{17}H_{25}N_2O^+$]; 79, (100) [Br^-].

1-(3-hydroxy-n-propyl)-3-(2,4,6-trimethylphenyl)imidazolium bromide ***3c***

3-Bromo-1-propanol (2.2 mL, 24.0 mmol) was added to a toluene solution (60 mL) of **2a** (3.72 g, 20.0 mmol). The mixture was stirred at 120°C for 15 h. During this time a cream solid precipitated in the flask. The suspension was cooled to room temperature, the solid was decanted, washed with toluene (2 x 15 mL) and dried in vacuo. A white solid was obtained. Yield: 4.47 g (69 %). ^{1}H NMR (δ, 250 MHz, $CDCl_3$): 9.64 (s, 1H, N-CH-N), 7.97 (t, J = 1.5 Hz, 1H, MesN-CH=C), 7.16 (t, J = 1.5 Hz, 1H, AlkN-CH=C), 6.99 (s, 2H, CH (Mes)), 4.85 (t, J = 4.9 Hz, 2H, N-CH_2), 4.03 (t, J = 4.8 Hz, 2H, CH_2-O), 3.54 (br, 1H, OH), 2.33 (s, 3H, *p*-

CH_3), 2.21 (q, J = 5.7 Hz, 2H, C-CH_2-C), 2.07 (s, 6H, *o*-CH_3). MS [DCI(NH_3)] m/z, (%): 245.2, (100) [$C_{15}H_{21}N_2O^+$]; 79.2, (100) [Br^-].

1-(2-bromoethyl)-3-(2,6-diisopropylphenyl)imidazolium bromide ***4b***

PBr_3 (0.83 mL, 8.80 mmol) was slowly added to a cold CH_2Cl_2 solution (70 mL, 0°C) of **3b** (2.59 g, 7.33 mmol). The mixture was stirred for 20 h at room temperature, diluted with CH_2Cl_2 (70 mL) and added to a cold, saturated $NaHCO_3$ solution (35 mL, 0°C). The organic phase was extracted and washed with a cold, saturated $NaHCO_3$ solution (1 x 10 mL, 0°C). Subsequently, it was dried ($MgSO_4$), filtered and the solvent was removed in vacuo to give a white solid. Yield: 2.38 g (78 %). ^{1}H NMR (δ, 500 MHz, $CDCl_3$): 10.07 (t, J = 1.6 Hz, 1H, N-CH-N), 8.67 (t, J = 1.6 Hz, 1H, (DIP)N-CH=C), 7.44 (t, J = 7.9 Hz, 1H, *p*-CH (DIP)), 7.20 (d, J = 7.9 Hz, 2H, *m*-CH (DIP)), 7.13 (t, J = 1.6 Hz, 1H, AlkN-CH=C), 5.15 (t, J = 5.4 Hz, 2H, N-CH_2), 3.96 (t, J = 5.4 Hz, 2H, CH_2-Br), 2.23 (h, J = 6.8 Hz, 2H, C<u>H</u>-(CH_3)$_2$), 1.09 (d, J = 6.8 Hz, 12H, CH-(C<u>H</u>$_3$)$_2$), 1.05 (d, J = 6.8 Hz, 12H, CH-(C<u>H</u>$_3$)$_2$); ^{13}C NMR (δ, 125.8 MHz, $CDCl_3$): 145.35 (*o*-C (DIP)), 138.21 (N-CH-N), 131.85 (*p*-CH (DIP)), 129.98 (N-C (DIP)), 124.57 (*m*-CH (DIP)), 124.39 ((DIP)N-CH=), 123.94 (AlkN-CH=), 50.73 (CH_2-N), 32.00 (CH_2-Br), 28.50 (C<u>H</u>-(CH_3)$_2$), 24.47 (CH-(C<u>H</u>$_3$)$_2$), 24.00 (CH-(C<u>H</u>$_3$)$_2$). Mp 73-75°C. Anal. cal. for $C_{17}H_{24}Br_2N_2$; C: 49.06, H: 5.81, N: 6.73 %; found: C: 48.71, H: 6.11, N: 6.43%. MS (ESI) m/z, (%): 335, (100) [$C_{17}H_{24}BrN_2^+$]; 79, (100) [Br^-].

1-(3-bromo-n-propyl)-3-(2,4,6-trimethylphenyl)imidazolium bromide ***4c***

PBr_3 (1.1 mL, 11.5 mmol) was slowly added to a cold CH_2Cl_2 solution (80 mL, 0°C) of **3c** (3.26 g, 10 mmol). The mixture was stirred for 15 h at room temperature, diluted with CH_2Cl_2 (80 mL) and added to a cold, saturated $NaHCO_3$ solution (25 mL, 0°C). The organic phase was extracted and washed with cold, saturated $NaHCO_3$ (1 x 10 mL, 0°C). Subsequently, it

was dried ($MgSO_4$), filtered and the solvent was removed in vacuo to give a pale yellow solid. Yield: 3.37g (87 %). ^{1}H NMR (δ, 500 MHz, $CDCl_3$): 10.23 (s, 1H, N-CH-N), 8.23 (s, 1H, MesN-CH=C), 7.23 (s, 1H, AlkN-CH=C), 6.95 (s, 2H, CH (Mes)), 4.86 (t, J = 6.8 Hz, 2H, N-CH_2), 3.48 (t, J = 6.3 Hz, 2H, CH_2-Br), 2.63 (q, J = 5.2 Hz, 2H, C-CH_2-C), 2.29 (s, 3H, *p*-CH_3), 2.02 (s, 6H, *o*-CH_3); ^{13}C NMR (δ, 125.8 MHz, $CDCl_3$): 141.28 (*p*-C (Mes)), 137.78 (N-CH-N), 134.10 (*o*-C (Mes)), 130.62 (N-C (Mes)), 129.85 (CH (Mes)), 124.04 (AlkN-CH=), 123.39 (MesN-CH=), 48.79 (N-CH_2), 33.01 (C-CH_2-C), 29.13 (CH_2-Br), 21.11 (*p*-CH_3), 17.72 (*o*-CH_3). Mp 148-149°C. Anal. cal. for $C_{15}H_{20}Br_2N_2$; C: 46.42, H: 5.19, N: 7.22%; found: C: 46.30, H: 4.92, N: 7.11%. MS (ESI) m/z, (%): 399, (100) [$C_{15}H_{20}BrN_2^+$]; 79-81, (100) [Br^-].

1-(2-diphenylphosphinoethyl)-3-(2,6-diisopropylphenyl)imidazolium bromide ***5b***

$KPPh_2$, freshly made from *t*-BuOK (337 mg, 3.00 mmol) and $HPPh_2$ (0.54 mL, 3.15 mmol) in DMSO (8mL), was added to a DMSO solution (8 mL) of **4b** (1.19 g, 2.86 mmol). The solution was allowed to stir for 2 h at room temperature. The solvent was then removed under vacuum. Methanol (5 mL) was added to quench the excess $KPPh_2$, then removed under vacuum. Dichloromethane (10 mL) was added and the resulting mixture was filtered and diethyl ether (100 mL) was added. The resulting precipitate was separated by filtration and dried in vacuo. The product was obtained as a white, air-sensitive solid. Yield: 1.37 g (92 %). ^{1}H NMR (δ, 200 MHz, $CDCl_3$): 10.20 (s, 1H, N-CH-N), 7.85 (s, 1H, MesN-CH=C), 7.46 (t, J = 7.8 Hz, 1H, *p*-CH (DIP)), 7.39 (m, 4H, *o*-CH (C_6H_5)), 7.30 (m, 6H, *m*/*p*-CH (C_6H_5)), 7.23 (d, J = 8 Hz, 2H, *m*-CH (DIP)), 7.07 (s, 1H, AlkN-CH=C), 4.84 (d of t, J = 12.4 Hz – J = 6.9 Hz, 2H, N-CH_2), 2.84 (t, J = 6.8 Hz, 2H, CH_2-P), 2.25 (h, J = 6.8 Hz, 2H, C<u>H</u>-$(CH_3)_2$), 1.17 (d, J = 6.6 Hz, 6H, CH-(C<u>H</u>$_3$)$_2$), 1.07 (d, J = 6.9 Hz, 6H, CH-(C<u>H</u>$_3$)$_2$); ^{31}P NMR (δ, 81 MHz, $CDCl_3$): -20.77 (CH_2-PPh_2) (data consistent with those found in the literature [13]).

1-(3-diphenylphosphinopropyl)-3-(2,4,6-trimethylphenyl)imidazolium bromide ***5c***

$KPPh_2$, freshly made from *t*-BuOK (152 mg, 1.35 mmol) and $HPPh_2$ (0.25 mL, 1.42 mmol) in DMSO (3mL), was added to a DMSO solution (2 mL) of **4c** (500 mg, 1.29 mmol). The solution was allowed to stir for 15 h at room temperature. The solvent was then removed under vacuum. Methanol (5 mL) was added to quench the excess $KPPh_2$, then removed under vacuum. Dichloromethane (10 mL) was added and the resulting mixture filtered. The filtrate was concentrated (ca. 1.5 mL) and diethyl ether (20 mL) was added. The resulting precipitate was separated by filtration and dried in vacuo. The product was obtained as a white, air-sensitive solid. Yield: 500 mg (79%). ^{1}H NMR (δ, 200 MHz, $CDCl_3$): 10.35 (t, J = 1.7 Hz, 1H, N-CH-N), 7.75 (t, J = 1.8 Hz, 1H, MesN-CH=C), 7.36 (t, J = 7.8 Hz, 1H, *o*-CH (C_6H_5)), 7.28 (m, 6H, *m*/*p*-CH (C_6H_5)), 7.16 (t, J = 1.7 Hz, 1H, AlkN-CH=C), 6.92 (s, 2H, CH (Mes)), 4.76 (d of t, J = 25.6 Hz – J = 6.5 Hz, 2H, N-CH_2), 2.97 (d of t, J = 23 Hz - J = 6.5 Hz, 2H, CH_2-P), 2.27 (s, 3H, *p*-CH_3), 2.63 (m, 2H, C-CH_2-C), 1.98 (s, 6H, *o*-CH_3); ^{31}P NMR (δ, 81 MHz, $CDCl_3$): -14.1 (s, CH_2-PPh_2) (data consistent with those found in the literature [13]).

2. 3. Synthesis of Nickel(II) complexes:

1-(2-diphenylphosphinoethyl)-3-(2,6-diisopropylphenyl)imidazolium nickel tribromide ***1b***

$NiBr_2$(DME) (410 mg, 1.33 mmol) was added to a solution of **5b** (700 mg, 1.34 mmol) in THF (20 mL). The mixture was stirred at room temperature for 30 min to give a green solution. The solvent was removed under vacuum and $CHCl_3$ (20 mL) was added. The mixture was filtered and the solvent removed to give a green solid. Yield: 953 mg (97 %). ^{1}H NMR (δ, 200 MHz, $CDCl_3$): ^{1}H NMR (δ, 250 MHz,d_6-$(Me)_2CO$): 20.79 (br s), 7.05 (br s), 6.69 (br s), 6.13 (br s), 3.86 (br s), 2.94 (br s), 2.62 (br s), 1.30 (br s), 0.23 (br s), 0.07 (br s),

-2.22 (br s); mp 157-159°C. Anal. cal. for $C_{29}H_{34}Br_3NiN_2P$; C: 47.07, H: 4.63, N: 3.79%; found: C: 46.72, H: 4.85, N: 3.59 %. MS (ESI) m/z, (%): 441.6, (100) [$C_{29}H_{34}N_2P^+$]; 79, (100) [Br^-].

1-(3-diphenylphosphinopropyl)-3-(2,4,6-trimethylphenyl)imidazolium nickel tribromide ***1c***

$NiBr_2(MeCN)_2$ (312 mg, 1.01 mmol) was added to a suspension of **5c** (435 mg, 0.88 mmol) in THF (10 mL). The mixture was stirred at room temperature for 1 h. The precipitate was filtered, the green solid/oil obtained was washed with THF (2 x 5 mL), $CHCl_3$ (2 x 10 mL) and dried under vacuum to give a green solid. Yield: 612 mg (97 %). Green crystals were obtained by diffusion of diethyl ether into an acetonitrile solution. ^{1}H NMR (δ, 250 MHz,d_6-$(Me)_2CO$): 20.72 (br s), 8.81 (br s), 8.63 (br s), 7.92 (s), 7.23 (s), 6.13 (s), 6.02 (br s), 4.53 (br s), 3.94 (br s), 3.70 (br s), 2.39 (br s), 2.23 (br s), 1.86 (s), -0.34 (br s), -2.43 (br s); mp 226-227°C. Anal. cal. for $C_{27}H_{30}Br_3NiN_2P$; C: 45.55, H: 4.25, N: 3.93%; found: C: 45.12, H: 3.95, N: 3.79%. MS (FAB, MNBA matrix) m/z, (%): 413 (100) [$C_{27}H_{30}N_2P^+$]; 631 (0.5) [$C_{27}H_{30}Br_2NiN_2P^+$].

2.4. Standard procedure for Kumada-Corriu reactions:

The aryl halide (1 mmol) and diethyleneglycol-di-*n*-butylether (30 μL as internal standard) were mixed with **1a**, **1b** or **1c** (3 mol % based on aryl halide) in THF (1 mL). The arylmagnesium halide (1.5 mmol) was slowly added to the mixture. Reactions were kept at room temperature (between 23-25°C) for 18 h and quenched with a minimum of ethanol. In order to remove the catalyst and the magnesium salt, mixtures were filtered on silica with ether as solvent. The resulting mixtures were analysed by gas chromatography.

2.5. X-ray analyses:

A single crystal was mounted under inert perfluoropolyether at the tip of a glass fibre and cooled in the cryostream of an Oxford-Diffraction XCALIBUR CCD diffractometer. Data were collected using the monochromatic MoKα radiation (λ= 0.71073). The Final unit cell parameters were obtained by the least-squares refinement of a large number of selected reflections. Only statistical fluctuations were observed in the intensity monitors over the course of the data collection.

The structure was solved by direct methods (SIR97 [22]) and refined by least-squares procedures on F^2 with the SHELXL-97 program [23] using the integrated system WINGX(1.63) [24]. Hydrogen atoms attached to carbon atoms were introduced at calculated positions and treated as riding on their parent atoms [d(CH)= 0.96-0.98 Å] with a displacement parameter equal to 1.2 (C_6H_5, CH_2, OH) or 1.5 (CH_3) times that of the parent atom. Owing to the poor quality of the crystal, only reflections with theta below 23.3° were used in the refinement procedure. The Molecular view was realised with the help of ORTEP-III [25] . Crystal data and refinement parameters are shown in Table 1.

Table 1.

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 299074. 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; e-mail: deposit@ccdc.cam.ac.uk).

3. Results and discussion

Following our recent discovery that the nickel(II) complexes **1a** and **1d** are excellent precatalysts for the coupling of phenylmagnesium chloride and 4-chloroanisole [19], it was of interest to see whether small structural changes in the phosphine-imidazolium ligand could affect the properties or catalytic activity. For this purpose, we considered two modifications: (*i*) replacement of the *ortho* substituents on the aryl group of the imidazolium moiety by bulkier isopropyl substituents; (*ii*) an increased length of the tether from 2 to 3 carbons, thus forming a 7-membered metallacycle instead of a 6-membered one in the putative phosphino-carbene complex (Figure 1).

Ligands **5b** and **5c** were prepared by a natural extension of the procedure previously described for ligand **5a** [19]. Thus, 2-bromoethanol reacted with *N*-(2,6-diisopropylphenyl)imidazole to give imidazolium salt **3b** in good yield. Analogously, the reaction of 3-bromopropanol with *N*-mesitylimidazole gave imidazolium salt **3c** in good yield (in this case, the procedure described by Fürstner [26] was slightly modified and allowed us to improve the yield from 28% to 69%). Bromination of **3b** and **3c** with PBr_3 gave compounds **4b** and **4c**. Finally, nucleophilic substitution with $KPPh_2$ gave the expected imidazolium salts **5b** and **5c**, with Br^- as the anion, in good to excellent yields.

Zwitterionic nickel(II) complexes **1b** and **1c** were obtained, like the previously reported **1a** [19], in excellent yields by stirring a mixture of the desired ligand and $NiBr_2L_2$ for 1 h in THF at room temperature (Scheme 2). Like **1a**, the two new complexes are green, paramagnetic compounds, with a distorted tetrahedral geometry. They have been characterized by NMR, elemental analysis and mass spectrometry, and by an X-Ray diffraction study for **1c** (Figure 2). The paramagnetism is indicated by the large paramagnetic shift of certain resonances in the ^{1}H NMR spectrum. Unfortunately, we did not manage to isolate the corresponding carbenic Ni(II) complexes, obtained by deprotonation of the

imidazolium moiety in the presence of $LiN(SiMe_3)_2$. However, the deprotonation of **1a-c** induced a colour change to yellow-brown, consistent with the formation of diamagnetic, square-planar complexes. An NMR monitoring of the deprotonation of **1a** confirmed the formation of nickel phosphine-carbene complexes. Indeed, the ^{31}P NMR spectrum shows two sharp, very close signals at 3.28 ppm (major) and 2.99 ppm (minor), in addition to a sharp signal at –18.3 ppm which could correspond to the free phosphine. In the ^{13}C NMR spectrum, two small doublets were observed in the typical region of coordinated NHC's at respectively 168.3 ppm (J_{PC} = 108.2 Hz) and 159.85 ppm (J_{PC} = 35.2 Hz). A selective ^{31}P decoupling experiment showed that these two doublets are coupled to the phosphorus nuclei resonating at 3.28 and/or 2.99 ppm, but not to the one at –18.3 ppm. The presence of two doublets, with very different J_{PC} coupling constants, could be explained by the formation of two carbenic complexes (Figure 1): a monomer, bearing the chelating carbene-phosphine ligand (*cis* coupling), and a dimer, with the carbene and the phosphine being in *trans* on the nickel. Moreover, we did not observe the characteristic ^{1}H NMR signal at ca. 10.5 ppm corresponding to the acidic proton of the imidazolium moiety. The ^{31}P NMR spectrum of the deprotonation product of **1c** shows a similar pattern, with two close singlets at –5.2 and –5.5 ppm, and a very small signal at –15.0 ppm.

A view of compound **1c** is illustrated in Figure 2. The Ni atom is tetrahedrally coordinated by the phosphorus atom of the phosphine group and by three bromine atoms. The Ni-P distance is comparable with the value found in $[NiBr_3(PPh_3)]^-(C_{24}H_{20}As)^+$ (2.323(1) Å) [27]. The Br atoms are rotationally staggered with respect to the phenyl and the imidazolium groups. The three Br-Ni-Br angles show a significant deviation from their mean, 112.8(1)°, with two values greater than the ideal tetrahedral angle. The mesityl group is found roughly orthogonal to the imidazolium ring with a dihedral angle of 88.2(4)°, as previously observed

in [1-(2,4,6-$Me_3C_6H_2$)imidazolium-3-{CH_2C(*t*-Bu)=N(*i*-Pr)}]bromide [28]. The internal bond lengths and angles of the imidazolium ring are unexceptional and lie within the range expected [29]. It is interesting to note that there are three weak intermolecular C-H…Br(1) hydrogen bond interactions (Table 2), the shortest one being with the acidic imidazolium proton.

The new complexes, together with the previously reported complex **1a**, were tested as precatalysts for the coupling reaction between a variety of aryl chlorides and Grignard reagents, extending the previous study of the coupling of 4-chloroanisole with phenylmagnesium chloride catalyzed by **1a** [19]. The corresponding trichloride complex **1d** was not further investigated, because our previous study showed that the activity does not depend on the nature of the halide ligand. As we have previously shown [19], the catalytic results are independent on whether the Grignard reagent or an external base (e.g. $LiN(SiMe_3)_2$) is used to deprotonate the precatalysts. Therefore, we consider that a chelating phosphine-carbene coordination mode is present in the catalyst as indicated by the NMR results described above. The results are given in Table 3. A more detailed analysis of the product distribution yields the results shown in Tables 4 and 5.

Some general trends emerge from this work. Complex **1a**, bearing a mesityl group on the imidazolium moiety, is a bit more active than **1b**. Both complexes, with the notable exceptions of the couplings involving the CF_3-substituted aryl chloride substrate (runs 2 and 8), also show an equal or slightly better activity than the $Ni(acac)_2$/IPr system [18], as can be seen from the kinetic studies (Figures 3 and 4). Indeed, in the reaction of 4-chloroanisole with phenylmagnesium chloride, the 4-chloroanisole conversion reached 95% with **1a** and 82 % with **1b** after 1 h (Figure 3). On the other hand, complex **1b** was a bit more selective than **1a**

and gave less by-products (Tables 4 and 5) [30]. Both are more selective than the $Ni(acac)_2$/IPr system.

In most cases, complex **1c** showed a poorer activity than **1a** or **1b**, as can be seen from Table 3 and Figure 3. It seems that the formation of a 7-membered cycle slows the reaction down. For several substrates, complex **1c** also shows a reduced selectivity, even relative to the $Ni(acac)_2$/IPr system.

One noticeable exception was observed with 4-chlorobenzotrifluoride, where conversions were low, with up to 71% starting material left for entry 2 (Table 4) and 66% for entry 8 (Table 5). A similar behaviour was reported for a monophosphine-based system, namely $Ni(acac)_2/P(t\text{-}Bu)_3$ (up to 53% starting material left), whereas the use of a simple imidazolium salt gave excellent conversions under the same conditions (Table 4, entry 2) [18]. A GC monitoring of this reaction provided insight as to the possible cause of this reduced activity.

The rate of conversion is initially high but dramatically drops after ca. 2 h. This result clearly indicates that the catalyst is rather active at the early stages of the reaction but dies as the reaction progresses. This stability problem appears closely related to the simultaneous presence of CF_3 groups and a phosphine in the ligand system.

Finally, the presence of ortho substituents relative to the chlorine atom had a dramatic effect on conversion with **1c**, but a much less pronounced effect with **1b**. A curious effect, for which we cannot offer an obvious rationalization, is the significantly lower activity of **1a** relative to **1b** for entry 11, whereas about the same activity of the two catalysts is observed for entry 5.

4. Conclusion

Zwitterionic complexes of Ni(II), bearing phosphine/imidazolium ligands, have been prepared and show high activities and selectivities for the coupling of aryl chlorides with aryl Grignard reagents at room temperature. We have observed that small structural changes, such as increasing the length of the ligand tether from 2 to 3 carbons, could have a dramatic effect on the catalytic activity. Very high conversions have been achieved, except in the case of 4-chlorobenzotrifluoride, where the presence of a phosphine moiety in the catalyst seems to hamper the reaction. We are now studying the coordination chemistry of these ligands on other metals, and the catalytic properties of the resulting complexes will be tested in due course.

5. Acknowledgements

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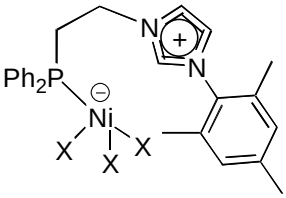
[30] the reaction of a Grignard reagent with 1-chloro-2,6-dimethylbenzene was carried out but only gave 5 to 10% of the expected heterocoupling product, which is comparable to the results found in the literature.

Tables and figures:



1a X = Br
1d X = Cl

Table 1. Crystal data and structure refinement for **1c**.

Empirical formula	$C_{27}H_{30}Br_3N_2NiP$	
Formula weight	711.94	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P b c a	
	a = 13.2103(8) Å	α= 90°.
Unit cell dimensions	b = 14.6501(9) Å	β= 90°.
	c = 30.0552(17) Å	γ = 90°.
Volume	5816.6(6) $Å^3$	
Z	8	
Density (calculated)	1.626 Mg/m^3	
Absorption coefficient	4.862 mm^{-1}	
F(000)	2832	
Crystal size	0.23 x 0.13 x 0.11 mm^3	
Theta range for data collection	2.86 to 23.25°.	
Index ranges	-14<=h<=14, -16<=k<=16, -29<=l<=33	
Reflections collected	32586	
Independent reflections	4176 [R(int) = 0.1041]	
Completeness to theta = 23.25°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.5426 and 0.4162	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4176 / 0 / 311	
Goodness-of-fit on F^2	1.236	
Final R indices [I>2sigma(I)]	R1 = 0.1019, wR2 = 0.1407	
R indices (all data)	R1 = 0.1290, wR2 = 0.1524	
Largest diff. peak and hole	0.716 and -0.468 e.$Å^{-3}$	

Table 2. Hydrogen bonds for **1c** [Å and °].

C-H…Br(1)	d(C-H)	d(H...Br)	d(C...Br)	<(CHBr)
C(1)-H(1)...Br(1)^{i}	0.93	2.76	3.566(11)	146.0

C(11)-H(11A)...Br(1)^{i}	0.97	2.90	3.666(13)	137.1
C(3)-H(3)...Br(1)^{ii}	0.93	2.92	3.707(13)	143.5

Symmetry transformations used to generate equivalent atoms:
(i) x-1/2,y,-z+3/2 ; (ii) -x+2,y+1/2,-z+3/2

Table 3. Cross-coupling reactions of aryl chlorides with arylmagnesium chloride or bromide. GC yield (%) of heterocoupling product **8**.[a][b]

Entry	R^1	E	R^2	X	Cat. **1a** [c]	Cat. **1b** [c]	Cat. **1c** [c]	IPr/Ni(acac)$_2$[d]
1	H	N	H	Cl	>99	>99	>99	>99
2	4-CF_3	C	H	Cl	37	53	29	96
3	4-CH_3	C	H	Cl	86	96	63	81
4	4-OCH_3	C	H	Cl	95	92	80	71
5	2-CH_3	C	H	Cl	78	82	23	73
6	bromomesitylene	C	H	Cl	4	3	7	5
7	H	N	4-OCH_3	Br	>99	>99	>99	>99
8	4-CF_3	C	4-OCH_3	Br	36	33	42	>99
9	H	C	4-OCH_3	Br	99	98	76	93
10	4-CH_3	C	4-OCH_3	Br	92	87	89	88
11	2-CH_3	C	4-OCH_3	Br	48	87	12	77

[a] For the meaning of R^1, R^2, E and X and for the nature of the possible reaction products, see Scheme 3.

[b] Conditions: 1.0 eq aryl halide, 1.5 eq aryl Grignard, 3 mol% **1a-c**, THF, 25°C, t = 18 h.

[c] GC yield using diethyleneglycol-di-n-butylether as the internal standard. The relative yields in percent are normalized to the reagent in defect (**6**): **6**+**8**+**9**+**10** = 100.

[d] Ref. [18].

Table 4. Detailed results of cross-coupling reactions with phenylmagnesium chloride.[a]

Entry	R	E	Cat. **1a**	Cat. **1b**	Cat. **1c**	IPr/Ni(acac)$_2$
1	H	N	100/0/0/0/6	100/0/0/0/17	100/0/0/0/21	100/0/0/0/4
2	4-CF_3	C	37/63/0/0/30	53/47/0/0/30	29/71/0/0/27	96/4/0/0/4
3	4-CH_3	C	86/2/5/7/17	96/2/1/1/10	63/32/4/1/15	81/7/3/9/11
4	4-OCH_3	C	95/4/0/1/19	92/6/1/1/22	80/18/1/1/19	71/19/1/9/16
5	2-CH_3	C	78/10/12/0/24	82/11/7/0/20	23/67/10/0/22	73/9/10/8/15
6	bromomesitylene	C	4/64/32/0/27	3/71/26/0/23	7/53/40/0/26	5/80/15/0/12

[a] The product distribution is given as **8**/**6**/**9**/**10**/**11**; the amount of **10** was approximated by comparison of the peak integrations.

Table 5. Detailed results of cross-coupling reactions with 4-anisylmagnesium bromide.[a]

Entry	R	E	Cat. **1a**	Cat. **1b**	Cat. **1c**	IPr/Ni(acac)$_2$
7	H	N	100/0/0/0/7	100/0/0/0/6	100/0/0/0/10	100/0/0/0/1
8	4-CF_3	C	36/63/1/0/17	33/66/1/0/15	42/57/1/0/16	100/0/0/0/8
9	H	C	99/0/0/1/4	98/1/0/1/6	76/23/0/1/4	93/3/3/1/16
10	4-CH_3	C	92/7/0/1/5	87/11/1/0/3	89/10/1/0/5	88/5/4/3/15
11	2-CH_3	C	48/45/6/1/6	87/9/3/1/5	12/83/5/0/5	77/20/0/3/10

[a] The product distribution is given as **8**/**6**/**9**/**10**/**11**; the amount of **10** was approximated by comparison of the peak integrations.

Figure 1. Proposed structures of Ni(II) carbenic complexes from **1a:** monomer (*cis* coordination) and dimer (*trans* coordination).

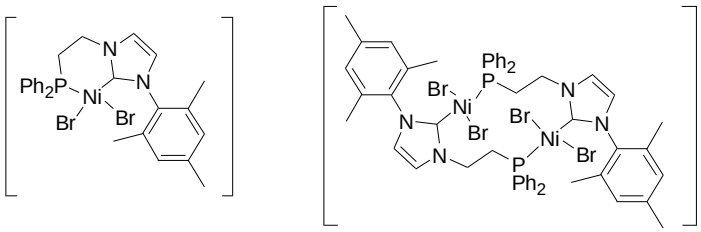


Figure 2. Molecular view of compound **1c** with atom labelling scheme. H atoms have been omitted for clarity. Selected bond lengths (Å) and bond angles (°): Ni(1)-P(1) 2.330(3); Ni(1)-Br(1) 2.3723(18); Ni(1)-Br(2) 2.3774(19); Ni(1)-Br(3) 2.3518(19); N(1)-C(11) 1.476(13); N(1)-C(1) 1.327(12); N(1) C(3) 1.365(14); N(2)-C(1) 1.313(12); N(2)-C(2) 1.362(14); N(2)-C(211) 1.448(13); C(2)-C(3) 1.326(16); P(1)-Ni(1)-Br(1) 100.52(10); P(1)-Ni(1)-Br(2) 105.26(9); P(1)-Ni(1)-Br(3) 110.73(10); Br(1)-Ni(1)-Br(2) 106.07(8); Br(1)-Ni(1)-Br(3) 112.77(8); Br(2)-Ni(1)-Br(3) 119.57(8); N(1)-C(1)-N(2) 108.7(10); C(1)-N(1)-C(3) 107.7(10); C(1)-N(2)-C(2) 108.7(10); N(1)-C(3)-C(2) 107.8(11); N(2)-C(2)-C(3) 107.1(11).

(TIFF file)

Figure 3. Conversion of 4-chloroanisole *vs* time with **1a-c** (Table 3, entry 4).

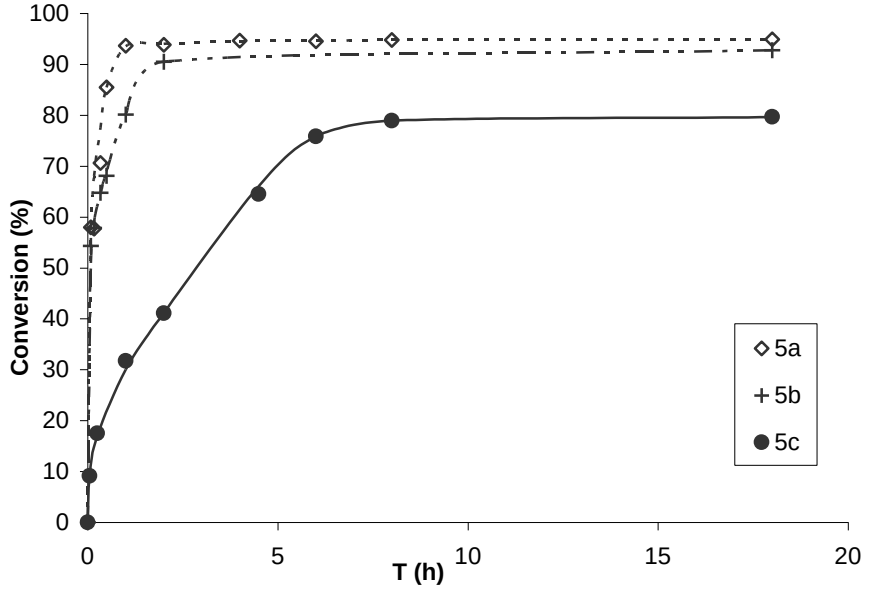


Figure 4. Conversion of 4-chlorotoluene *vs* time with **1a-c** (Table 3, entry 10) and comparison with the $Ni(acac)_2$/IPr system.

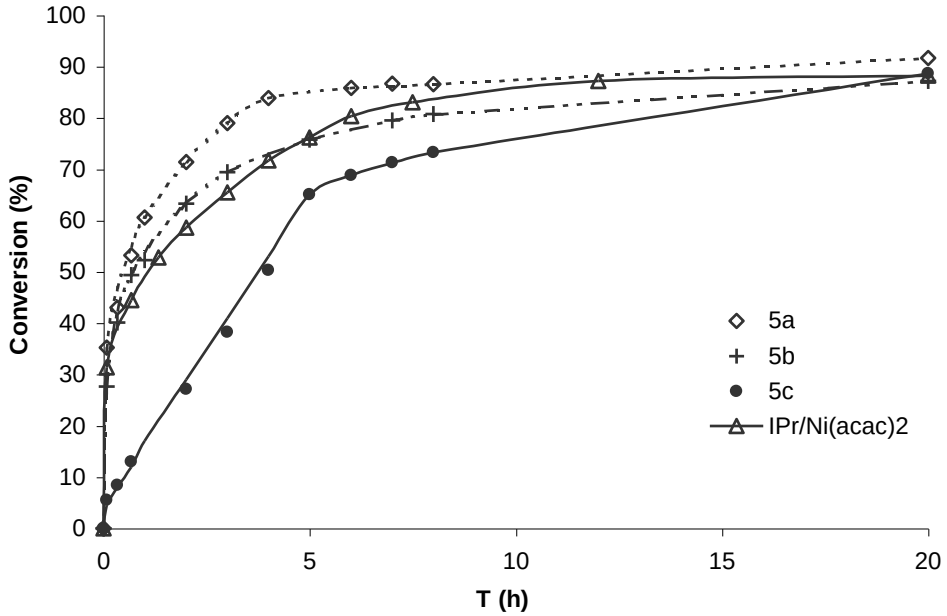
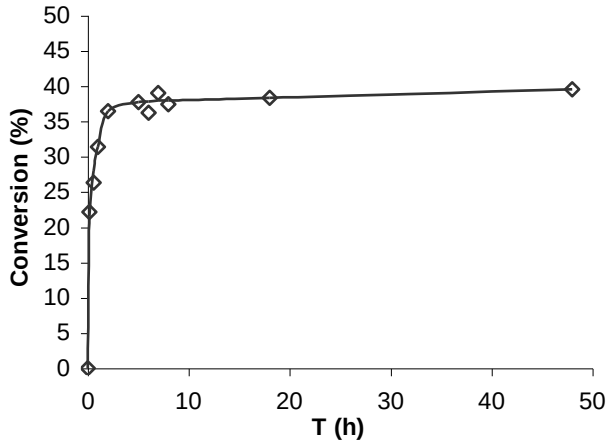
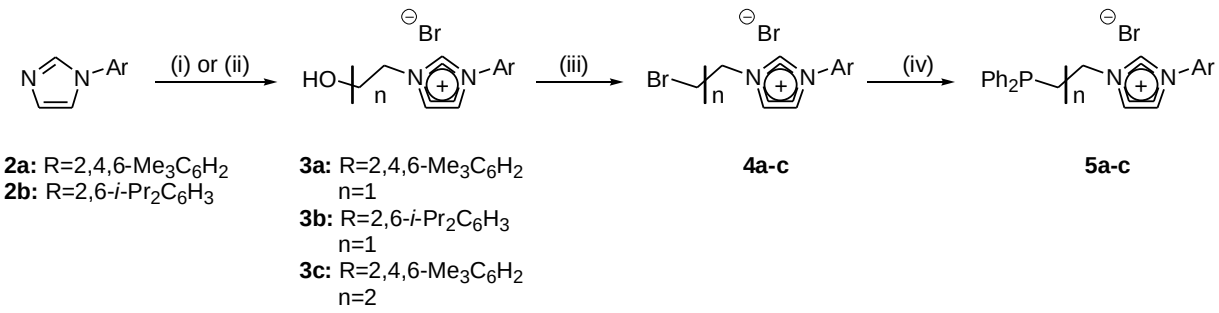


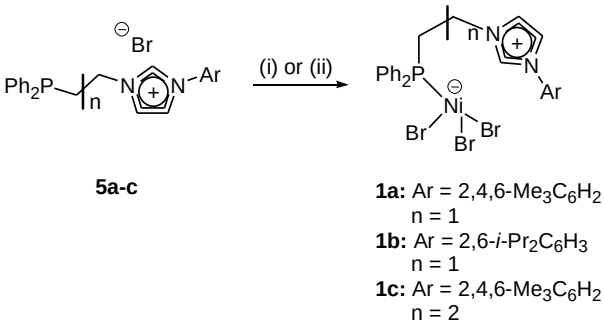
Figure 5. Conversion of 4-chlorobenzotrifluoride *vs* time with **1a**.



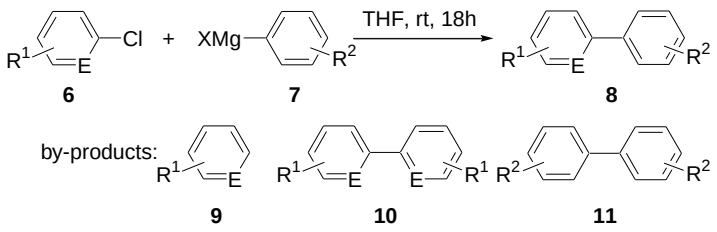
Scheme 1. *Reagents and conditions*: (i) 2-bromoethanol, toluene, 120 °C, 18 h; (ii) 3-bromo-1-propanol, toluene, 120 °C, 15 h; (iii) PBr_3, CH_2Cl_2, 0 °C, 20 h; (iv) $HPPh_2$, *t*-BuOK, DMSO, rt, 2 h (**5a,b**), 15 h (**5c**).



Scheme 2. *Reagents and conditions*: (i) $NiBr_2$(DME), THF, rt, 30 min to 1h (**1a,b**); (ii) $NiBr_2(MeCN)_2$, THF, rt, 1h (**1c**).



Scheme 3. Reagents and products for the catalytic Kumada-Corriu reaction (for the results, see Tables 3, 4 and 5).


THF, rt, 18h
by-products: