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Pyridin- and quinolinylidene nickel carbene complexes as effective catalysts for the Grignard cross-coupling reaction

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Abstract

A series of complex compounds that contain *N*-heterocyclic carbene (NHC) and *N*-heterocyclic carbene ligands with a remote heteroatom (*r*NHC) have been prepared in good yields and characterized. [Cl(NHC)$(PPh_3)_2$Ni]BF_4 and [Cl(*r*NHC)$(PPh_3)_2$Ni]BF_4 also combine the stability of carbene complexes with the activity of phosphine complexes and some are active and effective precatalysts for aryl-coupling in the Kumada–Corriu reaction. Aryl chlorides can be used as substrates. Their performance in catalysis as well as their easy preparation make the new compounds superior to other comparable mixed carbene–phosphine compounds known thus far.

Keywords: Kumada–Corriu coupling; *N*-Heterocyclic carbenes; Remote heteroatom *N*-Heterocyclic carbenes; Nickel

1. Introduction

Carbon–carbon bond formation in the presence of a transition metal catalyst is a key step in many synthetic protocols of organic chemicals, natural products, as well as in a variety of industrial processes [1–3]. One important example of such a catalytic transformation is the Grignard cross-coupling reaction [4], that has been used in a wide range of synthetic and industrial applications [1,5] since first independently reported in 1972 by Kumada and co-workers [4a] and Corriu and Masse [4b]. For example, the coupling of aromatic Grignard compounds with aryl halides offers a convenient synthetic access to biaryls, terphenyls, and oligoaryls that have become important building blocks for the synthesis of natural products, liquid crystals, polymers, and ligands in transition metal complexes [6]. The Kumada–Corriu reaction, however, is still not properly optimized [7]. For example, biaryl byproducts are observed due to unwanted homo-coupling of the organic groups in the Grignard compound, leading to difficulties in purification of the main cross-coupled product. Moreover, only a limited number of functionalities are tolerated in this reaction. Methoxy substituents, for example, are activated under the standard reaction conditions [8].

N-Heterocyclic carbenes are strong σ-donor ligands and were thus applied successfully in a variety of transition metal-catalyzed transformations [9,10]. They are especially effective when the oxidative addition of an aryl halide to the active metal is the rate determining step.

Imidazolin-2-ylidenes were introduced in the Herrmann group to stabilize the metal center in nickel-catalyzed Kumada–Corriu cross-coupling [11,12] replacing commonly used phosphine ligands and giving superior catalytic performance. The catalyst is generated by in situ deprotonation of an imidazolium salt by an excess of Grignard reagent in the presence of a nickel(II) salt and is highly efficient in the activation of C–Cl– bonds [12].

In recent communications we have shown by quantum mechanical calculation that the introduction of new types of carbene ligands derived from pyridine and quinoline, especially those with remote heteroatoms (*r*NHCs) [13,14], provide even stronger σ-bonding than the now well-known imidazolin-2-ylidene compounds. Based on these early results a more detailed

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study was undertaken in which related Ni carbene complexes were utilized.

We present here the first systematic study of using both NHC (carbene carbon next to N) and *r*NHC (carbene carbon removed from N) complexes of Ni(II) – with the ligands of the *N*-methylpyridinylidene and quinolinylidene types and the complexes prepared by oxidative addition – in Kumada–Corriu cross-couplings of aromatic Grignard compounds with aryl chlorides.

2. Experimental

2.1. General procedures

NMR spectra (^{1}H, ^{13}C, ^{31}P) were recorded either on a Jeol JMX-GX 400, a Jeol JMX-GX 270 or a Bruker DPX 400 instrument. Chemical shifts, δ are given in ppm. The spectra were calibrated to the residual protons of the solvent or to the ^{13}C signals of the solvent. FAB-MS spectra were measured on a Finnigan MAT 90 mass spectrometer (xenon/*p*-nitrobenzyl alcohol). Elemental analyses were carried out by the Microanalytical Laboratory at the TU München. Unless otherwise stated, all manipulations were carried out using standard Schlenk techniques. All solvents for use in an inert atmosphere were purified by standard procedures and distilled under nitrogen immediately prior to use. Other chemicals were obtained from commercial sources and used without further purification.

2.2. Synthesis of 2-chloro-3-methyl-N-methylquinolinium tetrafluoroborate (**4**)

2-Chloro-3-methylquinoline (1.01 g, 5.69 mmol) was dissolved in a mixture of dichloromethane (30 ml) and acetonitrile (10 ml). $[Me_3O][BF_4]$ (0.843 g, 5.69 mmol) was added over a period of 1.5 h at room temperature. After stirring overnight, the solvent was removed in vacuo. The residue was washed twice with THF (50 ml), filtered and dried in vacuo (white powder, yield: 92%).

^{1}H NMR (399.78 MHz, [*d*6]DMSO, 25 °C): $\delta = 8.52$ (s, 1H), 8.37 (s, $J = 7.6$ Hz, 1H), 8.30 (pseudot, $J = 8.4$ Hz, 7.2 Hz, 1H), 8.22 (d, $J = 8.4$ Hz, 1H), 7.99 (pseudot, $J = 7.6$ Hz, 7.2 Hz, 1H), 4.38 (s, 3H, NCH_3), 2.87 (s, 3H, CH_3); $^{13}C\{^{1}H\}$ NMR (100.53 MHz, [*d*6]DMSO, 25 °C): $\delta = 161.8$, 138.8, 135.6, 129.5, 127.8, 121.9, 120.1, 114.4, 29.4 (NCH_3), 17.4 (CH_3); MS (FAB-MS): *m*/*z* (relative intensity) 192 $[M]^+$ (100); elemental analysis calcd for $C_{11}H_{11}NClBF_4$ (279.47): C 47.27, H 3.97, N 5.01; found: C 47.19, H 3.97, N 4.63.

2.3. Synthesis of 4-chloro-N-methylquinolinium tetrafluoroborate (**6**)

Compound **6** was prepared in the same manner as **2**, with the same amounts of $[Me_3O][BF_4]$, but with 4-chloro-*N*-methylquinoline as the organic substrate. Recrystallization of the white powder from dichloromethane (−20 °C) was necessary to afford the pure product (colourless crystals, yield: 84%).

^{1}H NMR (399.78 MHz, [*d*6]DMSO, 25 °C): $\delta = 9.76$ (d, $J = 6.8$ Hz, 1H), 9.12 (d, $J = 8.4$ Hz, 1H), 8.98 (d, $J = 7.6$ Hz, 1H), 8.91 (pseudot, $J = 8.4$ Hz, 7.2 Hz, 1H), 8.61 (pseudot, $J = 7.6$ Hz, 7.2 Hz, 1H), 8.13 (d, $J = 6.8$ Hz, 1H), 5.08 (s, 3H, NCH_3); $^{13}C\{^{1}H\}$ NMR (100.53 MHz, [*d*6]DMSO, 25 °C): $\delta = 152.4$, 150.2, 139.6, 136.8, 131.8, 127.5, 126.6, 123.1, 120.5, 45.9 (NCH_3); MS (FAB-MS): *m*/*z* (relative intensity) 178 $[M]^+$ (100), 443 $[(2M) + BF_4]^+$ (4); elemental analysis calcd for $C_{10}H_9NClBF_4$ (265.44): C 45.25, H 3.42, N 5.28; found: C 45.06, H 3.41, N 5.28.

2.4. Synthesis of 4-chloro-2-methyl-N-methylquinolinium tetrafluoroborate (**7**)

Compound **7** was prepared in the same manner as **2**, with the same amount of $[Me_3O][BF_4]$, but with 4-chloro-2-methylquinoline as the organic substrate (white powder, yield: 90%). ^{1}H NMR (399.78 MHz, [*d*6]DMSO, 25 °C): $\delta = 8.63$ (d, $J = 7.1$, 1H), 8.51 (d, $J = 8.0$ Hz, 1H), 8.48 (s, 1H), 8.30 (pseudot, $J = 8.0$ Hz, 7.7 Hz, 1H), 8.09 (pseudot, $J = 7.1$ Hz, 7.7 Hz, 1H), 4.40 (s, 3H, NCH_3), 3.04 (s, 3H, CH_3); $^{13}C\{^{1}H\}$ NMR (100.53 MHz, [*d*6]DMSO, 25 °C): $\delta = 161.8$, 155.2, 150.6, 140.6, 136.5, 130.8, 126.6, 125.8, 120.3, 38.5 (NCH_3), 23.2 (CH_3); MS (FAB-MS): *m*/*z* (relative intensity) 192 $[M]^+$ (100), 471 $[(2M) + BF_4]^+$ (2); elemental analysis calcd for $C_{11}H_{11}NClBF_4$ (279.47): C 47.27, H 3.97, N 5.01; found: C 47.00, H 4.07, N 4.80.

2.5. Synthesis of chloro-(N-methyl-3-methylquinolin-2-ylidene)bis(triphenylphosphine)–nickel(II) tetrafluoroborate (**12**)

To 0.470 g (0.424 mmol) of $Ni(PPh_3)_4$ dissolved in toluene (40 ml), 1 mol equiv. of **4** (0.119 g, 0.424 mmol) was added and the reaction mixture was stirred overnight at 60 °C. After cooling to room temperature, the precipitate was filtered off, washed with toluene, dissolved in dichloromethane and filtered through Celite. Precipitation with pentane afforded complex **12** (yellow powder, yield: 79%).

^{1}H NMR (299.65 MHz, CD_2Cl_2, 25 °C): $\delta = 7.67 - 7.20$ (m, 35H, 30 phosphineH + 5 quinolineH); 4.75 (s, 3H, NCH_3); 3.13 (s, 3H, CH_3); $^{13}C\{^{1}H\}$ NMR (75.41 MHz, CD_2Cl_2, 25 °C): $\delta = 209.5$ (t, $^{2}J(^{31}P, ^{13}C) = 30.3$ Hz, carbeneC); 140.4, 139.8, 135.0 (quinolineC); 134.6 (pseudos, phosphineC); 132.3 (quinolineC); 132.0 (s, phosphine4C); 129.4 (m, ipsoC, phosphineC); 128.97, 128.7, 127.5, 115.6 (quinolineC); 49.7 (NCH_3); 24.0 (CH_3). $^{31}P\{^{1}H\}$ NMR (121.41 MHz, CD_2Cl_2, 25 °C): $\delta = 18.79$ (s). MS (FAB-MS): *m*/*z* (relative intensity) 774 $[M]^+$ (4), 512 $[M - PPh_3]^+$ (26), 476 $[M - PPh_3–Cl]^+$ (6), 192 $[M - 2PPh_3]^+$ (14); elemental analysis calcd for $C_{47}H_{41}NClBF_4P_2Ni$ (862.73): C 65.43, H 4.79, N 1.62; found: C 65.54, H 4.76, N 1.52.

2.6. Synthesis of chloro-(N-methylquinolin-4-ylidene)bis(triphenylphosphine)nickel(II) tetrafluoroborate (**14**)

Complex **14** was prepared in the same manner as **12**, with the same amount of $Ni(PPh_3)_4$, but with **6** as the organic substrate. Recrystallization of the yellow powder from

dichloromethane/pentane was necessary to afford the pure product (yellow crystals, yield: 46%)

^{1}H NMR (270.17 MHz, CD_2Cl_2, 25 °C): $\delta = 7.83 - 7.22$ (m, 36H, 30 phosphineH + 6 quinolineH); 3.88 (s, 3H, NCH_3); $^{13}C\{^1H\}$ NMR (67.9 MHz, CD_2Cl_2, 25 °C): $\delta = 215.5$ (t, $^2J(^{31}P, ^{13}C) = 25.2$ Hz, carbeneC); 136.9, 135.0 (quinolineC); 134.3 (t, $J = 4.6$ Hz, phosphineC); 132.6, 131.9 (quinolineC); 130.8 (s, phosphine4C); 129.9 (quinolineC); 129.2 (t, $J = 22.2$ Hz, ipsoC); 128.8 (quinolineC); 128.2 (t, $J = 4.6$ Hz, phosphineC), 127.7, 117.6 (quinolineC); 37.8 (NCH_3); $^{31}P\{^1H\}$ NMR (161.83 MHz, CD_2Cl_2, 25 °C): $\delta = 21.86$ (s); MS (FAB-MS): *m/z* (relative intensity) 498 $[M - PPh_3]^+$ (11), 463 $[M - PPh_3 - Cl]^+$ (2); 235 $[M - 2PPh_3]^+$ (7); elemental analysis calcd for $C_{46}H_{39}NClBF_4P_2Ni$ (848.71): C 65.10, H 4.63, N 1.65; found: C 65.33, H 4.50, N 1.77.

2.7. Synthesis of chloro-(N-methyl-2-methylquinolin-4-ylidene)bis(triphenylphosphine)–nickel(II) tetrafluoroborate (**15**)

Complex **15** was prepared in the same manner as **12**, with the same amount of $Ni(PPh_3)_4$, but with **7** as the organic substrate (yellow powder, yield: 60%).

^{1}H NMR (399.78 MHz, CD_3CN, 25 °C): $\delta = 9.56$ (s, 1H, quinolineH); 7.49–7.19 (m, 34H, 30 phosphineH + 4 quinolineH); 3.59 (s, 3H, NCH_3); 2.12 (s, 3H, CH_3); $^{13}C\{^1H\}$ NMR (100.53 MHz, CD_3CN, 25 °C): $\delta = 212.4$ (t, $^2J(^{31}P, ^{13}C) = 31.3$ Hz, carbeneC); 146.3, 136.5 (quinolineC); 134.3 (m, phosphineC); 134.7, 133.1, 132.0, 131.3 (quinolineC); 130.8 (s, phosphine4C); 129.4 (t, $J = 16.8$ Hz, ipsoC); 128.2 (m, phosphineC); 127.1, 117.6 (quinolineC); 36.9 (NCH_3); 21.6 (CH_3); $^{31}P\{^1H\}$ NMR (161.83 MHz, CD_3CN, 25 °C): $\delta = 22.41$ (s); MS (FAB-MS): *m/z* (relative intensity) 512 $[M - PPh_3]^+$ (22), 192 $[M - 2PPh_3]^+$ (41); elemental analysis calcd for $C_{47}H_{41}NClBF_4P_2Ni$ (862.73): C 65.43, H 4.79, N 1.62; found: C 65.83, H 4.79, N 1.58.

2.8. Synthesis of dichlorobis(1,3-dimesitylimidazolin-2-ylidene)–nickel(II) (**19**)

A 0.398 g (1.31 mmol) amount of 1,3-dimesitylimidazolin-2-ylidene [15] dissolved in 3 ml of THF was slowly added to a suspension of 0.373 g (0.57 mmol) of $NiCl_2(PPh_3)_2$ in 11 ml of THF. After 20 min of stirring at room temperature the solvent was evaporated under vacuum. The violet-red product was washed three times with 2.5 ml ice cold hexane and then recrystallized from dichloromethane/hexane (−20 °C) (violet-red crystals, yield: 58%). ^{1}H NMR (399.78 MHz, C_6D_6, 25 °C): $\delta = 6.97$ (s, 8H, Ar–H), 5.94 (s, 4H, NC_2H_2N), 2.42 (s, 12H, *p*-CH_3), 2.16 (s, 24H, *o*-CH_3); $^{13}C\{^1H\}$ NMR (100.53 MHz, C_6D_6, 25 °C): $\delta = 169.82$ (carbeneC), 136.96 (ipsoC), 136.83 (*p*-C), 136.68 (*o*-C), 129.21 (*m*-C), 122 (NC_2H_2N), 21.11 (p-CH_3) 19.26 (*o*-CH_3); MS (FAB-MS): *m/z* (relative intensity) = 736 $[M]^+$ (7), 699 $[M - Cl]^+$ (6), 664 $[M - 2Cl]^+$ (4), 529.5 (4.1), 425.8 (22.6), 338.1 (65.83), 304.2 (75) [carbene], 302.2 (100); elemental analysis calcd for $C_{42}H_{48}Cl_2N_4Ni$ (736.26): C 68.31, H 6.55, N 7.59; found: C 68.78, H 6.36, N 7.20.

Table 1
Crystallographic data for complex **12**

Chemical formula	$[C_{47}H_{41}ClNNiP_2]BF_4 \cdot CH_2Cl_2$
Formula weight	947.64
Crystal system	Orthorhombic
Space group	$Pca2_1$
a, *b*, *c* (Å)	31.740(5), 12.836(2), 10.820(2)
α, β, γ (°)	90, 90, 90
Volume (Å^3)	4408.2(12)
Colour, shape	Yellow, block
Z	4
μ (mm^{-1})	0.747
θ (°)	1.71–25.67
Crystal size (mm^3)	0.25 × 0.19 × 0.10
Index range	$-33 \le h \le 38$, $-11 \le k \le 15$, $-13 \le l \le 13$
No. of reflections collected	23 545
No. of independent reflections	8261
Parameters	542
$R_1(F_0^2 > 2\sigma F_0^2)$	0.0463
wR_2 (all data)	0.0624

$R_1 = \sum||F_0| - |F_c||/\sum|F_0|; wR_2 = [\sum[w(F_0^2 - F_c^2)^2]/\sum w(F_0^2)^2]^{1/2}$.

2.9. Crystallography for complex **12**

The X-ray diffraction data was collected (Table 1) on a Bruker SMART Apex CCD diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) at 100 K. Data reduction was carried out using standard methods from the software package Bruker SAINT [16]. Empirical corrections were performed using SCALEPACK [17] and SMART data was treated with SADABS [18–20]. The structure was solved using direct methods. All non-hydrogen atoms were refined anisotropically by full matrix least squares calculations on F^2 using SHELXL-97 [21] within the X-Seed environment [22]. The hydrogen atoms were fixed in calculated positions. ORTEP-III for Windows [23] was used to generate the figure at the 50% probability level.

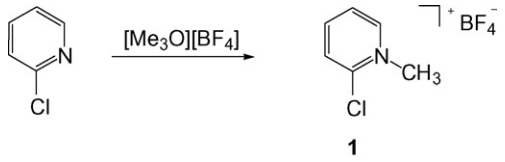
2.10. Kumada–Corriu reaction

A typical procedure for C–Cl activation of: 0.0046 g of $Ni(acac)_2$ (0.018 mmol) and 0.018 mmol azolium salt or 0.018 mmol of the Ni(II) complex were suspended in 1.2 ml of dry and degassed THF in an argon atmosphere. After addition of 61.1 μl of 4-chlorobenzene (0.0675 g, 0.6 mmol) and 33.6 μl of the internal standard, diethyleneglycol-di-*n*-butylether (0.0297 g), the mixture was stirred for 5 min at room temperature before catalysis was initiated by dropwise addition of 0.9 ml of the Grignard reagent, phenylmagnesium bromide (0.7 mmol, 1 M in THF). After the desired run time, 0.4 ml of the reaction mixture was removed, quenched by addition of 0.4 ml of methanol, diluted with 0.2 ml THF and examined by GC/FID.

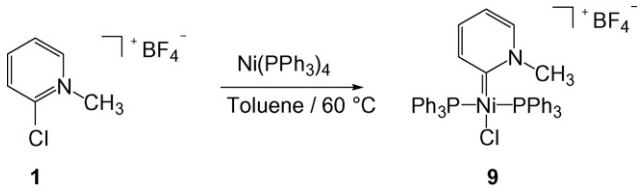
3. Results and discussion

3.1. Synthesis and characterization of pyridinium and quinolinium salts

The target ligand precursor **1**, for example, was prepared according to Scheme 1 and the other cations **2**–**7** (Fig. 1) were



Scheme 1. Ligand preparation.



Scheme 2. Complex synthesis.

synthesized similarly by alkylating the corresponding chloropyridine (**2**), or chloroquinoline (**3**–**7**) substrates with one equivalent of Meerwein's salt in a dichloromethane/acetonitrile (3/1) mixture [24]. Compounds **1**–**3** and **5** have already been described in detail [14] and the synthesis of **8** is described by Raubenheimer et al. [25]. Washing with cold THF yielded compounds **4**, **6** and **7** as colourless powders in an average yield of approximately 90%. Compounds **4**, **6** and **7** were characterized by NMR spectroscopy, mass spectrometry and elemental analysis.

3.2. Syntheses and spectroscopic characterization of pyridin- and quinolinylidene Ni(II) complexes

Cationic complexes of Ni(II) (**9**–**17**, Fig. 2) were obtained by oxidative addition of $Ni(PPh_3)_4$ to the ligand precursors **1**–**8** at 60 °C according to Scheme 2. Compounds **9**–**11**, **13**, **16** and **17** have already been described in detail in our previous work mentioned above [14]. Compound **17** representing a precatalyst that contains a standard NHC ligand does not belong to the same family as the rest and was included for comparison. Filtration through Celite and precipitation with pentane afforded the compounds **12**, **14** and **15** (Fig. 2) as yellow powders in good to excellent yields. Elemental analyses and solution NMR spectra confirmed the expected compositions and structures. The crystal and molecular structures of compound **12** were determined by single-crystal X-ray diffraction methods.

The single resonance observed for the compounds **12**, **14** and **15** in the ^{31}P NMR spectrum in a narrow range between 18.66 and 22.41 ppm, show clearly the equivalence of the two phosphorus ligands in each compound, indicating trans positioning of these ligands in solution. This is also true for the other, previously published, Ni(II) complexes shown in Fig. 2

The carbene carbon atoms in complexes **12**, **14** and **15** resonate at δ values 209.5, 215.5 and 212.4 in their ^{13}C NMR spectra. All of them show a downfield shift of approximately 40–60 ppm compared to previously reported thiazole-derived Ni(II) carbene complexes in the literature [26]. All carbene carbon signals appear as triplets with coupling constants between 25 and 30 Hz, again indicating the trans arrangement of the two phosphines in solution.

Only the FAB-MS spectrum of complex **12** shows weak signals corresponding to *m*/*z*-values for the cationic complex peaks, $[M]^+$. All other spectra contain signals for the $[M - PPh_3]^+$ and the $[M - 2PPh_3]^+$ fragments. The FAB-MS spectra of **12** and **14**, in addition, indicate the formation of the $[M - PPh_3–Cl]^+$ ion.

Note that the easy preparation of these Ni(II) carbene complexes using cheap and commercially available starting materials, short reaction times as well as a straightforward workup procedure, are major advantages compared to most other nickel carbene complexes used before in related catalytic applications.

3.3. Crystal and molecular structure of complex *12*

The crystal and molecular structure of **12**, a six-membered, one-N NHC complex (Fig. 3), was determined by X-ray diffraction techniques. Single crystals of the complex were grown

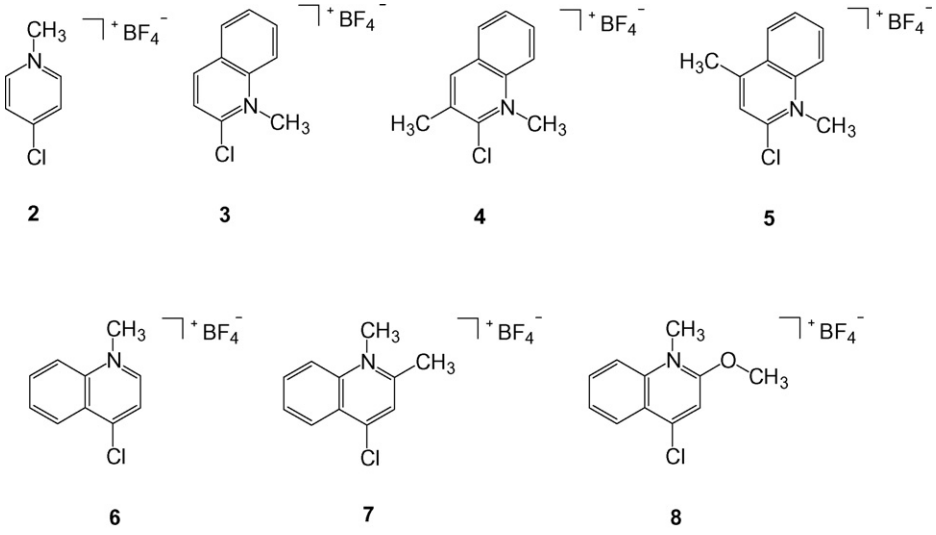


Fig. 1. Ligand precursors **2**–**8**.

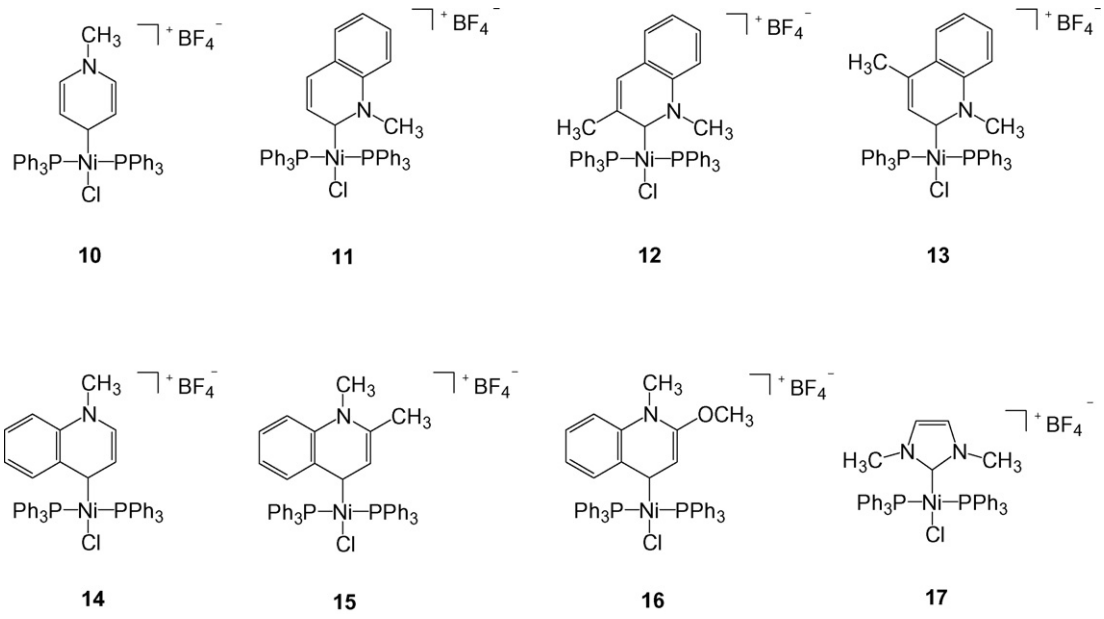


Fig. 2. Carbene complexes **10**–**17**.

by vapour diffusion of pentane into a dichloromethane solution. Selected bond lengths and angles are presented in Table 2. The cationic Ni complex occurs in a distorted square planar environment with deviations of 0.010(1), 0.102(2), −0.112(1), −0.112(1) and 0.110(2) Å from the least squares plane through Ni(1), Cl(1), P(1), P(2) and C(2). The two phosphine ligands are situated trans to each other. The carbene ligand is orientated almost perpendicular to this plane, with an interplanar dihedral angle of 86.03°.

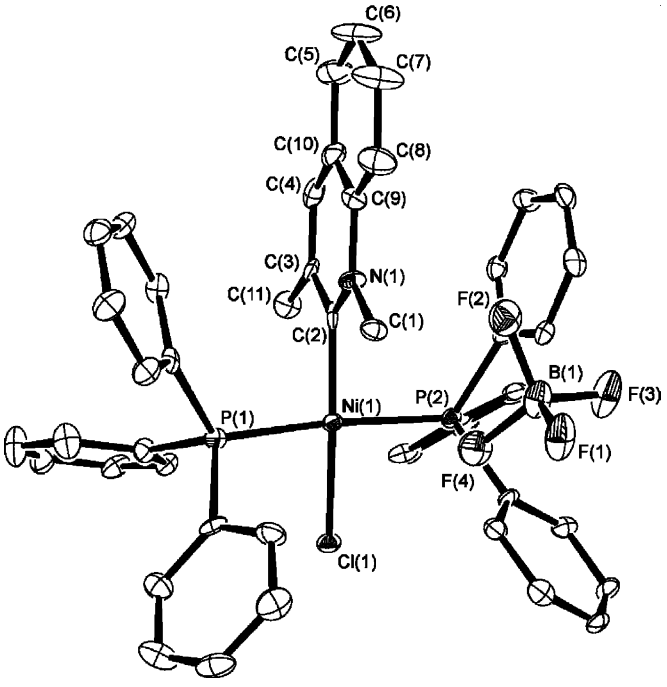


Fig. 3. Molecular structure of **12**; hydrogen atoms and CH_2Cl_2 solvent molecule are omitted for clarity.

The Ni–C(carbene) bond distance of 1.874(5) Å, falls well within the 1.83–1.98 Å range observed in a variety of Ni(II) carbene complexes [14,26]. The Ni–Cl separation (2.200(1) Å) does not differ significantly from the previously reported separation of 2.203 Å for the trans-chloro(1-methyl-1,2-dihydropyridin-2-ylidene)bis(triphenylphosphine)nickel(II) tetrafluoroborate complex [14]. This suggests similar trans-influences of the carbene ligands in the two complexes. No significant intermolecular interaction is observed. The Ni complexes are stacked in the direction of the *c*-axis and form channels with the CH_2Cl_2 solvent molecules included therein.

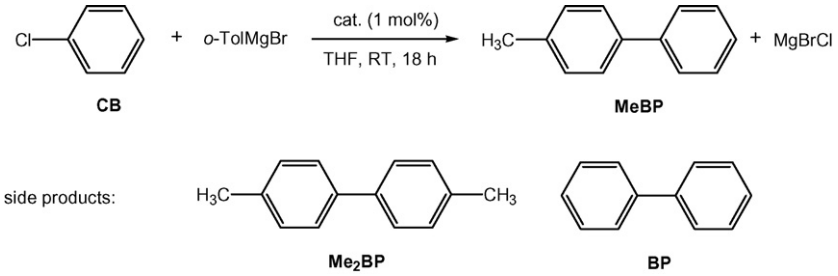
3.4. Kumada–Corriu coupling

The catalyst complexes in **9**–**17** (Scheme 2 and Fig. 2) were all screened for their activity and efficiency in the Kumada–Corriu reaction and the results obtained are summarized in Tables 3–5. For a better comparison with existing literature results, the diphosphine Ni(II) complex **18**, the

Table 2
Selected bond lengths (Å) and angles (°) in **12**

Ni(1)–C(2)	1.874(5)	C(3)–C(4)	1.363(8)
Ni(1)–P(1)	2.225(2)	C(4)–C(10)	1.408(8)
Ni(1)–P(2)	2.234(2)	C(10)–C(9)	1.399(8)
Ni(1)–Cl(1)	2.200(1)	C(9)–N(1)	1.397(7)
C(2)–C(3)	1.439(8)	N(1)–C(1)	1.464(7)
C(3)–C(11)	1.499(8)	N(1)–C(2)	1.352(7)
C(2)–Ni(1)–Cl(1)	174.6(2)	C(2)–C(3)–C(4)	120.0(5)
P(1)–Ni(1)–P(2)	172.5(1)	C(3)–C(4)–C(10)	120.9(5)
P(1)–Ni(1)–C(2)	93.8(2)	C(4)–C(10)–C(9)	119.9(5)
P(1)–Ni(1)–Cl(1)	86.7(1)	C(10)–C(9)–N(1)	117.3(5)
P(2)–Ni(1)–C(2)	90.7(2)	C(9)–N(1)–C(2)	124.4(5)
P(2)–Ni(1)–Cl(1)	89.4(1)	N(1)–C(2)–C(3)	117.4(5)
C(2)–C(3)–C(11)	119.4(5)	C(2)–N(1)–C(1)	118.3(4)

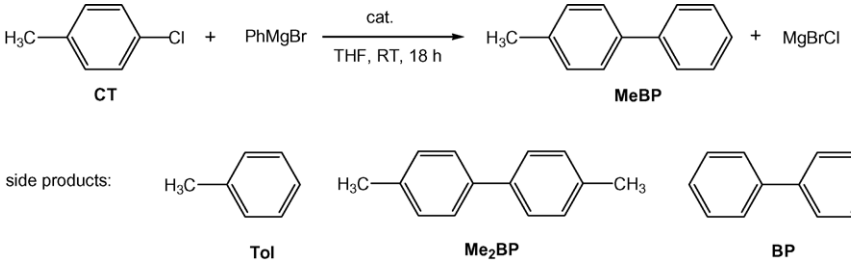
Table 3
Kumada–Corriu reaction of chlorobenzene with *o*-TolMgBr catalyzed by the Ni(II)-complexes **9–17** as well as the benchmark catalyst systems **18–20**



No.	Cat.	CB (%)[a]	MeBP (%)[a]	BP (%)[a]	Me_2BP (%)[a]
1	**9**	24	59	4	8
2	**10**	26	68	5	11
3	**11**	25	65	4	9
4	**12**	32	78	4	9
5	**13**	4	92	6	9
6	**14**	25	81	5	9
7	**15**	16	83	5	8
8	**16**	51	42	4	10
9	**17**	50	43	3	15
10	**18**	26	68	5	14
11	**19**	94	4	0	2
12	**20**	0	99	4	10

1.0 mol equiv. aryl chloride, 1.5 mol equiv. Grignard, THF, RT, $t = 18$ h.
[a] Conversions and yields determined by GC using diethylenglycol-di-*n*-butylether as internal standard.

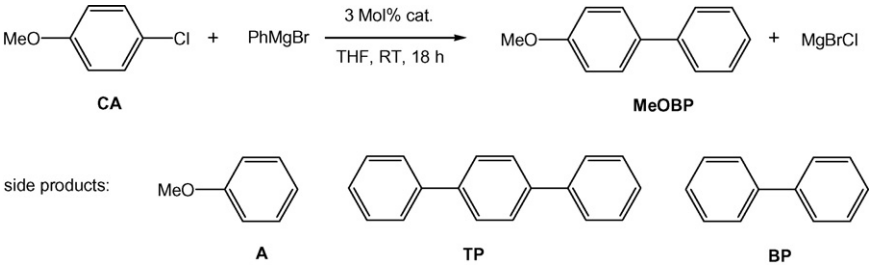
Table 4
Kumada–Corriu reaction of 4-chlorotoluene with phenyl-Grignard catalyzed by the Ni(II)-complexes **12–15** as well as the benchmark catalysts systems **18–20**



No.	mol%	Cat.	CT (%)[a]	MeBP (%)[a]	Tol (%)[a]	Me_2BP (%)[a]	BP (%)[a]
1	1	**12**	74	21	0	1	6
2	1	**13**	29	51	1	3	13
3	1	**14**	72	24	0	1	9
4	1	**15**	54	29	1	1	12
5	1	**18**	57	45	1	2	19
6	1	**20**	19	61	0	9	23
7	1	$Ni(acac)_2$	29	42	0	11	22
8	3	**12**	58	49	0	3	11
9	3	**13**	23	79	0	4	13
10	3	**14**	54	36	0	0	13
11	3	**15**	21	83	0	0	12
12	3	**18**	57	34	1	2	12
13	3	**19**	92	6	0	0	3
14	3	**20**	12	81	Not determined	Not determined	Not determined
15	3	$Ni(acac)_2$	40	48	0	2	29

1.0 equiv. aryl chloride, 1.5 equiv. Grignard, THF, RT, $t = 18$ h.
[a] Conversions and yields determined by GC using diethylenglykol-di-*n*-butylether as the internal standard.

Table 5
Kumada–Corriu reaction of 4-chloroanisole with phenyl-Grignard catalyzed by the Ni(II)-complexes **13**–**15** as well as the benchmark catalysts systems, **18**–**20**



No.	Cat.	CA (%)[a]	MeOBP (%)[a]	A (%)[a]	TP (%)[a]	BP (%)[a]
1	**13**	25	70	0	0	16
2	**14**	29	62	1	2	12
3	**15**	20	72	0	2	10
4	**19**	88	8	0	0	4
5	$Ni(acac)_2$	43	35	7	2	27
6	**20**	20	77	Not determined	Not determined	Not determined

1.0 equiv. aryl chloride, 1.5 equiv. Grignard, THF, RT, $t = 18$ h.
[a] Conversions and yields determined by GC using diethylenglycol-di-*n*-butylether as the internal standard.

biscarbene Ni(II) complex **19** as well as the in situ mixture **20** [$Ni(acac)_2$ + imidazolium salt] – representing the most active system for the Kumada–Corriu reaction known [11,12] – were included in the study. The results for the coupling of chlorobenzene with *o*-tolylmagnesium bromide (*o*-TolMgBr) using 1 mol% of catalyst, are summarized in Table 3 (Fig. 4).

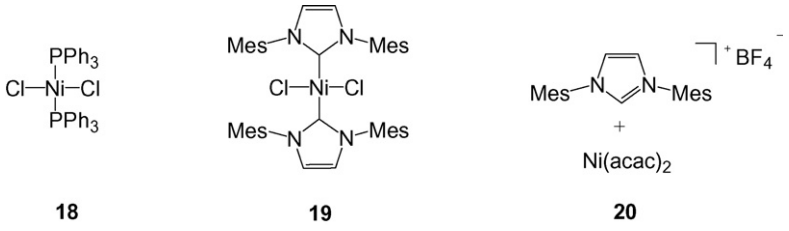
It can clearly be seen that some of the new pyridinylidene- and quinolinylidene-type nickel complexes are effective precatalysts for the Grignard cross-coupling. Under the chosen conditions compounds **12**–**15** are the most active new catalysts with **13** in the leading position affording a 92% yield of MeBP Table 3 (entry 5) – not far below presently the best, system **20**. Interestingly, all of the carbene ligands in the active complexes contain two rings and apart from the relatively simple ligand in **14**, they also have one or two C-bonded methyl groups attached to the pyridine ring. No simple discrimination between NHC- and *r*NHC-containing ligands is obvious. The imidazol-2-ylidene compound, **17**, only gives the sought after product in 43% yield.

An even better picture of the relative catalyst activities is given by the time-conversion curves depicted in Fig. 5. The reaction of chloro-benzene with *o*-TolMgBr was studied according to Kumada–Corriu using a catalyst concentration of 1.0 mol%. Compound **13** shows a significantly higher initial and overall activity compared to the imidazol-2-ylidene complex compound **17**, which performs poorly. The fact that most of the new one-N, NHC nickel(II) complexes are much more active than the standard five-membered, two-N NHC complex, **17**, indicates a huge potential for such ligands in C,C-coupling catalysis as well as in homogeneous catalysis in general. It is also remarkable that, unlike the situation with other NHC-containing catalysts, no induction period is observed, indicating a quick formation of the catalytically active {most likely Ni(0)} species.

For the activation of deactivated aryl chlorides, the four most active catalysts **12**–**15**, from the previous experiment, as well as the in situ system **20** and $Ni(acac)_2$ by itself were employed using catalyst concentrations of 1 mol% as well as 3 mol%. The results for the coupling of 4-chlorotoluene and 4-chloroanisole, respectively, with a phenyl-Grignard compound, are summarized in Tables 4 and 5. With the 1 mol% precatalyst concentrations the performances were not impressive and the discussion refers only to the 3 mol% experiments. Catalysts **13** and **15** show the highest activities with that of **15** achieving an 83% conversion to MeBP and thus just exceed the yield for the in situ system, **20** (compare entries 11 and 14, Table 4).

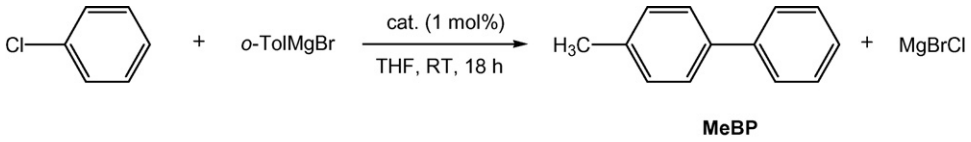
Even the strong deactivated 4-chloroanisole couples successfully when using 3 mol% of the catalyst **5**. Just as for 4-chlorotoluene, catalysts **13** and **15** again exhibit high activities, by furnishing ca. 70% of MeOBP (entries 1 and 3, Table 5).

These results prove that the new type of Ni(II) carbene complexes are suitable catalysts for C,C-coupling applications. They even compete successfully with the presently most successful catalyst system, **20**, for the Kumada–Corriu reaction. Optimiza-



18 19 20

Fig. 4. Catalyst precursors system for comparison.



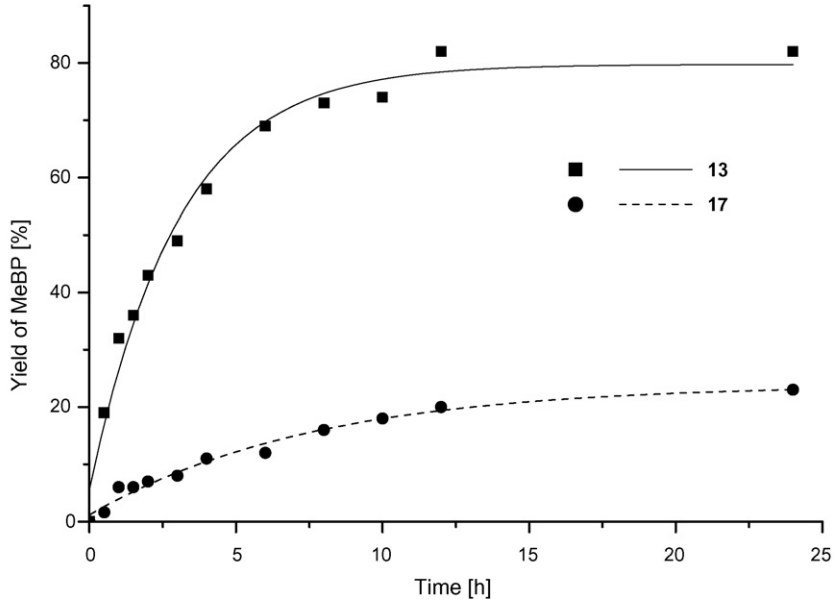


Fig. 5. Conversion growth curves using the catalysts **13** and **17**.

tion of the ligands in terms of their electronic effects as well as higher steric demand should lead to even higher activities.

All the precatalyst mixtures except the one that contained a bis(NHC) complex, **19** (entry 11, Table 3) turned immediately dark upon addition of the Grignard reagent – possibly a sign of reduction and Ni(0) active-catalyst formation. The reaction mixture of **19** remained visibly unchanged and this could be the reason for the very low yield of MeBP (Tables 3 and 4) produced. These observations correspond to those of Herrmann and Böhm [11,12] who also report a mono(carbene)Ni(0) intermediate as the catalytically active species in similar transformations.

4. Conclusion

The simultaneous presence of NHCs and phosphine ligands in complexes of Ni(II) increases both activity and stability of the catalytically active species in the Kumada–Corriu reaction. Our studies demonstrated that this is even more effective for mixed carbene–phosphine complexes with the carbene ligand, derived from chloro-pyridines and chloro-quinolinylidines, being of the NHC- or *r*NHC-type and containing only one N. We could show that these readily prepared new compounds from commercially available precursors are well suited as catalysts for Grignard cross-couplings in terms of both stability and activity. We expect that the new class of ligands will find application in other important catalytic processes as well and they should, individually, be considered as useful alternatives to classical NHCs as we ourselves shall show in future reports. Experiments, like the activation of aryl fluorides in this regard, are underway.

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