Polyhedron 30 (2011) 2051–2054

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Synthesis and use of *trans*-dichlorido-tetrakis-(*N*-R-imidazole)nickel(II) complexes in Kumada–Tamao–Corriu cross-coupling reactions

Neslihan Şahin [a,c], Hani El Moll [a], David Sémeril [a,*], Dominique Matt [a,*], İsmail Özdemir [b], Cemal Kaya [c], Loïc Toupet [d]

[a] *Université de Strasbourg, Laboratoire de Chimie Inorganique et Catalyse, UMR 7177 CNRS, 1 Rue Blaise Pascal, 67008 Strasbourg Cedex, France*
[b] *Department of Chemistry, Faculty of Science and Art, İnönü University, Malatya, TR 44280, Turkey*
[c] *Department of Chemistry, Faculty of Science, Cumhuriyet University, Sivas, TR 58140, Turkey*
[d] *Institut de Physique, UMR 6251 CNRS, Université de Rennes 1, Campus de Beaulieu, 35042-Rennes Cedex, France*

ARTICLE INFO

Article history:
Received 29 March 2011
Accepted 11 May 2011
Available online 18 May 2011

Keywords:
Imidazole ligands
Nickel
Kumada–Tamao–Corriu
Cross-coupling

ABSTRACT

Two dichlorido-tetrakis-(*N*-R-imidazole)nickel(II) complexes (R = 2,6-diisopropylphenyl (**1**); methyl (**2**)) have been synthesised. A single crystal X-ray diffraction study was carried out for **1**, which revealed a centrosymmetric complex with the nickel centre placed in an octahedral coordination environment. Both complexes showed high activities (TOFs up to 60200 mol(ArBr) mol(Ni)$^{-1}$ h^{-1}) in Kumada–Tamao–Corriu cross-coupling of arylhalides with arylgrignards. No significant differences in activity were observed between the two complexes.

1. Introduction

Imidazole ligands are of considerable interest in coordination chemistry. These aromatic five-membered ring systems contain two nitrogen atoms, a “pyridinic” one with an in-plane lone pair allowing metal binding and a trigonal “pyrrole” nitrogen possessing two electrons in an unhybridized orbital. Modification of the substituent of this latter nitrogen atom provides a straightforward way to modulate the steric and electronic properties of the flat pyrazole ligand. Metal ions that have been associated with imidazoles for catalytic purposes include iron, [1,2] ruthenium, [3–7] rhodium, [8] iridium, [8] nickel, [9] palladium [10–17] and copper [18–23]. A rapid survey of the chemical literature revealed that imidazole-based nickel complexes have, to the best of our knowledge, not yet been assessed in Kumada–Tamao–Corriu (KTC) cross-coupling reactions (Scheme 1), that is the coupling between a Grignard reagent and an arylhalide [24–26].

In the present work we describe the synthesis of two dichlorido-tetrakis-(*N*-(R)-imidazole)nickel(II) (R = 2,6-diisopropyl-aryl; R = Me) complexes, which differ essentially in steric bulk, and their utilisation in KTC catalysis. The X-ray structure of one of the complexes (R = 2,6-diisopropyl-aryl) is also reported.

2. Results and discussion

2.1. Synthesis and characterisation of nickel complexes 1 and 2

Complexes **1** and **2** were obtained in high yield from [$NiCl_2py_4$] (py = pyridine) by treatment with the appropriate imidazole ligand (Scheme 2). It is worth mentioning that complex **2** had previously been synthesised by reacting hydrated nickel chloride with four equivalents of *N*-methylimidazole in a mixture of ethanol and 2,2-dimethoxypropane [27]. Elemental analyses of the complexes were in agreement with the presence of four imidazole ligands. The mass spectrum of complex **1** revealed the presence of a strong peak at m/z = 485.34 having the isotopic profile expected for the dicationic species [**1**–2 Cl]$^{2+}$. In keeping with the octahedral geometry of the nickel(II) atom, complexes **1** and **2** exhibited paramagnetic behaviour. We noted that no NMR signals corresponding to hydrogen atoms of the imidazole ring could been seen in the range 0–12 ppm of the ^{1}H NMR spectrum. On the other hand, those belonging to the R substituents, which lie far from the nickel centre, appeared as broad signals.

2.2. X-ray diffraction studies of nickel complex 1

Single crystals of **1** suitable for X-ray diffraction study were obtained by diffusion of hexane into a dichloromethane solution of the complex (Fig. 1). The nickel atom of complex **1** assumes a centrosymmetric, (nearly) octahedral geometry with two axially

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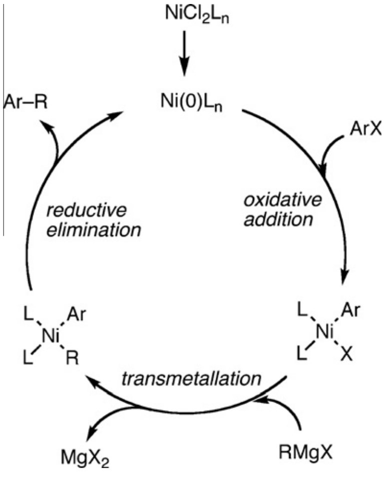
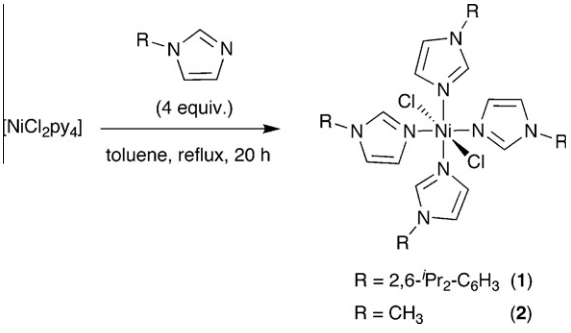
* Corresponding authors. Tel.: +33 368851719.
E-mail addresses: dsemeril@chimie.u-strasbg.fr (D. Sémeril), dmatt@chimie.u-strasbg.fr (D. Matt).

0277-5387/$ - see front matter
doi:10.1016/j.poly.2011.05.009



Scheme 1. Kumada–Tamao–Corriu cross-coupling reaction.



Scheme 2. Synthesis of the nickel complexes **1** and **2**.

located Cl atoms and four equatorial nitrogen atoms. Two *trans*-disposed imidazole rings are orthogonal to the N_4Ni plane. The other two imidazole rings are both inclined by 16.3° with respect to the equatorial plane, thereby minimising the steric interactions between isopropryl groups of adjacent imidazole ligands. The eigth NC(*H*) hydrogen atoms in alpha position to the coordinated N atom are involved in hydrogen bonding with one of the two chlorido atoms (CH···Cl bond lengths lying in the range 2.588–2.788 Å). The Ni–N (2.091(2) and 2.109(2) Å) and Ni–Cl (2.5380 (5) Å) bond lengths are comparable to those found in the recently reported complex dichlorido-tetrakis-(*N*-benzylimidazole)nickel(II) [28].

It is worth mentioning here that the isopropyl groups of paramagnetic **1** appear as two distinct (broad) signals (intensity 1:1), an observation which suggests the existence of a rotational barrier about the Ni–N bonds.

2.3. Utilisation of complexes *1* and *2* in Kumada–Tamao–Corriu cross-coupling

Complexes **1** and **2**, which are both stable in air, were studied in Kumada–Tamao–Corriu cross-coupling reactions. Reaction at 100 °C between 4-bromotoluene and phenylmagnesium bromide using 0.1 mol% of complex **1** led after 3 h to a conversion of 82.9% (Table 1, entry 1). Employing 2-tolylmagnesium chloride increased the reaction rate. For example, 4-bromotoluene was converted in 95.8% after 1 h applying a catalyst loading of 0.01 mol% (Table 1, entry 3). Reducing the amount of complex **1** to 0.001 mol% resulted in a conversion of 60.2%, which corresponds to a TOF of 60200 mol(ArBr) $mol(Ni)^{-1}$ h^{-1} (Table 1, entry 5). With the more sterically hindered 2-bromotoluene, high conversions were observed especially when 2-tolylmagnesium chloride reagent was used (Table 1, entries 7 and 9). Repeating these tests with complex **2** bearing the less encumbered methylimidazole ligand, led to slightly lower conversions. For example, arylations of 2-bromotoluene with 2-tolylmagnesium chloride were achieved in 85.7% and 84.5% yield using 0.01 mol% of complexes **1** and **2**, respectively (Table 1, entries 7 and 8).

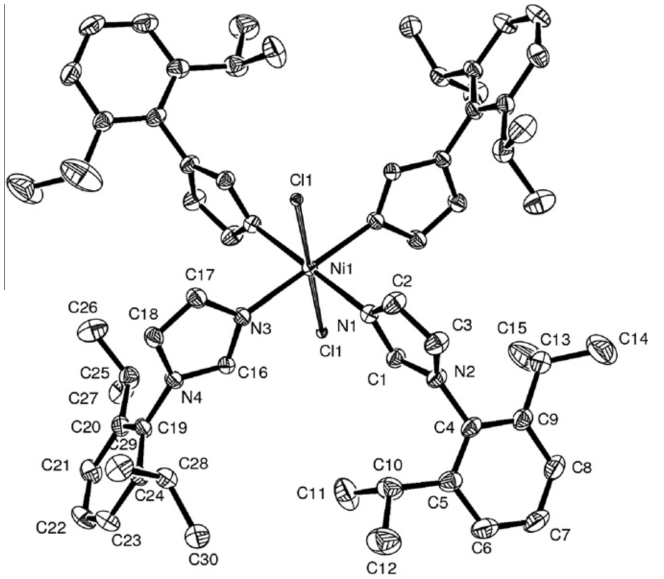


Fig. 1. ORTEP drawing of complex 1. Displacement ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (°): Ni(1)–Cl(1) 2.5380 (5), Ni(1)–N(1) 2.109(2), Ni(1)–N(3) 2.091(2), N(1)–C(1) 1.313(3), N(1)–C(2) 1.379(4), N(2)–C(1) 1.353(3), N(2)–C(3) 1.377(4), C(2)–C(3) 1.360(4); N(1)–Ni(1)–N(1) 180.0, Cl(1)–Ni(1)–Cl(1) 180.0, N(3)–Ni(1)–N(1) 93.72(8) and N(1)–Ni(1)–Cl(1) 89.36(6).

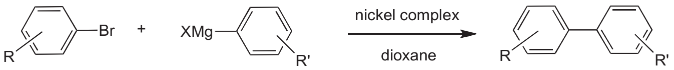
The two nickel complexes were further assessed in the cross-coupling of arylchlorides (Table 2). Using 1 mol% of **1** led to good conversions after 1 h at 100 °C. Thus, 4- and 2-chlorotoluene were converted in 45.2% and 44.1%, respectively, when 2-tolylmagnesium chloride was employed (Table 2, entries 4 and 9). Repeating the runs with the same substrates at room temperature for 24 h, led to conversions of 47.7% and 47.1%, respectively (Table 2, entries 5 and 10). As already observed with arylbromides, arylations carried out with complex **2** gave conversions similar to those obtained with complex **1**. These observations suggest that the substituent of the pyrrolic nitrogen is too far away from the catalytic center to exert any significant influence on the catalytic outcome.

3. Experimental

3.1. General considerations

All reactions were performed in Schlenk-type flasks under dry nitrogen. Solvents were dried by conventional methods and were distilled immediately prior to use. Routine ^1H was recorded with FT Bruker AV-300 spectrometer. ^1H NMR spectra were referenced to residual protiated solvent (7.26 ppm for $CDCl_3$). Chemical shifts and coupling constants are reported in ppm and in Hz, respectively. The catalytic solutions were analysed by using a Varian 3900 gas chromatograph equipped with a WCOT fused-silica column (25 m × 0.25 mm, 0.25 μm film thickness). Elemental analyses were performed by the Service de Microanalyse, Université de Strasbourg. 1-(2,6-diisopropylphenyl)imidazole [29] and $[NiCl_2(pyridine)_4)]$ [30] were prepared according to a literature procedure while 1-(methyl)imidazole was purchased from Sigma–Aldrich. Single crystals of **1** suitable for diffraction study were obtained by diffusion of hexane into a dichloromethane solution of

Table 1
Kumada–Tamao–Corriu cross-coupling of arylbromides using nickel complexes **1** and **2**.



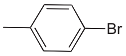
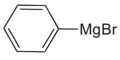
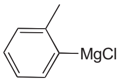
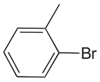
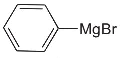
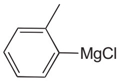
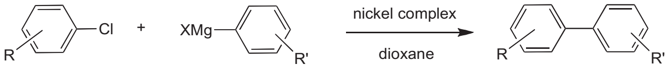
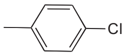
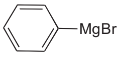
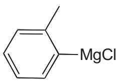
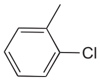
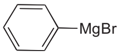
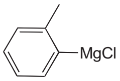
Entry	ArBr	ArMgX	Nickel complex (mol%)	Time (h)	Conversion (%)	Homocoupling (Ar′–Ar′ %)
1			**1** (0.1)	3	82.9	10.8
2			**2** (0.1)	3	73.1	13.6
3			**1** (0.01)	1	95.8	1.8
4			**2** (0.01)	1	91.7	2.1
5			**1** (0.001)	1	60.2	4.0
6			**1** (0.1)	5	51.6	15.6
7			**1** (0.01)	1	85.7	2.8
8			**2** (0.01)	1	84.5	3.2
9			**1** (0.001)	1	53.2	3.5

Table 2
Kumada–Tamao–Curriu cross-coupling of arylchlorides using nickel complexes **1** and **2**.



Entry	ArCl	ArMgX	Nickel complex	T (°C)	Time (h)	Conversion (%)	Homocoupling (Ar′–Ar′ %)
1			**1**	100	1	26.2	17.3
2			**2**	100	1	26.0	15.5
3			**1**	25	24	14.4	16.2
4			**1**	100	1	45.2	6.6
5			**1**	25	24	47.8	6.8
6			**2**	25	24	49.2	5.5
7			**1**	100	1	28.8	14.5
8			**1**	25	24	18.8	19.4
9			**1**	100	1	44.1	6.0
10			**1**	25	24	47.1	5.4
11			**2**	25	24	47.2	5.1

the complex. Formula of the crystals: $C_{30}H_{40}ClN_4Ni_{0.5}$, $Mr = 521.47$, triclinic, space group $\bar{P}$ $a = 8.8698(1)$, $b = 12.5988(3)$, $c = 13.6794(3)$ Å, $\alpha = 75.208$ (2), $\beta = 75.189(1)$, $\gamma = 83.720(2)°$, $V = 1427.30(5)$ Å^3, $Z = 2$, $D_x = 1.213$ mg m^{-3}, λ(MoKα) = 0.71073 Å, $\mu = 0.478$ mm^{-1}, $F(0\,0\,0) = 558$, $T = 130(2)$ K. The sample (0.28 × 0.26 × 0.20) was studied on an Oxford Diffraction Xcalibur Saphir 3 diffractometer with graphite monochromatized MoKα radiation. The data collection (Crysalis, 2004) ($2\theta_{max} = 27°$, omega scan frames *via* 0.7° omega rotation and 30 s per frame, range *hkl*: *h*, −11, 11; *k*, −16,16; *l*, −17,17) gave 18929 reflections. The data led to 5746 independent reflections from which 5049 with $I > 2.0\sigma(I)$ were observed. The structure was solved with SIR-97, [31] which revealed the non-hydrogen atoms of the molecule. After anisotropic refinement many hydrogen atoms were found with a Fourier Difference. The whole structure was refined with SHELX-97 [32] by the full matrix least-square techniques (use of F^2; *x*, *y*, *z*, β_{ij} for C, N, Cl and Ni atoms, *x*, *y*, *z* in riding mode for H atoms; 323 variables and 5049 observations with $I > 2.0\sigma(I)$; calc $w = 1/[\sigma^2(F_o^2) + (0.0691P)^2 + 2.3509P]$ where $P = (F_o^2 + 2F_c^2)/3$ with the resulting $R_1 = 0.0464$, $wR_2 = 0.1305$, $S_w = 1.035$, $\Delta\rho < 1.469$ eÅ^{-3}).

3.2. General procedure for the preparation of nickel complexes **1** and **2**

Imidazole (0.80 mmol) and $[NiC1_2py_4]$ (0.2 mmol) were dissolved in toluene (10 mL). The reaction mixture was refluxed for 20 h. After cooling to room temperature, the grey solution was filtered. The solid recovered was recrystallized in CH_2Cl_2/hexane to afford the desired product as blue–green crystals.

3.2.1. Dichlorido-tetrakis-(N-(2,6-diisopropylphenyl)imidazole)-nickel(II) (**1**)

Yield: 0.152 g (73%). ^1H RMN (300 MHz, $CDCl_3$, in the range 0–12 ppm): $\delta = 8.08$ (s br, 8H, arom. CH), 7.21 (t, 4H, arom. CH, $^3J = 5.8$ Hz), 3.29 (s br, 4H, $CH(CH_3)_2$), 1.41 (s br, 24H, $CH(CH_3)_2$), 1.20 (s br, 24H, $CH(CH_3)_2$). MS (ESI-TOF): $m/z = 777.42$ $[M-C_{15}H_{20}N_2-Cl]^+$, 549.27 $[M-C_{30}H_{40}N_4-Cl]^+$ and 485.34 $[M-2Cl]^{2+}$ (expected isotopic profile). *Anal.* Calc. for $C_{60}H_{80}N_8NiCl_2$: C, 69.10; H, 7.73; N, 10.74. Found: C, 69.03; H, 7.80; N, 10.72%.

3.2.2. Dichlorido-tetrakis-(N-methylimidazole)nickel(II) (**2**)

Yield: 0.071 g (78%). ^1H RMN (300 MHz, $CDCl_3$, in the range 0–12 ppm): $\delta = 4.06$ (s br, 12H, CH_3). *Anal.* Calc. for $C_{16}H_{24}N_8NiCl_2$: C, 41.96; H, 5.28; N, 24.46. Found: C, 42.05; H, 5.11; N, 24.37%.

3.3. General procedure for nickel-catalysed Kumada–Tamao–Corriu cross-coupling reactions

A dioxane solution containing the nickel complex, arylhalide (0.25 mmol), ArMgX (1.0 mmol, solution in THF), decane (0.025 mL, internal reference) and an additional amount of dioxane (so that the total reaction volume was 0.75 mL) were introduced into a Schlenk tube. After each catalytic run, a small amount (0.5 mL) of the solution was passed through a Millipore filter and analyzed by GC. The NMR spectral data of the products formed, 4-methylbiphenyl [33], 2-methylbiphenyl [34], 2,2′-dimethylbiphenyl [35], and 2,4′-dimethylbiphenyl [36] were in agreement with those reported in the literature.

4. Conclusion

We have prepared two octahedral dichlorido-tetrakis-(*N*-R-imidazole)nickel(II) complexes (R = 2,6-diisopropylphenyl (**1**); methyl (**2**)), having their four imidazole ligands located in the equatorial plane. Both complexes turned out to be active in Kumada–Tamao–Corriu cross-coupling of arylbromides, the observed TOFs reaching 60200 mol(ArBr) $mol(Ni)^{-1}$ h^{-1}. The complexes were also efficient in the arylation of deactivated arylchlorides at room temperature, provided 1 mol% of catalyst was used. Further work is aimed at synthesising analogues of complex **1** in which the imidazole substituent bears functional groups able to sterically interact with the metal centre. The reported results constitute the first examples of KTC cross-coupling based on Ni–imidazole complexes.

Acknowledgements

The scientific and technological research of Turkey (TÜBİTAK-BİDEB), International Research Fellowship Programme is gratefully acknowledged for a grant to N.S.

Appendix A. Supplementary data

CCDC 758051 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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