Journal of Organometallic Chemistry 813 (2016) 7–14

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

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

Facile Suzuki-Miyaura coupling of activated aryl halides using new CpNiBr(NHC) complexes

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ARTICLE INFO

Article history:
Received 17 January 2016
Received in revised form
12 March 2016
Accepted 16 March 2016
Available online 17 March 2016

Keywords:
Nickel
N-Heterocyclic carbene
Suzuki-Miyaura coupling

ABSTRACT

Nine new Ni(II)-NHC complexes, [CpNiBr(NHC)], were synthesised from nickelocene and the corresponding symmetric or asymmetric alkyl/-benzyl/phenylethyl imidazolium bromide ligands in relatively high yield. Access to each of the synthesised symmetric or asymmetric alkyl/benzyl/phenylethyl imidazolium bromide salts was obtained through deprotonation of imidazole, followed by treatment with an alkyl- or aryl halide, which is subsequently followed with reaction of a secondary alkyl-, benzyl-, or phenylethyl halide. The series of [CpNiBr(NHC)] exhibited catalytic activity in the Suzuki-Miyaura coupling of activated aryl halides with phenylboronic acid to give the respective biphenyl and biphenyl-containing products. In general, the more electron-donating NHC-bearing Ni complexes showed higher activity with aryl halides bearing electron-withdrawing functionalities including carboxaldehyde moieties. All complexes were characterised by ^{1}H and ^{13}C NMR spectroscopy, FT-IR spectroscopy, CHN and MS analyses, along with six selected single crystal X-ray structures that are reported here.

1. Introduction

N-Heterocyclic carbenes (NHCs) as a class of metal-stabilising "wonder ligands" remain the ligands of choice in many organometallic complexes, with specific application in homogeneous catalysis, organocatalysis, and medicinal chemistry [1–4]. This is mainly due to the support that NHCs provide through the possibility of reliable, predictable, and extensive steric- and electronic tuning [2,3b,5-7] in the design of a model complex with the specific application in mind. With the ever-increasing number of transition metal-NHCs reported, NHC-complexes of Rh [3a,8], Ru [9], Ni [7,10–14], Pd [4a,6b,15,16], Ag [17], and Au [17,18] remain to be the most abundant in literature, noting that Ni-NHC complexes received considerable attention only during the last decade [11,13,14]. The reaction of nickelocene with bis(alkyl/aryl)imidazolium halides to yield the complexes [CpNiX(NHC)] (X = Cl, Br, I), represents one of the most frequently employed and facile routes into cyclopentadienyl nickel(II) NHC systems [7,11–13,19,21,22]. Since the discovery of this atom-economical reaction by Cowley et al. [23] in 2000, the series of substituted [(η^5-C_5R_5)NiX(NHC)] (R = H, Me; X = Cl, Br, I, SPh) complexes has expanded to constitute a relatively well studied class of Ni(II) NHC complexes, predominantly employed in synthetic and catalytic applications [7,11–13,19,21,22].

In homogeneous catalysis, Ni-NHCs occupy an important position in carbon-carbon and carbon-heteroatom organic transformations offering access to an impressive array of valuable molecules which could previously be obtained only *via* expensive Ru and Pd catalysts [10,11b,12,15,19,20,24,25]. In the plethora of C-C coupling reactions, the Suzuki-Miyaura reaction has become one of the most studied for catalytic applications due to its tolerance of functional groups and low toxicity of its by-products [4d,15,19,20a,25,26]. Furthermore, [CpNiX(NHC)] (X = halide) and related systems have provided equal or improved catalytic activity in some C-C coupling reactions when compared to the traditional Pd catalysts [10,12,20,25,27]. In spite of this, the bromo complexes in the series of [CpNiBr(NHC)] compounds reported are few when compared to their chloro- and iodo-analogues [10,19]. The known [CpNiBr(NHC)] complexes (NHC = imidazolium backbone) reported to date have been illustrated in Fig. 1.

In this study, we expand the existing bromide series by reporting nine novel [CpNiBr(NHC)] complexes, where both symmetric- and asymmetric NHC ligands are employed. All new complexes synthesised were characterised, and their catalytic activity

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http://dx.doi.org/10.1016/j.jorganchem.2016.03.017
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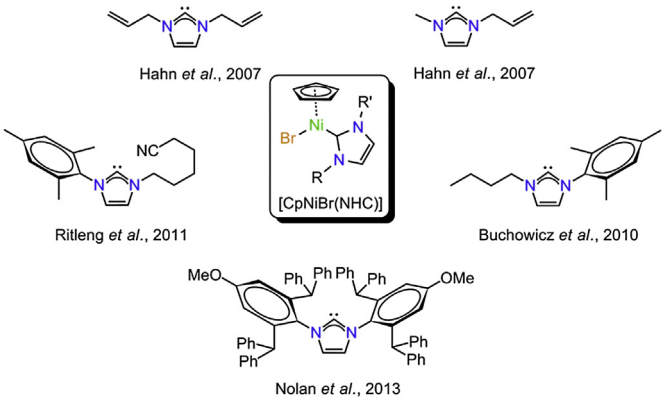

Fig. 1. Known [CpNiBr(NHC)] complexes reported by various groups [5a,11e,12,21,22b].

evaluated in the Suzuki-Miyaura (SM) coupling reaction using activated aryl chlorides and bromides. One of these substrates, 4-chlorobenzaldehyde, bearing an electron-withdrawing functional group, has to date not been fully investigated previously as a substrate in [CpNiX(NHC)] (X = halide) catalysed SM reactions.

2. Material and methods

2.1. General

All experiments were carried out under an argon atmosphere using standard Schlenk techniques. Solvents were dried prior to use using standard techniques [28]. Column chromatography was carried out under inert argon atmospheres using silica gel (particle size 0.063–0.200 mm) as the stationary phase. The imidazolium bromide ligands **L1** – **L9** (Fig. 2) with general formula [HImRR′]Br with R, R′ = Me, Bn, $(CH_2)_2$Ph, 4-NO_2Bn were synthesised and purified according to literature procedures [2,13,14,19,21]. NMR characterisation confirmed the molecular structures of the synthesised ligands (see Supplementary Information for data), which correlated with literature data. All other chemicals were purchased from Sigma-Aldrich and used without further purification. ^{1}H (300 MHz) and ^{13}C{H} (76 MHz) NMR spectra were recorded on a Bruker ARX-300 spectrometer using either $CDCl_3$, or $(CD_3)_2CO$ solutions. All measurements were performed at ambient temperature (~296 K), unless otherwise noted. Chemical shifts were referenced to the internal residual protio solvent impurity at δ_H 7.24 ($CDCl_3$) or 2.04 ($(CD_3)_2CO$); or carbon signals at δ_C 77.0 ($CDCl_3$), or 29.8 and 206.3 ppm ($(CD_3)_2CO$). Solid state FT-IR experiments were carried out on a Perkin Elmer Spectrum RXI FT-IR spectrometer as pressed KBr pellets in air. Microanalytical analyses (%CHNS) were obtained using a Thermo Scientific Flash 2000 elemental analyzer fitted with a TCD detector. All GC/MS analyses were carried out on a Hewlett Packard (HP) GC 1530A coupled to an Agilent 5975C mass selective detector (MSD). MS (ESI) and MS/MS measurements were performed on a Waters SYNAPT G2 LC-MS spectrometer.

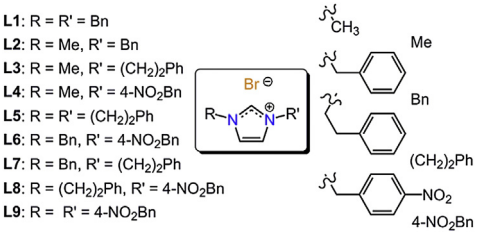

Fig. 2. R and R′ groups employed in ligands **L1** – **L9**.

2.2. General synthesis of [CpNiBr(NHC)] complexes (**1**–**9**)

A suspension of the alkyl/benzyl/phenylethyl imidazolium bromide (3 mmol) in THF (10 mL) with $[Ni(C_5H_5)_2]$ (0.57 g, 3 mmol) was heated under reflux between 3 and 16 h (depending on the NHC ligand). The reaction mixture was concentrated *in vacuo*, and purified by silica gel column chromatography, using gradient elution with hexane and dichloromethane. Red to red-brown powders were obtained in relatively high yields.

*[CpNiBr{*Im(*Bn*)$_2$*}]* (**1**): Yield: 79%. IR (cm^{-1}): 3168 (ν(=CH), w), 3136 (ν(=CH), w), 3110 (ν(=CH), w), 3028 (ν(-CH), w), 2929 (ν(-CH), w), 1569 (ν(=CH), w), 1495 (δ(-CH), *sym*, m), 1453 (δ(-CH), *sym*, s), 1430 (δ(-CH), *asym*, m), 1404 (δ(-CH), *asym*, s), 1358 (δ(-CH), s), 1230 (ν(-CN), s), 1028 (ν(CN), w), 794 (δ(=CH), s), 755 (s), 725 (δ(-CH), s), 715 (s), 685 (s). ^{1}H NMR ($CDCl_3$, δ_H) 5.12 (s, C_5H_5, 5H), 6.09 (dd, $^2J_{HH}$ = 15 and 65 Hz, CH_2, 4H), 6.79 (s, NC*H*, 2H), 7.26–7.40 (m, C_6H_5, 10H). ^{13}C{^{1}H}-NMR ($CDCl_3$, δ_C) 55.6 (s, CH_2), 91.7 (s, C_5H_5), 122.8 (s, N*C*H), 127.3 (s, C_6H_5), 127.6 (s, C_6H_5), 128.0 (s, C_6H_5), 128.2 (s, C_6H_5), 128.8 (s, C_6H_5) 129.2 (s, C_6H_5), 136.3 (s, *ipso*-C_6H_5), 166.9 (s, N*C*N). CHN (%): [$C_{22}H_{21}BrN_2Ni$]: C, 58.16 (58.46), H, 4.68 (4.68), N, 5.91 (6.20). MS (ESI): *m*/*z* 452.02 (M^+).

*[CpNiBr{*Im(*Me*)(*Bn*)*}]* (**2**): Yield: 77%. IR (cm^{-1}): 3168 (ν(=CH), w), 3132 (ν(=CH), w), 3104 (ν(=CH), w), 3053 (ν(-CH), w), 3029 (ν(-CH), w), 2924 (ν(-CH), w), 1564 (ν(=CH), w), 1518 (δ(-CH), *sym*, m), 1495 (δ(-CH), *sym*, m), 1454 (δ(-CH), *sym*, s), 1430 (δ(-CH), *asym*, m), 1404 (δ(-CH), *asym*, s), 1340 (δ(-CH), s), 1230 (ν(-CN), s), 1076 (ν(CN), w), 788 (δ(=CH), s), 725 (δ(-CH), s), 714 (s), 685 (s). ^{1}H NMR ($CDCl_3$, δ_H) 4.25 (s, CH_3, 3H), 5.16 (s, C_5H_5, 5H), 5.99 (d, $^2J_{HH}$ = 49 Hz, CH_2, 2H), 6.82 (d, $^3J_{HH}$ = 48 Hz, NC*H*, 2H), 7.20–7.31 (m, C_6H_5, 5H). ^{13}C{^{1}H}-NMR ($CDCl_3$, δ_C) 38.8 (s, CH_3), 55.1 (s, CH_2), 91.2 (s, C_5H_5), 121.9 (s, {Me}NCH), 123.6 (s, {Bn}NCH), 127.3 (s, C_6H_5), 127.6 (s, C_6H_5), 128.4 (s, C_6H_5), 136.0 (s, *ipso*-C_6H_5), 161.8 (s, N*C*N). CHN (%): [$C_{16}H_{17}BrN_2Ni$]: C, 50.96 (51.12), H, 4.31 (4.56), N, 7.75 (7.45). MS (ESI): *m*/*z* 375.99 (M^+).

*[CpNiBr{*Im(*Me*)((*CH*$_2$)$_2$*Ph*)*}]* (**3**): Yield: 74%. IR (cm^{-1}): 3156 (ν(=CH), w), 3124 (ν(=CH), w), 3100 (ν(=CH), w), 3054 (ν(-CH), w), 2922 (ν(-CH), w), 1604 (ν(=CH), s), 1519 (δ(-CH), *sym*, s), 1492 (δ(-CH), *sym*, m), 1460 (δ(-CH), *sym*, s), 1408 (δ(-CH), *asym*, s), 1339 (δ(-CH), s), 1233 (ν(-CN), s), 1081 (ν(CN), w), 786 (δ(=CH), s), 727 (δ(-CH), s), 714 (s), 697 (s). ^{1}H NMR ({CD_3}$_2$CO, δ_H) 3.41 (br s, NCH_2, 2H), 4.28 (s, CH_3, 3H), 4.95 (d, $^3J_{HH}$ = 29 Hz, $CH_2C_6H_5$, 2H), 5.20 (s, C_5H_5, 5H), 7.13 (s, NC*H*, 1H), 7.20 (s, NC*H*, 1H), 7.23–7.38 (m, C_6H_5, 5H). ^{13}C{^{1}H}-NMR ({CD_3}$_2$CO, δ_C) 37.7 (s, CH_3), 39.1 (s, NCH_2), 53.9 (s, $CH_2C_6H_5$), 92.0 (s, C_5H_5), 123.4 (s, {Me}NCH), 124.5 (s, {PhEt}NCH), 127.3 (s, C_6H_5), 127.6 (s, C_6H_5), 129.3 (s, C_6H_5), 129.9 (s, C_6H_5), 139.7 (s, *ipso*-C_6H_5), 161.3 (s, N*C*N). CHN (%): [$C_{17}H_{19}BrN_2Ni$]: C, 52.49 (52.36), H, 4.58 (4.91), N, 6.90 (7.18). MS (ESI): *m*/*z* 388.19 (M^+).

*[CpNiBr{*Im(*Me*)(*4-NO*$_2$*Bn*)*}]* (**4**): Yield: 69%. IR (cm^{-1}): 3168 (ν(=CH), w), 3132 (ν(=CH), w), 3109 (ν(=CH), w), 3053 (ν(-CH), w), 2929 (ν(-CH), w), 1674 (ν(NO), *asym*, m), 1516 (δ(-CH), *sym*, s), 1454 (δ(-CH), *sym*, s), 1430 (δ(-CH), *asym*, m), 1404 (δ(-CH), *asym*, s), 1344 (δ(-CH), s), 1230 (ν(-CN), s), 1166 (ν(NO), *sym*, m), 1108 (m), 1013 (ν(CN), w), 858 (m), 795 (δ(=CH), s), 726 (δ(-CH), s), 715 (s), 685 (s). ^{1}H NMR ($CDCl_3$, δ_H) 4.30 (s, CH_3, 3H), 5.19 (s, C_5H_5, 5H), 6.16 (d, $^2J_{HH}$ = 39 Hz, CH_2, 2H), 6.89 (d, $^3J_{HH}$ = 55 Hz, NC*H*, 2H), 7.46 (s, C_6H_4, 2H), 8.22 (s, C_6H_4 adjacent to NO_2, 2H). ^{13}C{^{1}H}-NMR ($CDCl_3$, δ_C) 25.6 (s, CH_3), 39.3 (s, CH_2), 91.8 (s, C_5H_5), 122.2 (s, {Me}NCH), 124.2 (s, C_6H_4), 124.6 (s, {4-NO_2Bn}NCH), 128.6 (s, C_6H_4 adjacent to NO_2), 143.8 (s, *ipso*-C_6H_4), 147.8 (s, *ipso*-C_6H_4 containing NO_2), 164.8 (s, N*C*N). CHN (%): [$C_{16}H_{16}BrN_3NiO_2$]: C, 45.64 (45.66), H, 3.52 (3.83), N, 9.61 (9.98). MS (ESI): *m*/*z* 418.98 (M^+).

*[CpNiBr{*Im((*CH*$_2$)$_2$*Ph*)$_2$*}]* (**5**): Yield: 71%. IR (cm^{-1}): 3120 (ν(=CH), w), 3101 (ν(=CH), w), 3048 (ν(-CH), w), 2922 (ν(-CH), w),