# Polyhedron 30 (2011) 1091-1094

Contents lists available at ScienceDirect

# Polyhedron

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

# Synthesis, characterization and application of pincer-type nickel iminophosphinite complexes

Jessica Sanford<sup>a</sup>, Catlin Dent<sup>a</sup>, Jason D. Masuda<sup>b</sup>, Aibing Xia<sup>a,\*</sup>

<sup>a</sup> Department of Chemistry, Mount Saint Vincent University, Halifax, Nova Scotia, Canada B3M 2J6 <sup>b</sup> The Maritimes Centre for Green Chemistry and The Department of Chemistry, Saint Mary's University, Halifax, NS, Canada B3H 3C3

# ARTICLE INFO

Article history: Received 1 November 2010 Accepted 11 January 2011 Available online 25 January 2011

Keywords: Nickel complexes Pincer types Unsymmetrical ligands Iminophosphinites Cross-coupling reactions The Kumada reaction

# ABSTRACT

Two pincer-type nickel iminophosphinite complexes,  $[(2-(CH=NR)-6-(OPR'_2)C_6H_3)NiCl]$  (R = 2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, R' = Ph (**2a**) or <sup>i</sup>Pr (**2b**)), were synthesized from the reactions of bis(1,5-cyclooctadiene)nickel(0) and corresponding iminophosphinite ligands. The solid state structures of the nickel pincer complexes were determined by X-ray single crystal diffraction studies. They were successfully employed in the Kumada reaction of non-activated aryl chlorides and phenylmagnesium bromide at room temperature. © 2011 Elsevier Ltd. All rights reserved.

#### 1. Introduction

The chemistry of pincer-type transition metal complexes has seen tremendous development over the past decade [1–5]. The pincer ligand systems are relatively easy to access and modify with desirable electronic and steric features. Pincer-type nickel complexes have attracted considerable attention in recent years due to their catalytic and electrochemical properties. They have been used as (pre)catalysts in a variety of organic transformations such as cross-coupling reactions [6-15] and olefin oligomerization reactions [16,17]. The strong donating groups of pincer ligands have been shown to lower the Ni(III)/Ni(II) reduction potential, leading to more effective catalysts [18-23]. While early reported nickel pincer complexes have been predominantly based on symmetrical pincer types such as bisphosphine (PCP) and bisamine (NCN), nickel complexes based on unsymmetrical ligand types have attracted increasing interest recently [12,15,19,24]. Here we wish to report two novel nickel complexes bearing unsymmetrical PCN-type iminophosphinite pincer ligands. The nickel complexes were easy to prepare and air-stable and have been employed successfully in Kumada reactions of non-activated aryl chlorides.

# 2. Results and discussion

# 2.1. Synthesis

We have recently reported the synthesis and catalytic application of a series of palladium complexes based on novel iminophosphinite ligands that were derived from 2-bromo-hydroxybenzaldehyde [25]. The pincer-type iminophosphinite ligands were easy to prepare and modify and could readily form complexes with palladium(0) or palladium(II) precursors [26]. In a fashion similar to the preparation of palladium iminophosphinite complexes, the analogous nickel complexes were prepared in simple steps. The synthetic route of the nickel complexes is outlined in Scheme 1. Condensation of commercially available 2-chloro-3hydroxybenzaldehyde and 2,6-diisopropylaniline in refluxing ethanol afforded the corresponding imine (1), which reacted readily with diphenylchlorophosphine or diisopropylchlorophosphine in the presence of 4-*N*,*N*-dimethylaminopyridine (DMAP). The resultant iminophosphinites were used without further purification to react with bis(1,5-cyclooctadiene)nickel(0), Ni(COD)<sub>2</sub>, at room temperature to give the desired nickel iminophosphinite pincer complexes (2a and 2b) in good yields. Both nickel complexes are air- and moisture-stable and can be recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/ hexane in the air. They are thermally robust and melt without decomposition at well over 200 °C. They have been fully characterized using NMR and FT-IT spectroscopic methods and X-ray single crystal analysis. Their elemental analysis results matched well with expected values.





<sup>\*</sup> Corresponding author. Tel.: +1 902 457 6543; fax: +1 902 457 6656. *E-mail address:* aibing.xia@msvu.ca (A. Xia).

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Scheme 1. Synthesis of pincer-type iminophosphinite nickel complexes.

#### 2.2. Characterization

The <sup>1</sup>H NMR spectra of imine **1** showed single resonance at 8.60 ppm for the proton of the imine (CH=N) group and 5.79 ppm for the proton of O–H group. Its IR spectrum showed strong absorption at 1631 cm<sup>-1</sup>, which is typical for the C=N function group. Both nickel iminophosphinite pincer complexes (**2a** and **2b**) are diamagnetic. Their <sup>1</sup>H NMR spectra showed upfield chemical shifts of the imine group to 7.98 and 7.95 ppm. The methyl groups in the isopropylphenyl moieties in the complexes split to two signals, compared to a single signal of those groups in the free imine **1**. The methyl groups in the isopropylphosphenyl group showed couplings with phosphorus ( $J_{PH}$  = 18.2 Hz) and adjacent hydrogen atoms ( $J_{HH}$  = 6.9 Hz). The <sup>31</sup>P NMR signals of the complexes are 200 and 148 ppm, respectively. The IR spectra of the iminophosphinite complexes showed red-shifts of the imine C=N stretch to 1577 and 1574 cm<sup>-1</sup>, for **2a** and **2b**, respectively.

Suitable crystals of **2a** and **2b** for X-ray analysis were grown from saturated solutions of dichloromethane and hexane at -10 °C. The molecular structures of the complexes were almost identical. A representative structure of **2b** is shown in Fig. 1. The structure of **2a** is included in the Supplementary data. Selected bond distances and angles for **2b** are listed in Table 1. Crystal data and structure refinement data for **2a** and **2b** are listed in Table 2. In the solid state of **2b**, the complex exists as a monomer, with Ni(II) ion adopting a distorted square-planar geometry. The bond angle of P–Ni–N is about 163°, suggesting significant strain in the core. The bond lengths for Ni–C (1.847 Å), Ni–N (1.986 Å), Ni–P (2.110 Å), and Ni–Cl (2.186 Å) are comparable to the reported values in related nickel complexes [19,24,27].

# 2.3. Catalytic studies

The nickel pincer complexes were evaluated in the Kumada reaction, which is of significant importance among the crosscoupling reactions because of its relative early discovery and important applications. The Kumada reaction was initially effected by nickel complexes [28], but their efficiencies have since been surpassed by more active palladium catalysts. However, there is continuing interest in the nickel catalysts due to their low cost and good activity. Recently important progress has been made in the nickel-catalyzed coupling of non-activated aryl chlorides, which are more desirable than the more reactive yet more expensive aryl bromides and iodides [7–10,12,13,15]. We chose 4-chlorotoluene, a neutral aryl chloride, and 4-chloroanisole, a deactivated aryl chloride as the organic substrates to react with phenylmagnesium bromide in THF at room temperature. Under 2 mol% nickel complex loading, **2a** gave modest conversion (~70%) for both aryl chlorides (Table 3, entries 1 and 3). However, **2b** gave near complete conversion (~99%) for the aryl chlorides (Table 3, entries 2 and 4). In all cases, the unsymmetrical biphenyls are the major products while the symmetrical biphenyls are minor biproducts. The improved efficiency of **2b** over **2a** may be attributed to better donating ability of the diisopropylphosphino group than that of the diphenylphosphino group.

#### 2.4. Conclusion

In summary, we have synthesized and characterized two novel iminophosphinite pincer nickel complexes. The diisopropylphosphinite complex was found to be very efficient in the Kumada coupling reaction of 4-chlorotoluene and 4-chloroanisole at room temperature. The nickel complexes were prepared in good yields under mild conditions and are air-stable and thermally robust, making them attractive candidates in catalytic studies. We are working to expand the scope of the novel complexes in other cross-coupling reactions. The results will be reported in due course.

# 3. Experimental

## 3.1. General procedures

All manipulations were performed under an argon atmosphere unless otherwise specified. All anhydrous solvents were purchased from Sigma–Aldrich Canada Ltd. and stored over 4 Å molecular sieves prior to use. Diphenylchlorophosphine, diisopropylchlorophosphine, 2-chloro-3-hydroxybenzaldehyde, 4-*N*,*N*-dimethylaminopyridine, and authentic biphenyl samples were purchased from Sigma–Aldrich Canada Ltd. and used as received. <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR spectra were recorded on a Bruker AV-500 spectrometer. The chemical shifts of <sup>1</sup>H and <sup>13</sup>C NMR spectra were referenced internally to the solvent signals. The chemical shifts of <sup>31</sup>P NMR spectra were referenced to an external standard using 85% H<sub>3</sub>PO<sub>4</sub>. Infrared spectra were collected on a Nicolet Avatar 330 FT-IR spectrometer. Elemental analyses were carried out by Guelph



Fig. 1. Molecular structure of 2b with 30% probability ellipsoids. Hydrogen atoms have been omitted for clarity.

Table 1	
Selected bond lengths (Å) and angles (°	) for <b>2b</b> .

Ni1-C7 Ni1-N1 Ni1-P1 Ni1-Cl1 C7-Ni1-N1 C7-Ni1-P1 N1-Ni1-P1 P1-Ni1-Cl1	1.847(3) 1.986(2) 2.1100(8) 2.1865(9) 82.55(10) 80.68(8) 163.15(7) 97.19(3)
N1-Ni1-P1	163.15(7)
PI-NII-CII C7-Ni1-Cl1 N1-Ni1-Cl1	97.19(3) 174.29(8) 99.67(7)

Table 2	
Crystal data and structure refinement for <b>2a</b> and I	2b.

	2a	2b
CCDC number	796787	796788
Formula	C <sub>31</sub> H <sub>31</sub> CINNiOP	C25H35CINNiOP
Formula weight	558.70	490.67
T (K)	296(2)	296(2)
Space group	P2(1)/n	P2(1)/c
a (Å)	9.197(1)	15.7468(7)
b (Å)	21.302(3)	9.8897(5)
<i>c</i> (Å)	14.281(2)	16.5849(8)
α (°)	90	90
β (°)	93.174(2)	94.100(1)
γ (°)	90	90
$V(Å^3)$	2793.6(7)	2576.2(2)
Ζ	4	4
$D_{\text{calc}}$ (g/cm <sup>3</sup> )	1.328	1.265
$\mu (\mathrm{mm}^{-1})$	0.871	0.935
F(0 0 0)	1168	1040
$\theta$ for Data collection (°)	2.39-25.00	1.30-25.00
No. of total reflections	18 245	16 658
No. of unique reflections	4862	4526
$R_1 \left[ I > 2\sigma(I) \right]$	0.0265	0.0356
$wR_2 [I > 2\sigma(I)]$	0.0677	0.0800
R <sub>1</sub> [all data]	0.0324	0.0575
wR <sub>2</sub> [all data]	0.0723	0.0924

# Table 3

Kumada coupling reactions of aryl chlorides<sup>a</sup>.



 $^{\rm a}\,$  1.0 mmol Aryl chloride, 1.5 mmol PhMgBr, 2 mol% nickel complex, 2 mL THF, room temperature, 22 h.

<sup>b</sup> GC yields based on unreacted aryl chlorides, average of two runs.

<sup>c</sup> Calibrated with authentic biphenyl samples.

Chemical Laboratories in Guelph, Ontario. Melting points were recorded on a Mel-Temp (Electrothermal) Apparatus and were uncorrected.

# 3.2. Synthesis

# 3.2.1. Synthesis of the imine (1)

2-Chloro-3-[(2,6-diisopropyl-phenylimino)methyl]phenol (1): 2-chloro-3-hydroxybenzaldehyde (3.13 g, 20.0 mmol) and 2,6diisopropylaniline (3.54 g, 20.0 mmol) were dissolved in 30 mL ethanol. Formic acid (10 drops) was added to the solution. The resultant yellow solution was refluxed with stirring for 48 h. After being cooled to room temperature, the reaction mixture was dried over anhydrous MgSO<sub>4</sub> and filtered. The filtrate was concentrated to dryness under reduced pressure, affording a yellow oil, which was recrystallized from hexanes to give the pale yellow solid **1**. Yield: 4.61 g (73%). M.p. 132–133 °C. *Anal.* Calc. for C<sub>19</sub>H<sub>22</sub>ClNO: C, 72.25; H, 7.02; N, 4.43. Found: C, 71.92; H, 7.17; N, 4.38%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500.13 MHz, ppm):  $\delta$  8.60 (s, 1H, CH=N), 7.87–7.82 (dd, *J* = 8.0, 1.6 Hz, 1H, Ar-H), 7.34 (t, *J* = 8.0 Hz, Ar-H), 7.20–7.13 (m, 4H, Ar-H), 5.79 (broad, 1H, OH), 2.97 (sept, *J* = 6.9 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 1.21 (d, *J* = 6.9 Hz, CH(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125.77 MHz, ppm):  $\delta$  158.95, 151.72, 148.87, 137.57, 133.41, 128.04, 121.63, 124.47, 123.09, 120.25, 118.57, 27.94, 23.51. IR (KBr, cm<sup>-1</sup>): *v* 3356(s), 2959(s), 2866(m), 1631(s), 1572(s), 1464(s), 1364(m), 1289(s), 1182(m), 1047(m), 780(s), 753(s), 708(m).

# 3.2.2. Synthesis of nickel pincer complexes, $[(2-(CH=NR)-6-(OPR'_2)-C_6H_3)NiCl]$ ( $R = 2,6^{-i}Pr_2C_6H_3$ )

General procedure: **1** (0.316 g, 1.00 mmol) and 4-*N*,*N*-dimethylaminopyridine (0.122 g, 1.00 mmol) were dissolved in THF (10 mL). To the solution was added diphenylchlorophosphine or diisopropylchlorophosphine (1.00 mmol) in THF (5 mL). The resultant mixture was stirred for 17 h at room temperature and filtered. To the filtrate was added bis(cyclooctadiene)nickel(0) (0.275 g, 1.00 mmol). The mixture was stirred under argon for 24 h. The volatiles were removed under reduced pressure to afford orange solids, which were washed with hexane (5 mL). The crude products were recrystallized from  $CH_2Cl_2$ /hexanes to afford the pure nickel complexes.

# 3.2.3. **2a**

R' = Ph: yield: 0.350 g (63%). M.p.: 269–270 °C. *Anal.* Calc. for C<sub>31</sub>H<sub>31</sub>ClNNiOP: C, 66.64; H, 5.59; N, 2.51. Found: C, 66.87; H, 5.85; N, 2.52%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500.13 MHz, ppm): δ 8.07 (m, 4H, Ar-H), 7.98 (d, *J* = 4.4 Hz, 1H, CH=N), 7.54–7.45 (m, 6H, Ar-H), 7.27–7.11 (m, 6H, Ar-H), 6.88 (m, 1H, Ar-H), 3.47 (sept, *J* = 6.9 Hz, 2H, *CH*(CH<sub>3</sub>)<sub>2</sub>), 1.39 (d, *J* = 6.9 Hz, 6H, CH(CH<sub>3</sub>)'(CH<sub>3</sub>)''), 1.18 (CDCl<sub>3</sub>, 125.77 MHz, ppm): δ 141.06, 131.93, 128.62, 122.95, 28.77, 24.34, 22.96 (some peaks not shown due to low solubility). <sup>31</sup>P NMR (CDCl<sub>3</sub>, 202.47 MHz, ppm): δ 199.94. IR (KBr, cm<sup>-1</sup>): v 2957(m), 1577(m), 1459(m), 1416(m), 1349(w), 1229(s), 1107(s), 1041(m), 875(m), 739(s), 687(s), 556(m), 478(m).

## 3.2.4. **2b**

R' = <sup>i</sup>Pr: yield: 0.410 g (84%). M.p. 237–239 °C. *Anal.* Calc. for C<sub>25</sub>H<sub>35</sub>ClNNiOP: C, 61.20; H, 7.19; N, 2.85. Found: C, 61.41; H, 7.32; N, 2.87%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500.13 MHz, ppm): δ 7.95 (d, *J* = 4.2 Hz, 1H, CH=N), 7.25–7.22 (m, 1H, Ar-H), 7.17–7.15 (m, 2H, Ar-H), 7.08 (m, 2H, Ar-H), 6.73 (m, 1H, Ar-H), 3.42 (sept, *J* = 6.9 Hz, 2H, Ar-CH(CH<sub>3</sub>)<sub>2</sub>), 2.39 (sept, *J* = 6.9 Hz, 2H, PCH(CH<sub>3</sub>)<sub>2</sub>), 1.51–1.46 (dd, 6H, *J* = 18.2, 6.9 Hz, PCH(CH<sub>3</sub>)'(CH<sub>3</sub>)''), 1.41–1.37 (m, 12H, overlapping PCH(CH<sub>3</sub>)'(CH<sub>3</sub>)'' and Ar-CH(CH<sub>3</sub>)'(CH<sub>3</sub>)''), 1.20 (d, *J* = 6.9 Hz, 6H, Ar-CH(CH<sub>3</sub>)'(CH<sub>3</sub>)''). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125.77 MHz, ppm): δ 172.47, 165.81, 147.10, 144.15, 140.88, 126.73, 126.36, 122.84, 121.46, 113.45, 113.33, 28.76, 28.21, 28.03, 24.13, 23.04, 16.67. <sup>31</sup>P NMR (CDCl<sub>3</sub>, 202.47 MHz, ppm): δ 148.13. IR (KBr, cm<sup>-1</sup>): ν 2962(s), 2867(m), 1574(m), 1541(s), 1466(s), 1351(m), 1215(s), 1180(m), 1045(m), 802(s), 748(s), 666(m).

# 3.3. General procedures for the Kumada reaction

A 25 mL Schlenk flask was charged with 4-chlorotoluene or 4chloroanisole (1.0 mmol), the nickel pincer complex **2a** or **2b** (0.020 mmol), and 2 mL THF. To the solution was added phenylmagnesium bromide (1.5 mmol) in THF. The mixture was stirred for 18 h at room temperature under argon. The reaction was quenched using 10 mL H<sub>2</sub>O and the reaction mixture was washed with diethyl ether. The combined organic layer was dried with MgSO<sub>4</sub> and filtered. The volatiles were removed under reduced pressure. The organic products were analyzed on an Agilent 6890 GC-FID instrument. The conversions and product ratios were calibrated relative to standards containing authentic samples of aryl halides and their biphenyl products.

# 3.4. X-ray structures

Crystals of **2a** and **2b** were grown by recrystallization methods using dichloromethane and hexanes as solvents at room temperature. Single crystals were mounted in thin-walled capillaries. The data were collected using the Bruker APEX2 software [29] package on a Siemens diffractometer equipped with an APEXII CCD detector, a graphite monochromator and Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). A hemisphere of data was collected in 1664 frames with 10 s exposure times. Data processing and absorption corrections were applied using APEX2 software package. The structure was solved (direct methods) and all non-H atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions using an appropriate riding model and coupled isotropic temperature factors. Thermal ellipsoid diagrams (30% probability level) were produced using Ortep-3 for Windows [30].

# Acknowledgements

We thank Natural Science and Engineering Research Council of Canada (NSERC) and Canada Foundation for Innovation (CFI) for financial supports.

# Appendix A. Supplementary data

CCDC 796787 and 796788 contain the supplementary crystallographic data for **2a** and **2b**. 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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