

Synthesis and structural characterization of aryloxo-functionalized N-heterocyclic carbene complexes of nickel(II)

Wan-Fei Li, Hong-Mei Sun, Zhi-Guo Wang, Mu-Zi Chen, Qi Shen *, Yong Zhang

The Key Laboratory of Organic Synthesis of Jiangsu Province, College of Chemistry and Chemical Engineering, Suzhou University, Suzhou 215006, China

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Abstract

The reaction of $\text{Ni}(\text{PPh}_3)_2\text{Br}_2$ with two equivalents of anionic aryloxo-functionalized N-heterocyclic carbene $[\text{NaO-4,6-di-}^t\text{Bu-C}_6\text{H}_2\text{-2-CH}_2\{\text{C}(\text{NCHCHNR})\}]$ ($\text{R} = ^i\text{Pr}$, NaL^1 ; $\text{R} = \text{Bz}$, NaL^2), which are generated in situ by the reaction of the corresponding salt H_2LCl with two equivalents of $\text{NaN}(\text{SiMe}_3)_2$, affords bis-ligand complexes of L_2^1Ni (**3**) and L_2^2Ni (**4**) in good yield, respectively. It is interesting to note that still the bis-ligand one not the mono-ligand $\text{Ni}(\text{II})$ halide is obtained, even the molar ratio of NaL^1 or NaL^2 to $\text{Ni}(\text{PPh}_3)_2\text{Br}_2$ is changed to 1:1. Complexes of **3** and **4** have been fully characterized including the X-ray structure determination. The structural analysis shows that each nickel atom in **3** or **4** is bonded to two bidentate ligands L^1 or L^2 , respectively, in a *cis* arrangement.

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Keywords: Functionalized N-heterocyclic carbene; Bidentate ligand; Nickel

1. Introduction

In recent years, tremendous efforts have been made towards the synthesis of transition metal complexes containing N-heterocyclic carbene (NHC) ligands [1]. N-heterocyclic carbenes (NHCs), as appealing alternatives to traditional phosphine ligands, have been widely used in organometallic chemistry due to their strong donor properties, easily tuned in electronic and steric effect by the diversity of nitrogen substituents, and the excellent catalytic behavior of their metal complexes in homogeneous catalysts [2]. The key point for new NHCs recently has been paid to the designation of the functionalized NHCs, since the introduction of pendant functional group to an NHC could result both in diverse metal complexes, and in an opportunity to better control the stability of active centers in catalytic reactions [3]. Recently, the anionic functionalized group, i.e., anionic amido, aryloxo, alkoxo-

tethered NHCs, have been designed and successfully applied in the synthesis of organometallic complexes, especially the early transition metal and lanthanide element complexes, in which the anionic group acts as an anchor and the tendency for ligand dissociation would be reduced efficiently [4].

NHCs becomes an important ligand in organometallic chemistry of nickel, several kinds of $\text{Ni}(\text{II})$ NHC complexes have been synthesized and some of them are excellent precatalysts in organic reactions. However, no examples to date of $\text{Ni}(\text{II})$ complex with an anionic functionalized NHC is reported. In view of the lack of such kind of $\text{Ni}(\text{II})$ complexes, the bidentate aryloxo-functionalized NHC precursor $[\text{HO-4,6-di-}^t\text{Bu-C}_6\text{H}_2\text{-2-CH}_2\{\text{CH}(\text{NCHCHN}^i\text{Pr})\}]\text{-Cl}$ ($^i\text{Pr} = \text{CH}(\text{CH}_3)_2$, $\text{H}_2\text{L}^1\text{Cl}$, **1**) and its analogue $[\text{HO-4,6-di-}^t\text{Bu-C}_6\text{H}_2\text{-2-CH}_2\{\text{CH}(\text{NCHCHNBz})\}]\text{-Cl}$ ($\text{Bz} = \text{CH}_2\text{C}_6\text{H}_5$, $\text{H}_2\text{L}^2\text{Cl}$, **2**) were designed and synthesized. The corresponding NHC of $\text{Ni}(\text{II})$ $[\text{O-4,6-di-}^t\text{Bu-C}_6\text{H}_2\text{-2-CH}_2\{\text{C}(\text{NCHCHN}^i\text{Pr})\}]_2\text{Ni}$ (L_2^1Ni , **3**) and $[\text{O-4,6-di-}^t\text{Bu-C}_6\text{H}_2\text{-2-CH}_2\{\text{C}(\text{NCHCHNBz})\}]_2\text{Ni}$ (L_2^2Ni , **4**) were synthesized by the reactions of $\text{Ni}(\text{PPh}_3)_2\text{Br}_2$ with **1** or **2** in the presence of $\text{NaN}(\text{SiMe}_3)_2$, respectively. Here, we would like to report the results.

* Corresponding author. Tel.: +86 512 6511 2513; fax: +86 512 6511 2371.

E-mail address: qshen@suda.edu.cn (Q. Shen).

2. Experimental

2.1. General procedures

All manipulations were performed under pure argon with rigorous exclusion of air and moisture using standard Schlenk techniques. Solvents were distilled from Na/benzophenone ketyl under pure argon prior to use. 2-Chloromethyl-4,6-di-*tert*-butylphenol [5], $(\text{PPh}_3)_2\text{NiBr}_2$ [6] and 1-benzyl-imidazole [7] was prepared by the literature methods, all other chemicals were obtained commercially and used as received unless stated otherwise. Elemental analysis was performed by direct combustion on a Carlo-Erba EA-1110 instrument. ^1H NMR spectra were measured on a Unity Inova-400 spectrometer at 25 °C.

2.2. Synthesis of H_2LCl

2.2.1. Synthesis of $\text{H}_2\text{L}^1\text{Cl}$ (1)

To a solution of 2-chloromethyl-4,6-di-*tert*-butylphenol (7.64 g, 30 mmol) in THF (20 mL) was added 1-isopropyl-imidazole (3.30 g, 30 mmol) in THF (30 mL). After stirring about 2–3 h at room temperature, the reaction mixture was filtered to collect the white powder, which was dried in vacuo. Yield 9.20 g (85%). ^1H NMR (400 MHz, CDCl_3 , 25 °C) δ : 10.27(s, 1H, NCHN) 7.35 (s, 1H, Ph-*H*), 7.25 (s, 1H, Ph-*H*), 7.19 (s, 1H, Ph-*H*), 7.09 (s, 1H, Ph-*H*), 5.84 (s, 2H, ArCH₂N), 4.64 (m, 1H, CH(CH₃)₂), 1.59 (d, 6H, CH(CH₃)₂), 1.39 (s, 9H, C(CH₃)₃), 1.29 (s, 9H, C(CH₃)₃). Anal. Calc. for C₂₁H₃₃ClN₂O: C, 69.11; H, 9.11; N, 7.67. Found: C, 68.18; H, 9.10; N, 7.62%.

2.2.2. Synthesis of $\text{H}_2\text{L}^2\text{Cl}$ (2)

1-Benzyl-imidazole (4.74 g, 30 mmol) was treated in a procedure similar to that for **1** to yield **2** (9.91 g, 80%). ^1H NMR (400 MHz, CDCl_3 , 25 °C) δ : 10.27(s, 1H, NCHN) 7.36 (d, 6H, Ph-*H*), 7.20 (s, 1H, Ph-*H*), 7.07 (d, 1H, Ph-*H*), 7.04 (s, 1H, Ph-*H*), 5.81 (s, 2H, ArCH₂N), 5.40 (s, 2H, PhCH₂N), 1.39 (s, 9H, C(CH₃)₃), 1.28 (s, 9H, C(CH₃)₃). Anal. Calc. for C₂₅H₃₃ClN₂O: C, 72.71; H, 8.05; N, 6.78. Found: C, 72.77; H, 8.03; N, 6.75%.

2.3. Synthesis of $\text{L}_2^1\text{Ni} \cdot 2(\text{C}_4\text{H}_8\text{O}_2)$ (3)

2.3.1. Procedure A

A Schlenk flask was charged with **1** (0.73 g, 2 mmol), THF (20 mL) and a stir bar. To this suspension was added dropwise two equivalents of $\text{NaN}(\text{SiMe}_3)_2$ (0.84 M, 4.8 mL) in THF at –78 °C. The reaction was stirred for 30 min and gradually warmed to room temperature for additional 10 min. Then the resulted solution was added slowly to a suspension of $\text{Ni}(\text{PPh}_3)_2\text{Br}_2$ (0.75 g, 1 mmol) in THF at –78 °C under stirring. The color of the solution from green to orange was immediately observed and indicated the occurrence of the reaction. The resulting solution

was gradually warmed to room temperature and then stirred for additional 12 h, filtered, and evaporated to dryness. The residue was extracted with toluene. Crystals suitable for elemental analysis and X-ray diffraction determination were obtained by recrystallization from 1,4-dioxane/ CH_2Cl_2 (5:1) at room temperature (1.33 g, 75%). ^1H NMR (400 MHz, C_6D_6 , 25 °C) δ 7.65 (1H, s, Ph-*H*), 7.61 (1H, s, Ph-*H*), 7.49 (1H, s, Ph-*H*), 7.01 (1H, s, Ph-*H*), 6.18 (2H, s, NCH), 5.73 (2H, s, NCH), 4.37 (2H, m, CH(CH₃)₂), 4.30 (2H, s, CH₂N), 4.27 (2H, s, CH₂N) 3.39 (16H, s, OCH₂CH₂O), 1.90 (18H, s, C(CH₃)₃), 1.47(18H, s, C(CH₃)₃), 1.10 (6H, d, CH(CH₃)₂), 0.27 (6H, d, CH(CH₃)₂); ^{13}C NMR (100 MHz, C_6D_6 , 25 °C): δ 164.6, 162.3, 140.8, 132.8, 124.4, 123.2, 122.8, 121.3, 116.8, 67.6, 55.0, 51.8, 36.5, 34.6, 32.8, 30.9, 25.1, 21.4. Anal. Calc. for C₅₀H₇₈N₄O₆Ni: C, 67.48; H, 8.84; N, 6.29. Found: C, 67.43; H, 8.81; N, 6.25%.

2.3.2. Procedure B

By the procedure analogous to that described above, the reaction of **1** (0.36 g, 1 mmol) and $\text{NaN}(\text{SiMe}_3)_2$ (0.84 M, 2.4 mL) with $\text{Ni}(\text{PPh}_3)_2\text{Br}_2$ (0.75 g, 1 mmol), **3** was obtained in 40% yield (0.71 g).

2.4. Synthesis of $\text{L}_2^2\text{Ni} \cdot 2(\text{C}_4\text{H}_8\text{O}_2)$ (4)

2.4.1. Procedure A

A Schlenk flask was charged with **2** (0.42 g, 1 mmol), THF (20 mL) and a stir bar. To this suspension was added dropwise two equivalents of $\text{NaN}(\text{SiMe}_3)_2$ (0.84 M, 2.4 mL) in THF at –78 °C. The reaction was stirred for 30 min and gradually warmed to room temperature for additional 10 min. Then, the resulted solution was added slowly to a suspension of $\text{Ni}(\text{PPh}_3)_2\text{Br}_2$ (0.38 g, 0.5 mmol) in THF at –78 °C under stirring. The resulting solution was gradually warmed to room temperature and then stirred for additional 12 h, filtered, and evaporated to dryness. The residue was extracted with toluene. Crystals suitable for elemental analysis and X-ray diffraction determination were obtained by recrystallization from 1,4-dioxane/ CH_2Cl_2 (5:1) at room temperature (0.68 g, 70%). ^1H NMR (400 MHz, C_6D_6 , 25 °C) δ 7.55 (2H, s, Ph-*H*), 7.51 (2H, s, Ph-*H*), 7.06 (10H, m, Ph-*H*), 5.96 (2H, s, NCH), 5.59 (2H, s, NCH), 4.39 (4H, d, CH₂N), 4.09 (4H, m, CH₂Ph), 3.39 (16H, s, OCH₂CH₂O), 1.87 (18H, s, C(CH₃)₃), 1.47(18H, s, C(CH₃)₃), ^{13}C NMR (100 MHz, C_6D_6 , 25 °C): δ 164.3, 162.2, 140.6, 136.3, 132.7, 129.6, 127.8, 124.5, 123.1, 122.3, 121.7, 121.3, 67.6, 55.2, 53.1, 36.6, 34.5, 32.9, 31.2. Anal. Calc. for C₅₈H₇₀N₄NiO₆: C, 71.23; H, 7.22; N, 5.73. Found: C, 71.24; H, 7.23; N, 5.70%.

2.4.2. Procedure B

By the procedure analogous to that described above, the reaction of **2** (0.42 g, 1 mmol) and $\text{NaN}(\text{SiMe}_3)_2$ (0.84 M, 2.4 mL) with $\text{Ni}(\text{PPh}_3)_2\text{Br}_2$ (0.75 g, 1 mmol), **4** was obtained in 42% yield (0.41 g).

2.5. Structure determination

Suitable single crystals of complexes **3** and **4** were each sealed in a thin-walled glass capillary for X-ray structural analysis. Diffraction data were collected on a Rigaku Mercury CCD area detector at 193(2) K. The structure was solved by direct methods and refined by full-matrix least-squares procedures based on F^2 . All non-hydrogen atoms were refined with anisotropic displacement coefficients. Hydrogen atoms were treated as idealized contributions. The structures were solved and refined using SHELXS-97 and SHELXL-97 programs, respectively. Crystal data and collection and main refinement parameters are given in Table 1. Selected bond lengths (Å) and angles (°) for **3** and **4** are given in Table 2.

3. Results and discussion

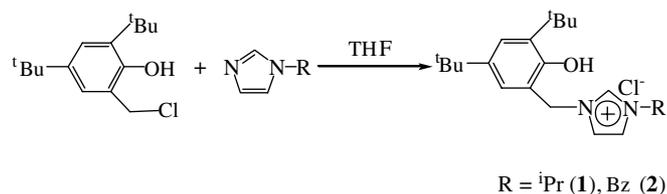
3.1. Syntheses and characterizations of **1** and **2**

Our aim was to understand the application of anionic-functionalized NHCs in organometallic chemistry of Ni(II). Taking into consideration that anionic aryloxo-functionalized NHCs are capable of binding metal atom through the aryloxo oxygen and the carbene carbon to provide an [O, C_{carbene}]-type chelation, we designed aryloxo-functionalized NHC ligands **L**¹ and **L**². Their precursors, H₂L¹Cl and H₂L²Cl, were synthesized conveniently in high yields via nucleophilic attack of a 1-alkylimidazole on a benzyl chloride by the method shown in Scheme 1. Thus, the reactions of 2-chloromethyl-4,6-di-*tert*-butylphenol with 1-isopropyl-imidazole or 1-benzyl-imidazole yielded the

Table 2
Selected bond lengths (Å) and angles (°) for **3** and **4**

3			
Ni(1)–O(1)	1.885(5)	Ni(1)–O(2)	1.882(4)
Ni(1)–C(8)	1.854(6)	Ni(1)–C(29)	1.861(6)
C(8)–Ni(1)–O(1)	91.9(2)	C(29)–Ni(1)–O(1)	176.6(2)
C(29)–Ni(1)–O(2)	91.3(2)	C(8)–Ni(1)–O(2)	177.0(2)
C(8)–Ni(1)–C(29)	91.5(3)	O(2)–Ni(1)–O(1)	85.3(2)
4			
Ni(1)–O(1)	1.893(2)	Ni(1)–O(1A)	1.893(2)
Ni(1)–C(8)	1.864(3)	Ni(1)–C(8A)	1.864(3)
C(8)–Ni(1)–O(1)	92.40(1)	C(8A)–Ni(1)–O(1)	177.86(9)
C(8A)–Ni(1)–O(1A)	92.40(1)	C(8)–Ni(1)–O(1A)	177.86(9)
C(8)–Ni(1)–C(8A)	89.73(2)	O(1A)–Ni(1)–O(1)	85.51(1)

corresponding precursors H₂L¹Cl (**1**) or H₂L²Cl (**2**) in 85% or 80% yields, respectively. The characterization of **1** and **2** were supported by elemental analysis and ¹H NMR spectroscopy. The ¹H NMR spectra of compounds **1** and **2** exhibit the characteristic resonances of imidazolium C₂-H signals at 10.27 ppm for **1** and 10.27 ppm for **2**, the *tert*-butyl protons signals in the region δ 1.29–1.39 ppm for **1** and δ 1.28–1.39 ppm for **2**, respectively.



Scheme 1. Synthesis of **1** and **2**.

Table 1
X-ray crystallographic data for **3** and **4**

	3	4
Empirical formula	C ₄₂ H ₆₂ N ₄ NiO ₂ · 2(C ₄ H ₈ O ₂)	C ₅₀ H ₅₄ N ₄ NiO ₂ · 2(C ₄ H ₈ O ₂)
Formula weight	889.87	977.89
Temperature (K)	193(2)	193(2)
λ (Mo Kα) (Å)	0.71070	0.71070
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2(1)/ <i>n</i>	<i>c</i> 2/ <i>c</i>
<i>a</i> (Å)	15.611(2)	31.636(1)
<i>b</i> (Å)	21.220(3)	10.892(3)
<i>c</i> (Å)	16.428(2)	22.620(8)
α (°)	90.00	90.00
β (°)	111.015(3)	134.002(5)
γ (°)	90.00	90.00
<i>V</i> (Å ³)	5080.1(1)	5607.0(3)
<i>Z</i>	4	4
<i>D</i> _{calcd} (g/cm ³)	1.164	1.159
Absorption coefficient (mm ⁻¹)	0.430	0.396
<i>F</i> (000)	1928	2088
Crystal size (mm)	0.44 × 0.43 × 0.28	0.45 × 0.40 × 0.30
2θ _{max} (°)	55.0	50.7
Number of reflections collected	56366	56366
Number of independent reflections	11619 (<i>R</i> _{int} = 0.0413)	26659 (<i>R</i> _{int} = 0.0594)
Goodness-of-fit on <i>F</i> ²	1.121	1.094
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	0.0755	0.0640

3.2. Synthesis and characterizations of **3** and **4**

The reaction of $\text{Ni}(\text{PPh}_3)_2\text{Br}_2$ with two equivalents of **1** or **2** in the presence of two equivalents of $\text{NaN}(\text{SiMe}_3)_2$ each yielded an orange Ni(II) complex in ca. 75% or 70% yield, respectively. Both of them were characterized to be the desired bis-ligand ones (**3** and **4**) by elemental analysis and ^1H NMR spectra (Scheme 2, Eq. 1). Attempt to synthesize mono-ligand complex by the same reactions at the molar ratio of 1:1 is unsuccessful (Scheme 2, Eq. 2). After workup, the same bis-ligand complexes **3** and **4** were isolated in reasonable lower yields of 40% and 42%, respectively. The results might be due to the additional of the second ligand being faster than the first one or the disproportionation of mono-ligand Ni(II) halide to a more stable bi-ligand complex [8]. The formations of **3** and **4** were supported by elemental analysis and NMR spectroscopy. In ^{13}C NMR spectra the signals for carbene carbon atoms of complexes **3** and **4** appear at δ 164.6, 162.3 ppm for **3** and δ 164.3, 162.2 ppm for **4**, respectively. These $\text{C}_{\text{carbene}}$ signals are comparable to those observed in Ni(II)-based NHC complexes [9]. However, it was noticed that two singlets, not one singlet, were observed for the peak of $\text{C}_{\text{carbene}}$ in each ^{13}C NMR spectrum, although the structure analysis of **3** or **4** showed them to be a C_2 symmetry at the center nickel atom of each complex (as shown in 3.3) [10]. Such characteristics of ^{13}C NMR spectra of **3** and **4** might be contributed to the existence of an equilibrium between a *cis* and *trans* isomer in solution of **3** and **4**, respectively. In fact, it was really observed that the signal of the carbene carbon in **3** or **4** was firstly appeared as a singlet (162.3 ppm for **3** and 162.2 ppm for **4**), and then another singlet (164.6 ppm for **3** and 164.3 ppm for **4**) gradually appeared nearly in the process of monitoring. In additional, it was also noticed that the signals of methylene protons of **3** and **4** appeared in ^1H NMR spectra both as a singlet at room temperature, even these signals should be doublets if the solid-state structures of **3** and **4** were retained in solution. These features might be related to the test's temperature. It was expected that the singlets could turn into the doublets at a temperature low enough.

Complexes **3** and **4** are soluble in protic solvents CH_2Cl_2 , DME, THF, 1,4-dioxane, diethyl ether and toluene, insoluble in hexane. They are thermally stable and will

melt at 165 °C for **3** and at 180 °C for **4**, respectively. It is worth mentioning that complexes **3** and **4** are much less sensitive to air and moisture, and both of them can even remain unchanged for a few days in open air.

3.3. Crystal structures of **3** and **4**

Crystals of **3** and **4** suitable for an X-ray crystal structure determination were grown from 1,4-dioxane/ CH_2Cl_2 at room temperature. The solid structures for **3** and **4** were shown in Figs. 1 and 2, respectively. The crystallographic data and selected bond distances and angles are listed in Tables 1 and 2, respectively.

The X-ray structural analysis revealed the complexes **3** and **4** have the similar solid-state structure. The center nickel atom of each complex coordinated to two bidentate ligands to form a distorted square-planar geometry (Figs. 1 and 2). The two chelating rings adopt a *cis* arrangement around the nickel atom, such that there is a C_2 symmetry at the nickel center. The two chelating rings slightly distort the coordination geometry of the nickel atom with the C–Ni–O bite angle being reduced to 85.3(2)° for **3** and 85.5(1)° for **4**. The two *cis* Ni– $\text{C}_{\text{carbene}}$ bonds of 1.854(6) and 1.861(6) Å for **3**; 1.864(3) and 1.864(3) Å for **4** are very close to these found in a bi-ligand picolyl-functionalized NHC supported Ni(II) complex [1.851(4) and 1.861(4) Å] reported by Jin and co-workers [10]. The Ni–O bond distances in **3** and **4** are comparable to those in known Ni(II) complexes [11]. In complex **3**, the dihedral angles of N-heterocyclic carbene planes (N1–N2–C8–C9–C10 and N3–N4–C29–C30–C31) with the plane formed by O1–O2–C8–C29 are 58.4° and 59.0°, respectively, while O1–O1A–C8–C8A in complex **4** both are 54.9°, which is smaller as compared with those in **3** and is somewhat more similar to those in the bis(bidentate)nickel(II) complexes (Ni(3-methyl-1-picolylimidazolin-2-ylidene) $_2\text{Cl}_2$, 44.6°; Ni(3-benzyl-1-picolylimidazolin-2-ylidene) $_2\text{Cl}_2$, 46.7°) [10]. The dihedral angles between the two carbene planes are 76.3° for **3** and 68.6° for **4**, respectively, suggesting that a benzyl group is less steric demanding than an isopropyl group. The structure differences between the two complexes

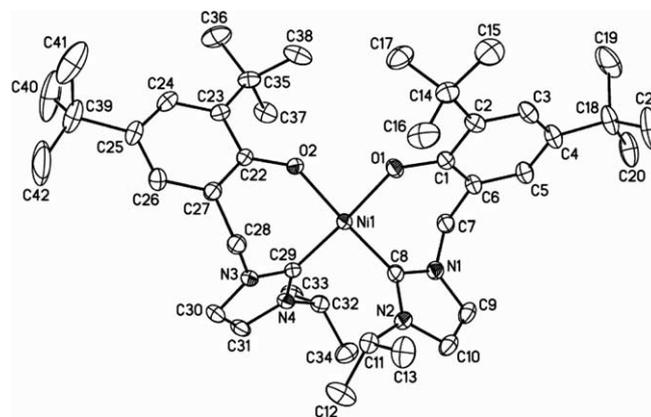
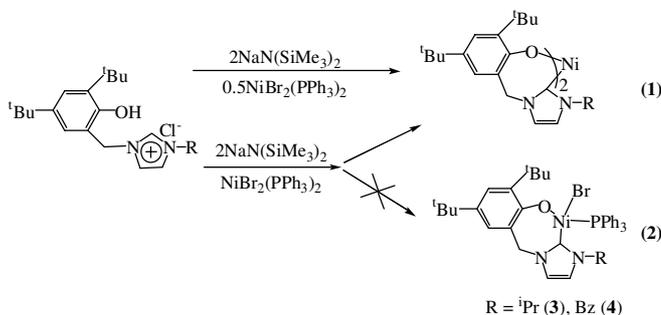


Fig. 1. The crystal structures of complex **3** showing 30% probability ellipsoids. The hydrogen atoms are omitted for clarity.



Scheme 2. Synthesis of **3** and **4**.

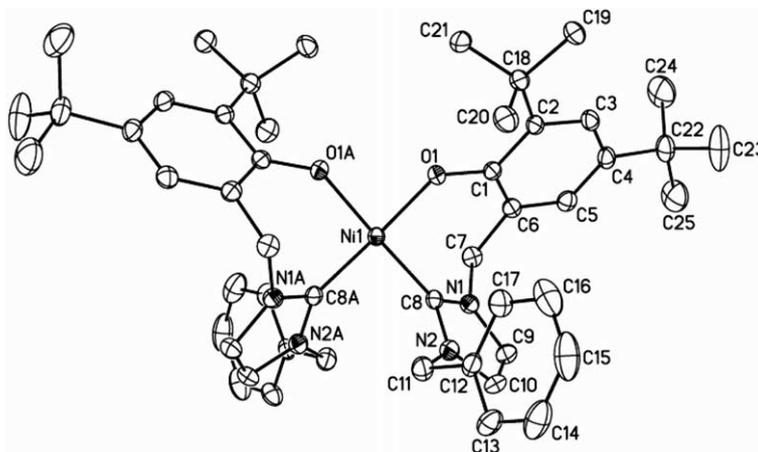


Fig. 2. The crystal structures of complex **4** showing 30% probability ellipsoids. The hydrogen atoms are omitted for clarity.

might be due to the steric hindrance of the substituent group of the ligand: an isopropyl group exerts greater steric hindrance than a benzyl group.

4. Conclusions

In summary, a novel kind of bidentate aryloxo-functionalized imidazolium chloride **1** and **2** was synthesized and the bis-ligand Ni(II) complexes **3** and **4** were obtained using **1** and **2** as the reactants. Further investigation on the applications of such complexes and the functionalized-NHC ligands in other metals is in progress.

Acknowledgments

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Appendix A. Supplementary data

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 279472 and 279473 for complexes **3** and **4**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2005.09.029.

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