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# Synthesis and X-ray crystal structure analysis of the first nickel bisoxazoline pincer complex

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#### Abstract

The reaction in toluene between 2-iodo-1,3-bis(4',4'-dimethyl-2'-oxazolinyl)benzene and Ni(COD)<sub>2</sub> gave [2,6-bis(4',4'-dimethyl-2'-oxazolinyl)phenyl-N,C<sup>1</sup>,N'liodonickle(II) isolated in 69% yield. The structure of this novel nickel bisoxazoline pincer complex was confirmed by a X-ray crystal structure analysis. © 2004 Elsevier B.V. All rights reserved.

Keywords: Bisoxazoline; Crystal structure; Nickel; Pincer complexes

## 1. Introduction

Complexes containing an anionic terdentate ligand ECE, where E is a neutral donor atom such as phosphorus, nitrogen or sulfur, are currently the subject of considerable attention, particularly in respect to their application in homogeneous catalysis [1]. A major subcategory of these so-called pincer complexes, and the subject of much of the work in this area, are NCN complexes 1 based upon, amongst others, the group 10 metals nickel, palladium and platinum [2]. Our own work in this area has focused on the synthesis of bisimine and bisoxazoline palladium and platinum complexes of general structures 2 [3] and 3 [4,5], and following halide abstraction with silver salts, application of the resulting cationic species as Lewis acid catalysts. Bisoxazoline complexes 3 are of particular interest for application in asymmetric catalysis, but to the best of our knowledge no corresponding nickel complex of structure 3 has been reported. In this note, we report on the

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synthesis, properties and X-ray crystal structure analysis of the first nickel bisoxazoline complex.



## 2. Results and discussion

Nickel complex 1a (X = Br) was first synthesised by the addition of Ni(COD)<sub>2</sub> to 2-bromo-1,3-(N,Ndimethylaminomethyl)benzene [2b]. This type of oxidative addition protocol has also been applied to the synthesis of palladium complexes 3a, generated in good yield on combination of Pd2(dba)3 and 2-bromo-1,3-bis(2'-oxazolinyl)benzenes [5a]. This type of approach thus appeared appropriate for the generation

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of a corresponding nickel bisoxazoline complex. To generate a precursor 2-halo-1,3-bisoxazoline we utilised the known regioselective lithiation of 1,3-bis(4',4'-dimethyl-2'-oxazolinyl)benzene [6] and followed this by the addition of iodine to give 2-iodo-1,3-bis(4',4'-dimethyl-2'-oxazolinyl)benzene 5 in 42% yield (Scheme 1). Dissolution of 5 in dry toluene, addition of  $Ni-(COD)_2$  and stirring the resulting mixture at room temperature resulted in a slow change in the colour of the mixture from yellow to orange. After nineteen hours, work-up of the reaction mixture gave novel complex 6, the identity of which was confirmed by an X-ray structure analysis of crystals obtained by the slow evaporation of a diethyl ether solution in air (Fig. 1). The resulting bright orange crystals have been stored in air at room temperature for several months without decomposition.

The structure of **6** reveals the shorter metal-nitrogen and metal-carbon bond distances expected of a first row transition metal complex compared to its second and third row congeners. For example, complex **3b** ( $\mathbf{R} = {}^{i}\mathbf{Pr}$ ,  $\mathbf{R}^{1} = \mathbf{H}$ ,  $\mathbf{X} = \mathbf{Cl}$ ) has a Pt-C bond length of 1.928(10) Å and Pt-N bond lengths of 2.032(10) and 2.035(10) Å [5c]. The corresponding values for one of



Fig. 1. Representation of one of the two independent crystal structures of **6** (corresponding values for the unshown second structure are given in parenthesis). Selected bond distances (Å) and angles (°): Ni(1)–C(11) = 1.859(4) [1.857(4)], Ni(1)–N(1) = 1.972(3) [1.968(3)] Ni(1)–N(2) = 1.977(3) [1.973(3)], Ni(1)–I(1) = 2.5804(5) [2.5861(5)] N(1)– C(5) = 1.298(5) [1.296(5)] N(2)–C(12) = 1.294(5) [1.292(5)], C(11)–Ni(1)–N(1) = 80.53(15) [80.38(15)] C(11)–Ni(1)–N(2) = 80.73 (15) [80.82(15)] N(1)–Ni(1)–N(2) = 161.04(13) [159.94(13)] C(11)–Ni(1)–I(1) = 172.61(11) [171.36(11)].

the two independent crystal structures of **6** are 1.895(4), 1.972(3) and 1.977(3) Å, respectively. As palladium–ligand bonds in complexes **3a** are longer than the corresponding platinum based bonds in **3b** [4d], metal– terdentate ligand bond lengths in group 10 bisoxazoline complexes follow the expected pattern Ni < Pt < Pd.

In a recent study, a large number of metal chlorides were examined as Lewis acid catalysts for the reaction of a silvl enol ether with a mixture of benzaldehyde and N-benzylideneaniline [7]. This revealed both NiCl<sub>2</sub> and PdCl<sub>2</sub> to be inactive whereas PtCl<sub>2</sub> showed weak activity for the activation of the imine. This result mirrors our recent findings that cationic Pt complexes derived from 3b are more active than the corresponding palladium complexes derived from 3a in the Michael reaction between ethyl α-cyanoacetate and methyl vinyl ketone [4d]. Nickel complexes 1a have previously been applied as catalysts for the Kharasch addition which proceeds via a radical mechanism and includes the formation of a nickel(III) complex [Ni(NCN)X<sub>2</sub>] as a persistent radical [8]. We were thus curious to examine the applicability of cationic Ni-bisoxazoline complexes as Lewis acid catalysts for the Michael reaction of activated nitriles. To generate the required complex we combined 6 with one equivalent of silver triflate in reagent grade acetone protected from light (Scheme 2). Analysis of the reaction mixture by TLC revealed consumption of the starting material, but attempted isolation of the expected cationic Ni(II) complex 7 only resulted in a green amorphous solid that could not be further purified. Some evidence for the formation of 7 was obtained from the mass spectrum (FAB) in which a signal arising from the molecular ion was observed (m/z 496, 53%), together with a signal arising from the loss of the triflate counter ion (m/z 347, 51%). The <sup>1</sup>H NMR of the reaction product in acetone-d<sub>6</sub> was broad and inconclusive and the <sup>13</sup>C NMR spectrum contained more peaks than expected. It is of note that a cationic analogue of 7 derived from 1 is sensitive to oxidation to Ni(III), and even that samples with no particular evidence of oxidation can still give broadened signals in a NMR spectrum [2b]. We thus attempted catalysis of the Michael reaction between ethyl cyanoacetate and methyl vinyl ketone on the crude product arising from the addition of silver triflate to 6. Addition of this (5 mol% based on 6) and 10% Hunigs base to a CH<sub>2</sub>Cl<sub>2</sub> solution of ethyl cyanoacetate and methyl vinyl ketone maintained at 4 °C, resulted in a





55% conversion to the Michael product 5-cyano-5-ethoxycarbonyl-2,8-nonadione after 1 h. However, subsequent analyses (2, 3 and 15 h) revealed no significant progression of the reaction revealing deactivation of the catalyst under the conditions employed.

#### 3. Conclusions

The first example of a nickel bisoxazoline complex was synthesised in good yield by the addition to Ni- $(COD)_2$  of 2-iodo-1,3-bis(4',4'-dimethyl-2'-oxazolinyl)benzene. The identity of the resulting complex **6** was confirmed by a X-ray crystal structure analysis. Attempted halide abstraction from **6** gave some evidence for the formation of the desired cationic complex **7**, but this could not be purified and appeared sensitive to oxidation. In contrast, the palladium and platinum congeners of **7** are stable easily isolated complexes, making these significantly better suited as Lewis acid catalysts for the transformation of organic substrates.

#### 4. Experimental

#### 4.1. General methods

Reactions were performed under an atmosphere of nitrogen employing standard Schlenk techniques. THF was distilled under nitrogen from sodium benzophenone ketal and toluene was distilled under nitrogen from molten sodium metal, other solvents were not specifically dried. Column chromatography was performed on  $SiO_2(40-63 \ \mu\text{m})$ . Compound **4** was prepared as previously reported [6].

# 4.2. Synthesis of 2-iodo-1,3-bis(4',4'-dimethyl-2'-oxazolinyl)benzene 5

To a solution of diisopropylamine (0.234 g, 2.31 mmol) in THF (1 mL), cooled to -78 °C, was added BuLi in hexanes (2.54 mmol) and the resulting mixture stirred at -78 °C for 20 min, followed by a further 30 min at room temperature. After re-cooling to -78 °C, this was added via cannula to a separate flask, also

cooled to -78 °C, containing a solution of 1,3bis(4',4'-dimethyl-2'-oxazolinyl)benzene **4** (0.210 g, 0.77 mmol) and TMEDA (0.330 g, 2.84 mmol) in THF (7 mL). After the addition the resulting deep red solution was stirred at room temperature for 5 h prior to the addition of iodine (0.400 g, 1.58 mmol). The solvent was removed in vacuo and the crude product dissolved in CH<sub>2</sub>Cl<sub>2</sub> (50 mL). After washing with aqueous sodium thiosulfate solution  $(5 \times 50 \text{ mL})$ , this was dried ( $MgSO_4$ ), filtered and the solvent removed in vacuo. Column chromatography of the residue (EtOAc) gave 5 as a pale brown crystalline solid (0.130 g, 42%). M.p. 103-110 °C; IR (v<sub>max</sub>; nujol) 1652 (C=N) cm<sup>-1</sup>; <sup>1</sup>H NMR ( $\delta$ ; CDCl<sub>3</sub>) 1.40 (12H, s, CH<sub>3</sub>), 4.14 (4H, s, OCH<sub>2</sub>), 7.37 (1H, t, J 7.7, 5-H), 7.50 (2H, d, J 7.4, 4- and 6-H);  ${}^{13}C{}^{1}H$  NMR ( $\delta$ ; CDCl<sub>3</sub>) 28.6 (CH<sub>3</sub>), 68.6 (C(CH<sub>3</sub>)<sub>2</sub>), 80.0 (OCH<sub>2</sub>), 96.2 (2-C), 128.2 (5-C), 132.0 (4- and 6-C), 137.0 (1- and 3-C), 163.7 (C=N); m/z (EI) 398 (M<sup>+</sup>, 56), 271 (4), 128 (18), 55 (85), 41 (100): (Found: M<sup>+</sup>, m/z (EI) 398.0498. C<sub>16</sub>H<sub>19</sub>IN<sub>2</sub>O<sub>2</sub> requires 398.0491).

# 4.3. Synthesis of [2,6-bis(4'4'-dimethyl-2'-oxazolinyl)phenyl-N,C<sup>1</sup>,N' ]iodonickel (II) **6**

A mixture of 5 (0.23 g, 0.6 mmol) and  $Ni(COD)_2$ (0.20 g, 0.7 mmol) were stirred in freshly distilled degassed toluene (20 mL) for 19 h at room temperature, by which time the reaction was deemed complete by TLC (CH<sub>2</sub>Cl<sub>2</sub>). The reaction mixture was filtered through silica eluting with ethyl acetate. The orange band was collected and the solvent removed in vacuo (for an extended period) to give [2,6-bis(4',4'-dimethyl-2'-oxazolinyl)phenyl-N,C<sup>1</sup>,N']iodonickle(II) as an orange/brown solid (0.184 g, 70% yield based on 5. A sample suitable for X-ray analysis was prepared by slow evaporation of a diethyl ether solution in air to give bright orange plates. M.p. 214 °C (decomp.); Anal. Found: C, 42.24; H, 4.22; N, 5.96. Calcd for C<sub>16</sub>H<sub>19</sub>IN<sub>2-</sub> NiO<sub>2</sub>: C, 42.06; H, 4.19; N, 6.13; IR (v<sub>max</sub>; CH<sub>2</sub>Cl<sub>2</sub>) 1616  $(C=N) \text{ cm}^{-1}$ ; <sup>1</sup>H NMR ( $\delta$ ; CDCl<sub>3</sub>) 1.63 (12H, s, CH<sub>3</sub>), 4.30 (4H, s, CH<sub>2</sub>), 7.07 (1H, app dd, J 5.9 and 8.6, Ar 4-H), 7.13 (2H, d, J 6.2, Ar 3- and 5-H);  ${}^{13}C{}^{1}H$  NMR ( $\delta$ ; CDCl<sub>3</sub>) 29.0 (CH<sub>3</sub>), 66.2 (C(CH<sub>3</sub>)), 84.4 (OCH<sub>2</sub>), 128.9 (4-C), 124.3 (3- and 5-C), 124.91 (2- and 3-C), 130.0 (1-C), 172.4 (C=N); MS (m/z; FAB) 329 (M<sup>+</sup> – I, 100%), 273 ( $M^+ - I - Ni$ , 51%), (*m*/*z*; ES) 273 ( $M^+ - I - Ni$ , 100%).

# 4.4. Attempted synthesis of [2,6-bis(4',4'-dimethyl-2'oxazolinyl)phenyl-N,C<sup>1</sup>,N' |nickel (II) triflate 7

[2,6-Bis(4',4'-dimethyl-2'-oxazolinyl)phenyl-N,C<sup>1</sup>,N']iodonickel(II) **6** (0.044 g, 0.1 mmol) and silver triflate (0.026 g, 0.1 mmol) were combined in acetone (10 mL) and stirred protected from light. After stirring at room temperature for 27 h the reaction mixture was filtered through celite, eluting with acetone, to remove a grey/ white precipitate, consistent with the formation of silver iodide. Removal of the solvent in vacuo gave a green amorphous solid (0.05 g, >99% yield, based on **6**). <sup>1</sup>H NMR ( $\delta$ ; 270 MHz, d<sub>6</sub>-acetone) broadened inconclusive spectrum; MS (*m*/*z*; FAB) 496 (M<sup>+</sup>, 53%) 347 (M – OTf, 51), 328 (100), 273 (100%).

# 4.5. The Michael reaction between ethyl cyanoacetate and methyl vinyl ketone

[2,6-Bis(4',4'-dimethyl-2'-oxazolinyl)phenyl-N,C<sup>1</sup>,N']iodonickel(II) **6** (0.0088 g, 0.02 mmol) and silver triflate (0.0052 g, 0.02 mmol) were combined in acetone (2 mL) and stirred protected from light under a nitrogen atmosphere for 24 h. The mixture was filtered through celite and the solvent removed in vacuo to give a brown/green solid (0.010 g). To this was added 1.5 mL of a solution comprising ethyl cyanoacetate (0.10 mL, 1 mmol), methyl vinyl ketone (0.24 mL, 2.9 mmol) and Hunig's base (0.02 mL, 0.1 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (3 mL). The reaction was maintained at 4 °C and analysed periodically by gas chromatography.

# 5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 225928 for **6**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc. cam.ac.uk or http://www.ccdc.cam.ac.uk).

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