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Synthesis of N,O-heterocyclic carbene and coordination to rhodium(I) and copper(I)

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ABSTRACT

5,7-Di-tert-butyl-3-phenyl benzoxazolium tetrafluoroborate **1** could be prepared by simple reaction of the corresponding aminophenol with triethyl orthoformate under acidic conditions. Both rhodium(I) and copper(I) complexes with benzoxazol-2-ylidene ligand were then efficiently synthesised in a straightforward and smooth manner involving the reaction of benzoxazolium salt 1 with metal precursor and an external base. The complexes have been fully characterised and used in metal-catalysed hydrosilylation of ketones, where they showed poor catalytic activity, presumably due to low stability of the complexes under those conditions.

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1. Introduction

N-heterocyclic carbenes (NHCs) have been established as a class of priviledged ligand in transition metal coordination chemistry since Arduengo and collaborators first isolated stable NHC species in 1991 [1,2]. They have provided the base for extensive research efforts in the development of catalysts and during the last decade, numerous applications of NHC complexes as phosphine mimics have been reported [3,4]. However, the reactivity of NHC complexes is different from that of the corresponding phosphine complexes and these differences may be connected with the nature of the metal-carbene bond, which remain subject of debate [2d].

NHCs and phosphines have different topography so that, to date, electronic and steric properties of phosphines can be readily varied whereas such easy modularity is less accessible for N-heterocyclic carbenes. Indeed, tuning the electronic components of NHCs may be of great interest for the development of highly active catalysts. The strategies are as follows: (i) attachment of electrondonating or electron-withdrawing groups [5], (ii) incorporation of additional heteroatoms into the backbone (e.g. nitrogen, boron and phosphorus) [6], (iii) substitution of heteroatoms (O, S and even P) [7].

Tuning the properties of the NHCs by substitution of nitrogen by a sulphur atom or an oxygen atom is an attractive approach that still remains underexploited so far (Chart 1). N,S-heterocyclic carbene complexes have been used with success in arylation of allylic alcohols [8], C-C coupling reactions [9] or olefin metathesis [10]. However, there are fewer examples of N,O-heterocyclic carbenes probably because such carbene complexes were originally obtained

by indirect methods via isocyanide derivatives [7,11]. However in 2005, Biffis and co-workers reported the synthesis of palladium bis-N,O-heterocyclic carbene complexes from oxazolium salts and palladium precursor [12]. The oxazolium precursors were prepared by direct alkylation of oxazole with methyl iodide or benzylic bromides. These bidentate ligands were found to catalyse the Heck type coupling reaction.

In this contribution, we report a straightforward synthesis of benzoxazolium salt directly obtained from the hydroxyaniline. The synthesis and coordination chemistry of the benzoxazol-2-ylidene as ligand with Rh(I) and Cu(I) is also discussed. Finally, some preliminary experiments on hydrosilylation reaction have been carried out.

2. Results and discussion

2.1. Synthesis of the Ligand

Biffis, Cavell and collaborators prepared oxazolium salts through the alkylation of oxazole with primary alkyl halides, a procedure that does not allow synthesis of N-aryl substituted oxazolium salts. We found that such *N*-aryl substituted precursors may be obtained directly from *N*-aryl 2-amino phenol. Therefore, 3,5-di-tert-butyl-2-hydroxy-N-phenylaniline [13] was reacted with one equivalent of tetrafluoroboric acid and excess of triethyl orthoformate. Stirring at room temperature the solution led to precipitation of benzoxazolium salt 1 (Scheme 1) as a white solid, which was obtained after workup in 60% yield. The oxazolium proton (OCHN) resonance is characteristically downfield shifted (δ = 10.25 ppm) and the carbon resonance was found to be at δ = 155.4 ppm. Molecular structure of **1** was also confirmed by X-ray diffraction studies as shown in Fig. 1.





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2.2. Coordination to rhodium(I) and copper(I)

For the coordination of precursor **1** as an N.O-heterocyclic carbene to rhodium or copper, the strategy based on the ligand transfer by a silver carbene complex was unsuccessful [14]. Reaction of 1 with 0.5 equivalent of Ag₂O leads to a mixture of undefined compounds. On the other hand, the in situ reaction of 1 with [RhCl(cod)]₂ and tBuOK was found to be successful. The reaction was carried out in THF at room temperature for 15 h. Filtration over celite and recrystallisation from THF/pentane gave the neutral rhodium complex 2 as yellow crystals in 91% yield (Scheme 2). The product slowly decomposes in solution but is stable in the solid state and under nitrogen. In the ¹³C NMR spectrum, the resonance of the carbene carbon nuclei of 2 was observed as a doublet at δ = 214.4 [¹J(¹⁰³Rh¹³C) = 57.1 Hz]. Two signals for the olefin hydrogen atoms CH_{cod} were observed by ¹H NMR spectroscopy indicating free rotation of the carbene around the C-Rh bond on the NMR timescale.

X-ray structure analysis confirms the molecular structure of **2** (Fig. 2). The coordination geometry around the metal centre is a distorted square plane with the N,O-heterocyclic carbene ring oriented almost orthogonally. The $C_{carbene}$ -Rh bond length is 1.988(2) Å and C_{cod} -Rh bond lengths are within the expected range. The Rh- C_{cod} distances *trans* to the carbene carbon atom are longer than those *trans* to the chloride [2.212(2)/2.244(2) versus 2.102(3)/2.121(2) Å]. This *trans* influence is also reflected in the difference in the C=C double bond lengths of the coordinated cod ligand [1.373(4) versus 1.403(3) Å].

In order to define the donating capacity of the carbene, we treated the rhodium complex **2** with CO gas in an attempt to form the corresponding rhodium carbonyl complex. When a solution of the complex was subject to CO gas bubbling, the yellow solution instantaneously turned to deep orange, which gradually decomposes. Proton NMR analysis showed a mixture of undefined products and unfortunately any attempt to isolate well-defined products were unsuccessful.

A similar procedure was used for the synthesis of the copper(I) complex. We first reacted CuCl with LiOtBu overnight in THF prior to addition of the benzoxazolium salt **1** in one portion (Scheme 3). The resulting suspension was then stirred at room temperature for 12 h. Removal of the formed white salt by filtration and evaporation of the solvent lead to the copper complex **3** in 65% yield (Scheme 3). Proton and carbon NMR analysis confirmed the formation of the N,O-heterocyclic carbene. In the ¹³C NMR spectrum, the resonance of the carbene carbon nuclei of **3** was observed at $\delta = 200.0$ ppm. Recrystallisation of the complex proved to be difficult and the X-ray data obtained were of insufficient quality for a refinement of the structure. However, the basic connectivities were



Fig. 1. Molecular structure of benzoxazolium **1**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): C(1)-N(1), 1.310(5); C(1)-O(1), 1.317(4); N(1)-C(1)-O(1), 112.8(3).



Scheme 2. Preparation of rhodium complex 2 from benzoxazolium 1.



Fig. 2. Molecular structure of compound **2**. Hydrogen atoms and a solvent molecule (THF) are omitted for clarity. Selected bond lengths (Å) and angles (°): C(1)–Rh(1), 1.988(2); C(1)–N(1), 1.341(3); C(1)–O(1), 1.358(3); C(22)–C(23), 1.403(3); C(27)–C(26), 1.373(4); C(22)–Rh(1), 2.102(3); C(23)–Rh(1), 2.121(2); C(26)–Rh(1), 2.212(2); C(27)–Rh(1), 2.244(2); Cl(1)–Rh(1)–C(1), 89.2(2); N(1)–C(1)–Rh(1)–Cl(1), -95.1.



Scheme 1. Synthesis of benzoxazolium salt 1 from 3,5-di-tert-butylcatechol. Reaction conditions: (i) aniline, NEt₃, heptane, reflux [13].



Scheme 3. Synthesis of the copper(I) complex 3.

verified and the complex was found to be a dimer in the solid state with bridging chlorides (see Electronic Supplementary Information for a view).

We tested the rhodium and copper complexes for their activity in the hydrosilylation reaction in order to evaluate their potential in catalysis. Standardised reaction conditions were applied (i.e. acetophenone, Ph_2SiH_2 , THF and CH_2Cl_2 as solvent, 1 mol% of precatalyst). The conversions were found to be below 2% after 48 h with both complexes, which is in contrast with NHC systems that usually display good activity under the same experimental conditions [15,16]. Although no black solids were observed, it appeared that the solutions gradually turned deep dark, which suggest us that a slow decomposition of the complexes occurs.

In summary, we have illustrated that the benzoxazolium salt **1** is a suitable precursor for the synthesis of N,O-heterocyclic carbene complexes. Its coordination capabilities have been established in the synthesis of rhodium(I) and copper(I) complexes. Preliminary results in hydrosilylation of ketones indicate that such systems exhibit low catalytic activity. Future work will explore the potential of this class of ligands with other transition metals (i.e. Pd, Pt).

3. Experimental

3.1. General procedures

All experiments were carried out under N₂ using standard Schlenk techniques or in a Mbraun Unilab glovebox. THF, dichloromethane and pentane were first dried through a solvent purification system (MBraun SPS) and stored for at least a couple of days over activated molecular sieves (4 Å) in a glovebox prior to use. CD_2Cl_2 and C_6D_6 were purchased from Eurisotope (CEA, Saclay, France), degassed under a N₂ flow and stored over activated molecular sieves (4 Å) in a glovebox prior to use. 3,5-Di-tert-butyl-2-hydroxy-*N*-phenylaniline was synthesised according to literature procedures. NMR spectra were recorded on Bruker AC 300 MHz NMR spectrometers at ambient temperature. ¹H and ¹³C chemical shifts are reported versus SiMe₄ and were determined by reference to the residual ¹H and ¹³C solvent peaks. Elemental analysis and mass analysis were performed by the Service de Microanalyse and Service de masse of Université de Strasbourg.

3.2. Preparation of the compounds

3.2.1. 5,7-Di-tert-butyl-3-phenyl benzoxazolium tetrafluoroborate (1)

HBF₄ (1.39 mL, 48% w/w) was added dropwise to a solution of 3,5-di-tert-butyl-2-hydroxy-*N*-phenylaniline (3.17 g, 10.6 mmol) in 50 mL of MeOH. After 30 min of stirring, the solvent was removed under vacuum and (EtO)₃CH (30 mL) was added. The resulting solution was stirred at room temperature under N₂ overnight to give a white suspension. The solid was filtered, washed with diethyl ether and dried in vacuo, giving 2.52 g of **1** (60% yield). ¹H NMR (300 MHz, CDCl₃): δ 10.25 (s, 1H), 7.86–7.72 (m, 6H), 7.36 (s, 1H), 1.58 (s, 9H), 1.38 (s 9H). ¹³C{¹H} NMR (75 MHz, CDCl₃): δ 155.4 (NCHO), 153.7, 146.1, 138.2, 132.3, 131.0, 130.2, 129.1,

125.1, 119.2, 107.9, 35.9 ($-CMe_3$), 35.0 ($-CMe_3$), 31.4 ($-C(CH_3)_3$), 29.8 ($-C(CH_3)_3$). HRMS (ESI) *m/z* (%): Calc. for C₂₁H₂₆NO ([$M-BF_4$]⁺) 308.2014, found: 308.2009 (100). *Anal.* Calc. for C₂₁H₂₆BF₄NO: C, 63.82; H, 6.63; N, 3.54. Found: C, 63.98; H, 6.78; N, 3.47%.

3.2.2. $[(C_{21}H_{26}NO)Rh(COD)Cl]$ (2)

In a glove box, a THF solution (5 mL) of [Rh(cod)Cl]₂ (100.0 mg, 0.20 mmol) and the benzoxazolium salt **1** (160.0 mg, 0.40 mmol) was precooled at -35 °C. tBuOK (48.0 mg, 0.42 mmol) was then added in one portion. The reaction mixture was stirred overnight at room temperature to yield a yellow solution, which was filtered over celite and evaporated to dryness. The product was recrystallised from THF/pentane layering to give 2 as yellow crystals in 91% yield (210 mg, 0.38 mmol). ¹H NMR (300 MHz, CDCl₃): δ = 8.10 (m, 2H), 7.68 (m, 3H), 7.26 (d, J = 1.8 Hz, 1H), 7.05 (d, J = 1.8 Hz, 1H), 5.13 (m, 2H, CH_{cod}), 3.35 (m, 2H, CH_{cod}), 2.12 (m, 4H, CH₂), 1.90 (m, 4H, CH₂), 1.56 (s, 9H, tBu), 1.30 (s, 9H, tBu). ¹³C NMR (75 MHz, CDCl₃): δ 214.4 (d, J = 57.1 Hz, NCO), 149.9, 148.9, 135.6, 135.0, 132.2, 129.5, 129.4, 126.9, 119.1, 105.3, 102.4 (d, J = 6.2 Hz), 69.3 (d, J = 14.9 Hz), 35.3, 34.7, 32.6 (CH_{2(cod)}), 31.7 (C(CH₃)₃), 30.0 (C(CH₃)₃), 28.5 (CH_{2(cod})). HRMS (ESI) *m/z*: Calc. for C₂₉H₃₇NORh ([M–Cl]⁺) 518.1930, found: 518.1926. Anal. Calc. for C₂₉H₃₇ClNORh: C, 62.88; H, 6.73; N, 2.53. Found: C, 63.02; H, 6.79; N, 2.45%.

3.2.3. [(C₂₁H₂₆NO)CuCl] (3)

In a glove box, a THF solution (5 mL) of CuCl (40.0 mg, 0.4 mmol) and LiOtBu (33.0 mg, 0.41 mmol) was stirred at room temperature. After 12 h, the resulting yellow solution was precooled at -35 °C prior to addition of a solution of 160 mg of benzoxazolium 1 dissolved in 2 mL of THF. After stirring overnight, the colourless solution was filtered over celite and the solvent was removed under vacuum. Toluene (5 mL) was added and the solution was filtered again over celite. Evaporation of the solvent and recristallisation from THF/pentane afforded 3 as colourless crystalline solid (104 mg, 0.26 mmol, 65% yield). ¹H NMR (300 MHz, CD_2Cl_2): δ = 7.69 (m, 5H), 7.48 (d, J = 1. Hz), 7.21 (d, J = 1.8 Hz), 1.56 (s, 9H), 1.33 (s, 9H). ¹³C NMR (75 MHz, CD₂Cl₂): δ 200.0 (NCO), 150.6, 148.4, 136.1, 134.4, 131.1, 130.4, 125.8, 121.3, 106.5, 35.3 (C(CH₃)₃), 34.6 (C(CH₃)₃), 31.2 (C(CH₃)₃), 29.6 (C(CH₃)₃). Anal. Calc. for C₂₁H₂₅ClCuNO: C, 62.06; H, 6.20; N, 3.45. Found: C, 62.34; H, 6.45; N, 3.52%. Note: We have been unable to obtain satisfactory crystal for X-ray diffraction studies. However, the basic connectivities were verified and the complex was found to be a dimer in the solid state with bridging chlorides. Electronic supporting information displays a view of the molecule ($C_{21}H_{25}ClCuNO$, space group: $P2_1/c$, a = 11.90930(10), b = 14.1890(2), c = 23.8492(4), β = 89.9970, cell volume: 4030.06 Å³).

3.3. Crystal structure determination

Single crystals of the compounds 1, 2 and 3 were mounted on a Nonius Kappa-CCD area detector diffractometer (Mo K α

| Table | 1 | | | | | | |
|-------|---|--|--|--|--|--|--|
|-------|---|--|--|--|--|--|--|

Details of the crystal structure determinations of the compounds 1 and 2.

| | 1 | 2 |
|---|---|----------------------|
| Formula | C ₂₁ H ₂₆ NOBF ₄ | C33H45ClNO2Rh |
| Formula weight | 395.24 | 626.06 |
| Crystal system | triclinic | monoclinic |
| Space group | ΡĪ | $P2_1/c$ |
| a (Å) | 10.7077(6) | 9.3524(2) |
| b (Å) | 15.5708(11) | 12.1837(3) |
| c (Å) | 16.1510(13) | 27.1533(4) |
| β (°) | 80.737(4) | 100.7890(10) |
| λ(°) | 89.455(4) | |
| V (Å ³) | 2524.0(3) | 3039.34(11) |
| Ζ | 4 | 4 |
| $d_{\rm c} ({\rm Mg}{\rm m}^{-3})$ | 1.040 | 1.368 |
| μ(Mo Kα) (mm ⁻¹) | 0.083 | 0.679 |
| Index ranges (independent | -13 to 13, -15 to 20, | -13 to 9, -15 to 17, |
| set) h, k, l | -20 to 20 | -38 to 34 |
| θ Range (°) | 1.3-27.4 | 1-30.0 |
| T (K) | 173(2) | 173(2) |
| F ₀₀₀ | 832 | 1312 |
| Reflections collected | 40 530 | 23 030 |
| Reflections unique, R _{int} | 11 392, 0.0755 | 8418, 0.05 |
| Data/restraints/parameters | 11 392/0/512 | 8418/0/350 |
| Goodness for fit on F^2 | 1.057 | 1.077 |
| R indices (observed data) | 0.1125, 0.3139 | 0.0415, 0.1063 |
| $R(F)$, $wR(F^2)$ | $[F > 3\sigma(F)]$ | $[F > 4\sigma(F)]$ |
| R indices (all data) R(F), wR(F ²) | 0.1898, 0.3542 | 0.0615, 0.1214 |
| Largest residual peaks (e Å ⁻³) | 1.16 and -0.573 | 1.645 and -1.111 |

 $\lambda = 0.71071$) complete conditions of data collection (Denzo software) [17] and structure refinements are in Table 1. The cell parameters were determined from reflections taken from one set of 10 frames (1.0° steps in phi angle), each at 20 s exposure. The structures were solved using direct methods (SHELXS97) and refined against F^2 using the SHELXL97 software [18]. The absorption was not corrected. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were generated according to stereo-chemistry and refined using a riding model in SHELXL97.

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Appendix A. Supplementary data

CCDC 723327 and 723328 contain the supplementary crystallographic data for **1** and **2**. 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

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2009.05.067.

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