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## Formation of N-coordinated 4H-benzo[d][1,3]oxazine from 2-(trimethylsiloxymethyl)- and 2-(hydroxymethyl)-phenyl isocyanides promoted by dirhodium(II) acetate

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## Abstract

The neutral dirhodium(II) acetate  $[Rh_2(OAc)_4]$  and the related cationic complex  $[Rh_2(OAc)_2(MeCN)_6](BF_4)_2$  react with 2-(trimethylsiloxymethyl)phenyl isocyanide (I) and/or 2-(hydroxymethyl)phenyl isocyanide (II) to give the corresponding adducts, in which the entering isocyanide occupies the axial position at the two rhodium centres. These complexes are stable in toluene, but they evolve in chloroform as a consequence of an intramolecular ligand rearrangement via oxygen attack to the coordinated carbon atom. With the neutral dirhodium acetate species the cyclization reaction affords the well characterized benzoxazine complex  $[Rh_2(OAc)_4(NC_6H_4-2-CH_2OC(H))_2]$  (4), whereas the cationic acetonitrile derivative rapidly evolves into a complex mixture. © 2006 Elsevier B.V. All rights reserved.

Keywords: Rhodium(II); Functionalized isocyanides; Benzo[d][1,3]oxazine complex

The reactivity of functionalized isocyanides towards metal complexes has been widely studied in the last years [1] and it has been demonstrated that it depends on several factors such as the nature of the functional group, the type of transition metal and its oxidation state. In this contribution we wish to report some results on the coordination of 2-(trimethylsiloxymethyl)phenyl isocyanide (I) and 2-(hydroxymethyl)phenyl isocyanide (II) (Fig. 1) to [Rh<sub>2</sub> (OAc)<sub>4</sub>] and of (II) to the cationic complex [Rh<sub>2</sub>(OAc)<sub>2</sub> (MeCN)<sub>6</sub>](BF<sub>4</sub>)<sub>2</sub>.

The investigated isocyanides are interesting ligands because they present both the isocyanide group and an easily accessible hydroxyl function, which upon 1,2-addition to the  $C \equiv N$  triple bond, would generate the N,O-heterocyclic carbene benzo[1,3]oxazin-2-ylidene, as it has been already reported with several palladium(II) and platinum(II) complexes [2]. In this context we have tested this particular ability of ligands (I) and (II) with dirhodium(II) metal centres, for which up to now only a single example of carbene complex has been reported in the literature [3].

The complexes  $[Rh_2(OAc)_4(CNC_6H_4-2-CH_2OR)_2]$  (1, R = SiMe<sub>3</sub>; **2**, R = H) and  $[Rh_2(OAc)_2(CH_3CN)_4(CNC_6H_4-2-CH_2OSiMe_3)_2]$  (BF<sub>4</sub>)<sub>2</sub> (**3**) were obtained in good yield by reaction of  $[Rh_2(OAc)_4]$  or  $[Rh_2(OAc)_2(MeCN)_6](BF_4)_2$ , respectively, with the functionalized isocyanides in 1/1 Rh/ isocyanide ratio (Scheme 1) [4].

Their <sup>1</sup>H and <sup>13</sup>C NMR spectra show the expected resonances for the functional groups present in the molecule and they indicate the C-coordination of the isocyanide function to the free apical positions of the metal precursor; the signals relative to the bridging acetate (or to the acetonitrile molecules) are in fact almost unaffected by coordina-

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Fig. 1. Functionalized isocyanides employed in this study [2].



Scheme 1.

tion of the isocyanide ligand. Rh(II)-Cax coordination is rather rare and involves as axial ligands isocyanides [5], CO [6], carbenes [3], alkenes [7], alkynes [8] or arenes [9]. In this context complex (3) represents the first example of Cax coordination in a dicationic rhodium(II) complex. The infrared spectra of complexes (1)-(3) confirm the proposed structure. In particular, complex (1) exhibits the N=C absorption at 2128 cm<sup>-1</sup> (force constant k(N=C)) ca. 1730 N/m) with a  $\Delta \tilde{v} = (\tilde{v}(N \equiv C)_{\text{coordinated}} - \tilde{v}(N \equiv C)_{\text{free}})$  [1a] of ca. 10 cm<sup>-1</sup>, whereas complex (3) shows an absorption at 2176 cm<sup>-1</sup> ( $k(N \equiv C) = 1810$  N/m) and the corresponding  $\Delta \tilde{v}$  is 45 cm<sup>-1</sup>. As already observed, a higher value of  $\Delta \tilde{v}$  reflects a greater electrophilicity of the isocyanide carbon, which is therefore more susceptible of nucleophilic attack [1a]. As expected the highest value is observed for the cationic dirhodium(II) complex, as a consequence of the positive charge localized on the metal center. This fact explains the instability in solution of complex (3), whose evolution is already observed during the record of the NMR spectrum in deuterated chloroform.

Complex (2) is characterized in the solid state by two  $N \equiv C$  absorptions at 2154 and 2138 cm<sup>-1</sup>; furthermore the solid state <sup>13</sup>C NMR spectrum shows two sets of signals for the carboxylato and isocyanide ligands. This non-equivalence of the axial ligands may be attributable to an intra- or intermolecular interaction (possibly via –OH hydrogen bonding) involving one of the two coordinated isocyanides, which is effective only in the solid state. In fact, both infrared and NMR spectra in solution shows the presence of a single set of signals.

Complex (1) is converted in methanol in the presence of a catalytic amount of  $F^-$  anions (tetrabutyl ammonium fluoride, TBAF) to the corresponding benzoxazine derivative (4), which was isolated in good yield as a purple solid (Scheme 2) [10].

The IR spectrum of complex (4) is characterized by the absence of the absorption band at  $2125 \text{ cm}^{-1}$ , relative to the N=C bond stretching, indicating an evolution of the system. However, the expected carbene derivative has not been obtained (Scheme 3): in the IR spectrum in fact the absorption band at ca. 3300 cm<sup>-1</sup> relative to the N-H bond stretching is absent; moreover, in the <sup>1</sup>H NMR spectrum there is no signal attributable to the N-H proton.

At the same time, the <sup>1</sup>H NMR spectrum of complex (4) exhibits a signal at 7.72 ppm attributable to the N=CH hydrogen and the <sup>13</sup>C NMR spectrum shows the corresponding carbon resonance at 157.2 ppm.

In order to shed light on the mechanism of this cyclization reaction and to identify possible carbene intermediates, the stability of complex  $[Rh_2(OAc)_4(CNC_6H_4-2-CH_2OH)_2]$  (2) has been studied in CDCl<sub>3</sub> solution. During the <sup>1</sup>H NMR investigation a slow evolution of complex (2) to the benzoxazine complex (4) has been observed, but we were unable to detect any carbene intermediate. Attempts to trap the carbene species by transfer to other substrates such as styrene or diazoacetate, were unsuccessful: in fact no cyclopropanation or coupling products were observed.

The chemical behaviour of the hydroxymethyl functional isocyanide (II) coordinated to dirhodium(II) metal species can be compared with that already described for a series of metal centers like Cr(0), W(0), Pd(II), Pt(II)[1b,2]. While with the first two electron-rich metals only coordination of the isocyanide is observed, without any activation towards nucleophilic attack of the pending OH, with the less electron rich Pd(II) and Pt(II) metal centers activation occurs to give intramolecular cyclization and final formation of the N,O-heterocyclic carbene com-





Scheme 3.

plexes. In the case of Rh(II) the activation gives rise to a final product involving the coordination of the N,O-heterocvclic ligand through the imino nitrogen instead of the carbene carbon. It has been recently reported for N,Nheterocyclic carbenes that N- or C-coordination markedly depends on the nature of the metal center [11] and the observed behaviour confirms the well known reluctance of dirhodium(II) towards C-carbene bonding [3]. The importance of the electron density at the metal on the degree of activation of the coordinated isocyanide is well demonstrated in the case of the cationic complex  $[Rh_2(OAc)_2(CH_3CN)_4(CNC_6H_4-2-H_2OSiMe_3)_2](BF_4)_2$  (3). The positive charge makes the metal more electrophilic and, as a consequence, the isocyanide carbon becomes more susceptible of nucleophilic attack even by the SiMe<sub>3</sub>-protected oxygen atom.

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- [4] [ $[Rh_2(OAc)_4(CNC_6H_4-2-CH_2OSiMe_3)_2$ ] (1). In this typical reaction to a suspension of [Rh<sub>2</sub>(OAc)<sub>4</sub>] (200 mg, 0.45 mmol) in toluene (25 mL) was added slowly and under vigorous stirring (I) (0.19 g, 1.0 mmol) dissolved in toluene (5 mL). The reaction mixture was stirred for 3 h at room temperature and then evaporated to small volume under reduced pressure. Treatment with *n*-hexane (10 mL) gave a light brown solid, which was filtered and dried under vacuum (73% yield). Anal. Calc. for C<sub>30</sub>H<sub>42</sub>N<sub>2</sub>O<sub>10</sub>Rh<sub>2</sub>Si<sub>2</sub> (M = 852.65): C, 42.26; H, 4.97; N, 3.29. Found: C, 43.04; H, 4.94; N, 3.30%. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  0.18 (s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>), 1.96 (s, 6H, CH<sub>3</sub>CO<sub>2</sub><sup>-</sup>), 5.17 (s, 2H, CH<sub>2</sub>OSi), 7.41–7.74 (m, 4H, C<sub>6</sub>H<sub>4</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  – 0.6 (Si(CH<sub>3</sub>)<sub>3</sub>), 24.2 (CH<sub>3</sub>CO<sub>2</sub><sup>-</sup>), 60.9 (CH<sub>2</sub>OSi), 124.2, 126.7, 127.3, 127.7, 130.1, 139.1 (C<sub>6</sub>H<sub>4</sub>), 194.4 (CH<sub>3</sub>CO<sub>2</sub><sup>-</sup>), the signal correspond-

ing to the isocyanide carbon C=N was not detected. FT IR (KBr,  $cm^{-1}$ ): 2953-2876, 2128 [ $v(C \equiv N)$ ], 1591, 1429, 1346, 1248, 1115, 1076, 880, 843, 750 and 696.  $[Rh_2(OAc)_4 (CNC_6H_4-2-CH_2OH)_2]$  (2). This compound was obtained from [Rh<sub>2</sub>(OAc)<sub>4</sub>] (200 mg, 0.45 mmol) and (II) (0.12 g, 0.9 mmol), as a yellow solid (52% yield). Anal. Calc. for  $C_{24}H_{26}N_2O_{10}Rh_2$  (*M* = 708.29): C, 40.70; H, 3.70; N, 3.96. Found: C, 40.27; H, 3.40; N, 3.70%. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  1.96 (s, 6H, CH<sub>3</sub>CO<sub>2</sub><sup>-</sup>), 3.80 (br, 1H, OH), 5.00 (2s, 2H, CH<sub>2</sub>O), 7.45-7.75 (m, 4H,  $C_6H_4$ ).<sup>13</sup>C{<sup>1</sup>H}NMR (CDCl<sub>3</sub>):  $\delta$  24.0 (CH<sub>3</sub>CO<sub>2</sub><sup>-</sup>), 61.8 (CH<sub>2</sub>O), 126.3, 126.5, 128.8, 129.8, 130.5, 139.5 (C<sub>6</sub>H<sub>4</sub>), 188.5 (C=N), 194.7  $(CH_3CO_2^-)$ .<sup>13</sup>C CP MAS NMR:  $\delta$  25.3 and 26.4  $(CH_3CO_2^-)$ , 61.2 (br, CH<sub>2</sub>O), 120.0–139.0 (br, C<sub>6</sub>H<sub>4</sub>), 140.0–148.0 (br, C<sub>6</sub>H<sub>4</sub>), 190.0–198.0 (br, C=N and CH<sub>3</sub>CO<sub>2</sub>). FT IR (KBr, cm<sup>-1</sup>): 3484, 3000–2930, 2154 and 2138 [v(C=N)], 1595, 1436, 981, 476, 460. FT IR (CHCl<sub>3</sub>, cm<sup>-1</sup>): 2143  $[v(C \equiv N)]$ .  $[Rh_2(OAc)_2(MeCN)_6(CNC_6H_4-2-CH_2OSiMe_3)_2]$ - $(BF_4)_2$  (3). This compound was obtained from  $[Rh_2(OAc)_2(MeCN)_6]$ (BF<sub>4</sub>)<sub>2</sub> (250 mg, 0.34 mmol) and (I) (0.14 g, 0.74 mmol), as a light brown solid (76% yield). Anal. Calc. for C34H48B2F8N6O6Rh2Si2 (*M* = 1072.39): C, 38.08; H, 4.51; N, 7.84. Found: C, 38.40; H, 4.43; N, 7.59%. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 0.17 (s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>), 2.09 (s, 3H, CH<sub>3</sub>CO<sub>2</sub>), 2.66 (s, 6H, CH<sub>3</sub>CN), 4.97 (s, 2H, CH<sub>2</sub>OSi), 7.47–7.68 (m, 4H, C<sub>6</sub>H<sub>4</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta - 0.5$  (Si(CH<sub>3</sub>)<sub>3</sub>), 3.9 (CH<sub>3</sub>CN), 23.3 (CH<sub>3</sub>CO<sub>2</sub><sup>-</sup>), 60.9 (CH<sub>2</sub>OSi), 123.4-138.6 (m, C<sub>6</sub>H<sub>4</sub>), 193.8 ( $CH_3CO_2^-$ ), the signal corresponding to the isocyanide carbon C N was not detected. FT IR (KBr,  $cm^{-1}$ ): 3072–2955, 2336, 2176[v(C=N) isocyanide], 1566, 1448, 1254, 1057, 870, 843, 762 and 714

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