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# The first example of Re(IV)-mediated nitrile-hydroxylamine coupling

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# Abstract

The metal-mediated coupling between the acetonitriles in *cis*-[Re<sup>IV</sup>Cl<sub>4</sub>(MeCN)<sub>2</sub>] and the *N*,*N*-dibenzylhydroxylamines  $R_2^3$ NOH (R<sup>3</sup> = CH<sub>2</sub>Ph, CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>Cl-*p*) proceeds smoothly in CH<sub>2</sub>Cl<sub>2</sub>/MeCN at 20–25 °C for ca. 15 min to accomplish new imino species *cis*-[ReCl<sub>4</sub>{NH=C(Me)ONR<sub>2</sub><sup>3</sup>}] (R<sup>3</sup> = CH<sub>2</sub>Ph, 1, CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>Cl-*p*, 2) in ca. 70% yield. The structures of the isolated compounds were based on elemental analyses (C, H, N), IR, FAB<sup>+</sup>-MS and on X-ray data for 1. © 2006 Published by Elsevier B.V.

Keywords: Nitriles; Rhenium(IV) complexes; Nucleophilic addition; Metal-mediated reactions; Dibenzylhydroxylamines; Imino complexes

Nucleophilic addition to nitriles, RC=N, represents an attractive way to new organic and coordination compounds with a variety of applications, e.g. in polymer industry, pharmacology, and environmental protection [1,2]. The reactivity of organonitriles has already been summarized in some comprehensive reviews [1,3,4], giving an idea that nitriles, in particular unreactive RCN species with donor R groups, should be subjected to additional electrophilic activation in order to perform the nucleophilic addition. One of the most effective routes to reach this activation is coordination to a metal center [1], and the benefits in reactivity could be so significant that coupling of coordinated nitriles might proceed with even weak HON-nucleophiles (i.e. oximes) to accomplish imino species, and the reaction opens up (upon liberation of the obtained ligands) a route to new uncommon or even unknown compounds in organic chemistry.

Recently we discovered that HON-nucleophiles, such as oximes and dialkylhydroxylamines, can effectively promote the conversion of phthalonitriles to phthalocyanines (PCs) [5]. In the case of oximes and in the presence of a metal salt (viz. NiCl<sub>2</sub>), the reaction proceeds via the formation of intermediate complex A (Fig. 1), generated through the double nucleophilic addition of  $R^1R^2C$ =NOH species by the oxygen to a nitrile carbon, which further reacts with 2 equiv. of phthalonitriles to form metal-Pcs [5].

Furthermore, it was recently observed [6] that the use of N,N-dialkylhydroxylamines, HONR<sub>2</sub><sup>3</sup>, as alternative HON-nucleophiles in the synthesis of PCs, leads to an enhancement of the reactivity, which suggests that the hydroxylamines have a higher nucleophilicity than the oximes. This relative behaviour has recently been confirmed by a kinetic study [7].

However, in contrast with the diversity of the addition reactions of various oximes to nitriles, coordinated to different metal centers, e.g. (Pt<sup>IV</sup>, Re<sup>IV</sup>, Rh<sup>III</sup>) [8a,8b,8c,8d], there are only a few works devoted to the hydroxylamine–nitrile coupling [7,9]. Thus, our previous studies demonstrate that the reaction of dialkyl- and dibenzylhydroxylamines (HONR<sub>2</sub><sup>3</sup>, R<sup>3</sup> = Me, Et, CH<sub>2</sub>Ph, CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-Cl-*p*) with coordinated nitriles in the platinum(II) and platinum(IV) complexes [PtCl<sub>n</sub>(RCN)<sub>2</sub>] (*n* = 2,4) and [Ph<sub>3</sub>-PCH<sub>2</sub>Ph][PtCl<sub>n</sub>(RCN)] (*n* = 3,5) affords, upon addition of the hydroxylamine oxygen to the carbon atom of the

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RC $\equiv$ N ligands, structurally relevant Pt<sup>II</sup>- and Pt<sup>IV</sup>-imino species [PtCl<sub>n</sub>{NH=C(Et)ONR<sub>2</sub><sup>3</sup>}<sub>2</sub>] or [Ph<sub>3</sub>PCH<sub>2</sub>Ph]-[PtCl<sub>n</sub>{NH=C(Et)ONR<sub>2</sub><sup>3</sup>}], correspondingly [9].

In order to widen the application of the higher nucleophilicity of dialkylhydroxylamines towards coordinated organonitriles as compared to oximes, we decided to extend the work to other metal-centers and focused our attention on Re<sup>IV</sup> nitrile complexes. Moreover, it is known that Re centers can activate nitriles towards either electrophilic or nucleophilic additions depending on the metal oxidation state (in contrast with the Pt<sup>II,IV</sup>-centers for which only electrophilic activation of nitriles is known [1]). In fact, the electron-rich Re<sup>I</sup>-phosphinic centers *trans*- and *cis*-{ReCl(Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>} strongly activate nitrile ligands towards electrophilic but not nucleophilic addition [10]. Thus, we have now investigated the activation of nitriles by the electron-poor Re<sup>IV</sup> center and report herein the first example of a Re<sup>IV</sup>-mediated nitrile–hydroxylamine HONR<sup>3</sup><sub>2</sub> (R<sup>3</sup> = CH<sub>2</sub>Ph, CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>Cl-*p*) coupling.

The coupling between the acetonitriles in *cis*-[ReCl<sub>4</sub> (MeCN)<sub>2</sub>] and the dibenzylhydroxylamines  $R_2^3$ NOH (R<sup>3</sup> = CH<sub>2</sub>Ph, CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>Cl-*p*), Scheme 1, proceeds smoothly in CH<sub>2</sub>Cl<sub>2</sub>/MeCN at 20–25 °C for ca. 15 min and the subsequent workup provides the isolation of the new imino species *cis*-[ReCl<sub>4</sub>{NH=C(Me)ONR<sub>2</sub><sup>3</sup>}] (R<sup>3</sup> = CH<sub>2</sub>Ph, 1,



Scheme 1. Re<sup>IV</sup>-mediated nitrile-hydroxylamine coupling.

CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>Cl-*p*, **2**) in ca. 70% yield [11]. The isolated compounds were characterized by elemental analyses (C, H, N), IR, FAB<sup>+</sup>-MS and also **1** by a single crystal X-ray diffraction [12]. Despite the numerous attempts to obtain the corresponding products of addition of dialkylhydroxylamines,  $R_2^3$ NOH (R<sup>3</sup> = Me, Et), or monosubstituted alkylhydroxylamine, R<sup>3</sup>NHOH (R<sup>3</sup> = Me), to *cis*-[ReCl<sub>4</sub>(MeCN)<sub>2</sub>], we were unable to isolate any significant quantities of the expected imine products, presumably due to their instability and/or occurrence of side reactions.

Compounds 1 and 2 gave satisfactory C. H. and N elemental analyses. The FAB<sup>+</sup>-MS spectra of both compounds display the molecular ion peaks and those derived from fragmentation, corresponding to the sequential loss of Cl ligands, viz.  $[M-nCl]^+$ , as observed previously for [ReCl<sub>4</sub>(imine)<sub>2</sub>] complexes [8b]. In the IR spectra, 1 and 2 display no band that could be assigned to a  $v(C \equiv N)$  stretching vibration (such a band appears at 2293 cm<sup>-1</sup> for the parent *cis*-[ReCl<sub>4</sub>(MeCN)<sub>2</sub>] [13]), but show one intense band in the range of  $1660-1595 \text{ cm}^{-1}$ assigned to v(C=N) of the newly formed imino group C=NH. These data match well with those obtained for the related complexes, e.g. cis-[ReCl<sub>4</sub>{NH=C(Me)ON=  $(CR^{1}R_{2}^{2})$  [8b], derived from the addition of oximes to Re-bound acetonitriles. The molecular structure of 1 has been determined by single-crystal X-ray diffraction analysis (Fig. 2).

Crystallographic data are summarized in [14,15], while selected bond lengths and angles are given in the legend to Fig. 2. The rhenium(IV) imino complex **1** has a slightly distorted octahedral geometry and both imino ligands are



Fig. 2. The crystal structure of *cis*-[ReCl<sub>4</sub>{NH=C(Me)ON(CH<sub>2</sub>Ph)<sub>2</sub>]<sub>2</sub>] (1). Selected bond lengths (Å) and angles (°) for 1 are Re(1)–N(1) 2.105(2), Re(1)–N(3) 2.108(2), Re(1)–Cl(1) 2.3322(5), Re(1)–Cl(2) 2.3638(5), N(1)–C(1) 1.277(3), C(1)–O(10) 1.351(2), O(1)–N(2) 1.482(2), N(2)– C(3) 1.486(3), C(1)–C(2) 1.482(3), Cl(1)–Re(1)–Cl(2) 81.31(2), N(1)–Re(1)–Cl(1) 172.18(5), N(1)–Re(1)–Cl(2) 83.52(5), C(1)–N(1)– Re(1) 137.27(14), N(1)–C(1)–O(10) 121.4(2), C(1)–O(10)–N(2) 112.10(15), N(1)–C(1)–C(2) 127.0(2); hydrogen bond: N(1)–H(1) 0.89, H(1) … N(2) 2.16 N(1) … N(2) 2.590(2), N(1)–H(1) … N(2) 113.1, N(3)–H(3) 0.91, H(3) … N(4) 2.16, N(3) … N(4) 2.658(2), N(3)– H(3) … N(4) 113.4.

mutually *cis* and in the *E*-configuration. The Re—Cl bond lengths [2.105(2) and 2.108(2) Å] and all bond angles around the Re center are as expected [16], and they are in a good agreement with those obtained for the related complexes *cis*-[ReCl<sub>4</sub>{NH=C(Me)ON=C(R)}<sub>2</sub>] (R = C<sub>5</sub>H<sub>10</sub>, C<sub>9</sub>H<sub>18</sub>) [8b]. The two C=NH bonds in **1** are equal within  $3\sigma$  [1.277(3) and 1.286(3) Å] and they correspond to typical values (1.26–1.29 Å) [16] for C=N double bonds. All other bond lengths and angles for compound **1** are not unusual and are within the expected limits [16]. Inspection of the N—H and NH···N distances and values of the H—N···H angles in the imine ligands clearly indicates that the *E*-configuration of these species is stabilized by a N—H···H hydrogen bond between the imine hydrogen and the hydroxylamine N atom.

Thus, we extended the nitrile–hydroxylamine coupling, previously observed only at Pt centers [7,9], to another metal and reported the first example of a Re<sup>IV</sup>-mediated integration between nitriles and hydroxylamines.

### Supplementary material

Crystal data for *cis*-[ReCl<sub>4</sub>{NH=C(Me)ON(CH<sub>2</sub>Ph)<sub>2</sub>}<sub>2</sub>] have been deposited at the Cambridge Crystallographic Data Centre (CCDC) with deposition No. 601861. Copies of this information may be obtained free of charge from 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 (manuscript code here).

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- [12]  $cis_{-}[ReCl_{4}\{NH=C(Me)ON(CH_{2}Ph)_{2}\}_{2}]$  (1): Anal. Calcd. for  $C_{32}H_{36}N_{4}Cl_{4}O_{2}Re: C, 45.94; H, 4.34; N, 6.70. Found: C, 45.47; H, 4.32; N, 6.50%. FAB<sup>+</sup>-MS, <math>m/z$ : 835 [M]<sup>+</sup>, 799 [M-Cl-H]<sup>+</sup>. IR, cm<sup>-1</sup>: 3268 m-w v(N-H), 1612 v(C=N), 1192 m v(C-O).  $cis_{-}[ReCl_{4}\{NH=C(Me)ON(CH_{2}C_{6}H_{4}Cl-p)_{2}\}_{2}]$  (2): Anal. Calcd. for  $C_{32}H_{32}N_{4}Cl_{8}O_{2}Re: C, 39.44; H, 3.31; N, 5.75. Found: C, 40.21; H, 3.12; N, 5.25%. FAB<sup>+</sup>-MS, <math>m/z$ : 973 [M]<sup>+</sup>, 903 [M-2Cl]<sup>+</sup>. IR, cm<sup>-1</sup>: 3262 m-w v(N-H), 1609 s v(C=N), 1206 m v(C-O).
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(refinement on  $F^2$ ), 392 parameters, 0 restraints. Lp and absorption corrections applied,  $\mu = 3.900 \text{ mm}^{-1}$ .

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