

Syntheses and characterization of novel ruthenium complexes based on 1,3-dicyanobenzene

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Abstract

The syntheses and full characterization of novel ruthenium complexes based on 1,3-dicyanobenzene are described. Crystal structures are reported for both [1,3-(*cis*-RuCl(P(CH₃)₃)₄N≡C)₂C₆H₄][PF₆]₂ (**1cis**) and [1,3-(*trans*-RuCl(dppe)₂N≡C)₂C₆H₄][H₂PO₄]₂ (**3'**). Ligand substitution in the homobimetallic complex (**3**) leads easily to the monometallic analogue, [1,3-(*trans*-RuCl(dppe)₂N≡C)-C₆H₄(C≡N)][PF₆] (**4**). A heterobimetallic complex, [1,3-(*trans*-RuCl(dppe)₂N≡C)C₆H₄(C≡N-FeCp(dppe))][PF₆]₂ (**5**), of satisfactory purity is also obtained.

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1. Introduction

Organonitriles represent a class of sterically undemanding, neutral monodentate ligands; they form stable complexes with transition metals and may stabilize the metal in different oxidation states, thereby providing convenient precursors [1–3]. Nitrile complexes can be readily prepared from other nitrile complexes by nitrile exchange reaction [1]. The coordination chemistry of ruthenium(II) with tertiary phosphines [4,5] and chelating diphosphine ligands [6–9] received much attention in the last decades because of their potential application in the field of homogeneous catalysis [10]. The chemistry of ruthenium(II) phosphines with simple, monodentate nitriles (i.e. acetonitrile) has been thoroughly investigated [11–15] and also a series of ruthenium(II) dihydrogen complexes have been prepared [16,17]. Garcia et al. synthesised a series of iron(II) and ruthenium(II) nitrile complexes [18–21], as model donor–

acceptor systems, to probe the effects of structural variation on non-linear optical (NLO) properties [22,23]. However, relatively few papers are reported on transition metal-coordinated polynitriles [24–26] including those [27,28] developed into metallodendrimers [29–31].

As a part of our research program on the field [27,28], we wished to prepare a series of ruthenium(phosphine) complexes based on 1,3-dicyanobenzene (1,3-DCB or *m*-DCB) that can theoretically behave as mono- and/or bidentate ligands. Janczak and Kubiak determined and compared the crystal structures of all isomers (*o*- [32], *m*- [33], and *p*- [34]) of dicyanobenzene. The ring distortions occurring within each structure were analyzed in terms of the distribution of the charge density caused by the two highly polar nitrile groups. We intended to utilize 1,3-DCB as a bifunctional model compound and its ruthenium complexes as potential building blocks for nitrile-based metallodendrimer synthesis. During the course of this work, Fillaut et al. reported the synthesis of wire-like mono- and poly-nuclear molecules based on the core *trans*-[Ru(alkynyl)(nitrile)(dppe)₂][PF₆] using 1,4-DCB as

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a bridging ligand [35]. Cordiner et al. have recently described a series of Group 8 benzonitrile complexes including homobimetallic ruthenium and iron complexes of 1,4-DCB [36].

2. Results and discussion

1,3-DCB was reacted overnight with different ruthenium precursors (2.5 molar ratio) in refluxing 1,2-dichloroethylene (DCE), TlPF₆ was used as a chloride abstracting agent (Chart 1). As a standard work-up procedure, after filtration of TlCl and evaporation of the solvent under vacuum, the residue was washed with diethyl ether, and reprecipitated from concentrated dichloromethane solution by addition of diethyl ether. ³¹P NMR was used to determine the composition of the yielded microcrystalline powders (Table 1). ¹H and ¹³C NMR assignments were also made when pure compounds were successfully isolated.

The reaction of 1,3-DCB with *trans*-RuCl₂(P(CH₃)₃)₄ gave a mixture of different components, making full ¹H NMR assignment impossible. However, the formation of the expected dicationic complex, [1,3-(*cis*-RuCl(P(CH₃)₃)₄N≡C)₂C₆H₄][PF₆]₂ (**1cis**), as the main product (68–70%), was confirmed based on ³¹P NMR analysis and from the integration ratio between the aromatic and methyl protons in the ¹H NMR spectrum. The formation of a well-known, undesired binuclear side product, resulting from a rearrangement into this halide-bridged dimer, [Ru(PMe₃)₃]₂[μ-Cl]₃[PF₆]₃ (8–10%) can also be detected from both the ³¹P NMR (21.5 ppm) [37] and TOF-MS analysis (*m/z* = 765.1 Da). Despite failed purification efforts, single crystals of **1cis** suitable for X-ray analysis were obtained at micro-scale levels. This was achieved by

the slow diffusion of diethyl ether into its dichloromethane solution. The X-ray structure of **1cis** was thus successfully determined (see Section 4.8).

The reaction of 1,3-DCB with *trans*-RuCl₂(dppm)₂ (dppm = bis(diphenylphosphino)methane) yielded highly complicated ¹H and ³¹P NMR spectra. The ³¹P NMR spectrum showed four multiplets, which were assigned to [1,3-(*cis*-RuCl(dppm)₂N≡C)₂C₆H₄][PF₆]₂ (**2**, 85–87%). The pair of triplets (13–15%) observed in the spectrum at 0.59 and –25.04 ppm (with *J*(³¹P–³¹P) = 36.6 Hz) was attributed to the previously characterised ruthenium(II) complex, *cis*-RuCl₂(dppm)₂ [38]. The formation of this complex can be explained by the thermal isomerization of the starting *trans*-RuCl₂(dppm)₂ complex [6]. The presence of four multiplets in **2** suggests the non-equivalency of the phosphorus donor atoms when the chelating dppm ligand is used for complexation. Similar ³¹P NMR patterns were observed for the previously described, related acetonitrile complexes, *cis*-[RuCl(CH₃CN)(dppm)₂]₂X, (X = BF₄ [12], X = PF₆ [11]). The bis-(acetonitrile) complexes, *cis*-[Ru(CH₃CN)₂(dppm)₂]₂X₂ (X = OTf [13], X = PF₆ [11]), also retained this stereochemistry with the four-membered ring diphosphine. However, the Higgins' group observed that the stereochemical outcome of ligand substitution reactions in related complexes can often be controlled simply by the order of addition of the reagents [12,39]. The low symmetry of the molecule, originating from the *cis* stereochemistry of **2**, explains the highly complex ¹H NMR spectrum in the aromatic region. The presence of **2** was also confirmed by TOF-MS, which shows the proper distribution of peaks around *m/z* = 2083.39 [M⁺–(PF₆)] and 1938.41 Da equivalent to [M⁺–(PF₆)₂].

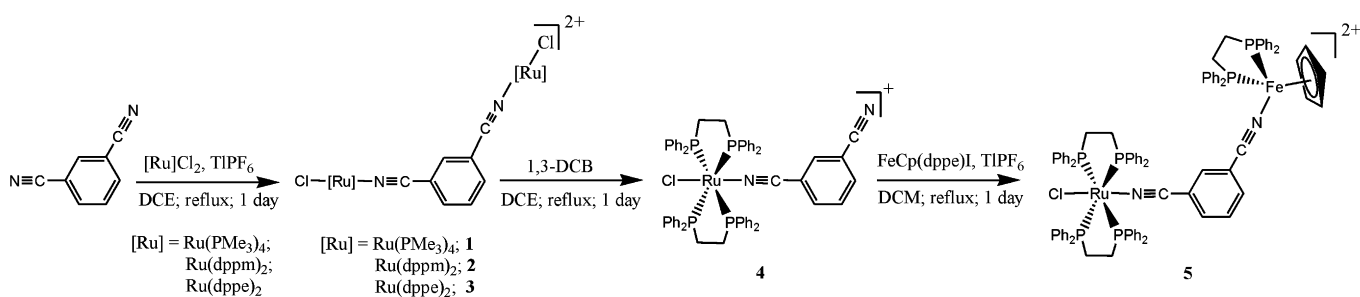


Chart 1. Reaction scheme (PF₆[−] counter ion(s) omitted).

Table 1
The composition of the reaction mixtures as analyzed by ³¹P NMR

| Ru-precursor | Composition |
|--|--|
| <i>trans</i> -RuCl ₂ (P(CH ₃) ₃) ₄ | [1,3-(<i>cis</i> -RuCl(P(CH ₃) ₃) ₄ N≡C) ₂ C ₆ H ₄][PF ₆] ₂ (1cis , 68–70%) [1,3-(<i>trans</i> -RuCl(P(CH ₃) ₃) ₄ N≡C) ₂ C ₆ H ₄][PF ₆] ₂ (1trans , 21–23%) [Ru(P(CH ₃) ₃) ₃] ₂ [μ-Cl] ₃ [PF ₆] ₃ (8–10%) |
| <i>trans</i> -RuCl ₂ (dppm) ₂ | [1,3-(<i>cis</i> -RuCl(dppm) ₂ N≡C) ₂ C ₆ H ₄][PF ₆] ₂ (2 , 85–87%) <i>cis</i> -RuCl ₂ (dppm) ₂ (13–15%) |
| <i>cis</i> -RuCl ₂ (dppe) ₂ | [1,3-(<i>trans</i> -RuCl(dppe) ₂ N≡C) ₂ C ₆ H ₄][PF ₆] ₂ (3 , 100%) |

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