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Cyclometalated ruthenium(II) complexes of benzo[*h*]quinoline (bzqH)$[Ru(bzq)(NCMe)_4]^+$, $[Ru(bzq)(LL)(NCMe)_2]^+$, and $[Ru(bzq)(LL)_2]^+$ (LL = bpy, phen)

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ABSTRACT

Cyclometalation of benzo[*h*]quinoline (bzqH) by $[RuCl(\mu\text{-}Cl)(\eta^6\text{-}C_6H_6)]_2$ in acetonitrile occurs in a similar way to that of 2-phenylpyridine (phpyH) to afford $[Ru(bzq)(MeCN)_4]PF_6$ (**3**) in 52% yield. The properties of **3** containing 'non-flexible' benzo[*h*]quinoline were compared with the corresponding $[Ru(phpy)(MeCN)_4]PF_6$ (**1**) complex with 'flexible' 2-phenylpyridine. The $[Ru(phpy)(MeCN)_4]PF_6$ complex is known to react in MeCN solvent with 'non-flexible' diimine 1,10-phenanthroline to form $[Ru(phpy)(phen)(MeCN)_2]PF_6$, being unreactive toward 'flexible' 2,2′-bipyridine under the same conditions. In contrast, complex **3** reacts both with phen and bpy in MeCN to form $[Ru(bzq)(LL)(MeCN)_2]PF_6$ {LL = bpy (**4**) and phen (**5**)}. Similar reaction of **3** in methanol results in the substitution of all four MeCN ligands to form $[Ru(bzq)(LL)_2]PF_6$ {LL = bpy (**6**) and phen (**7**)}. Photosolvolysis of **4** and **5** in MeOH occurs similarly to afford $[Ru(bzq)(LL)(MeCN)(MeOH)]PF_6$ as a major product. This contrasts with the behavior of $[Ru(phpy)(LL)(MeCN)_2]PF_6$, which lose one and two MeCN ligands for LL = bpy and phen, respectively. The results reported demonstrate a profound sensitivity of properties of octahedral compounds to the flexibility of cyclometalated ligand. Analogous to the 2-phenylpyridine counterparts, compounds **4**–**7** are involved in the electron exchange with reduced active site of glucose oxidase from *Aspergillus niger*. Structure of complexes **4** and **6** was confirmed by X-ray crystallography.

1. Introduction

Cyclometalated ruthenium and osmium complexes have a diverse spectrum of challenging chemical and biochemical properties and potential applications. They are involved in a rapid electron exchange with the active sites of various oxidoreductases and mediate the electron transfer between the enzymes and an electrode [1–6]. Among intriguing chemical features of the ortho-metalated ruthenium derivative of 2-phenylpyridine **1** is a remarkably different reactivity toward two structurally similar bidentate diimine ligands, *viz.* 2,2′-bipyridine and 1,10-phenanthroline (Scheme 1). The ligand substitution reaction between yellow compound **1** with phen cleanly affords brownish compound $\mathbf{2}_{phen}$ in acetonitrile, whereas the bpy ligand just changes the color of **1** into brownish-red without any ligand replacement under identical conditions [4,7]. Photochemical properties of $\mathbf{2}_{phen}$ and $\mathbf{2}_{bpy}$ are also different. Irradiation of $\mathbf{2}_{phen}$ and $\mathbf{2}_{bpy}$ in methanol at room temperature causes photosolvolysis of two and one MeCN ligands, respectively [4]. However, physico-chemical properties of 2,2′-bipyridine and 1,10-phenanthroline are very close and the reasons for such different chemistries, particularly for compound **1**, are still unclear and as such need to be studied more deeply. The major structural dissimilarity of 2,2′-bipyridine and 1,10-phenanthroline is their in-plane rigidity. Nitrogens of bpy have a higher mobility due to a rotation of the pyridine rings around the C–C bond. This is prohibited for phen. The mobility of the *C* and *N* donor centers of *o*-2-phenylpyridinato ligand is obviously similar to that of bpy. Thus, the chemistries described previously [1,4,5] involved combinations of ligands *CN*-flexible–*NN*-flexible and *CN*-flexible–*NN*-nonflexible, orthoruthenated *o*-2-phenylpyridinato being always a flexible partner. In order to verify this flexibility hypothesis, we were intrigued to see the properties of the structurally similar orthoruthenated compounds with the "inverse" structural motives, *viz.* with *CN*-nonflexible–*NN*-flexible and *CN*-nonflexible–*NN*-nonflexible structural combinations.

Therefore we decided to prepare a new ruthenacyclic motif with a rigid and planar benzoquinolate fragment (Scheme 1, bottom).

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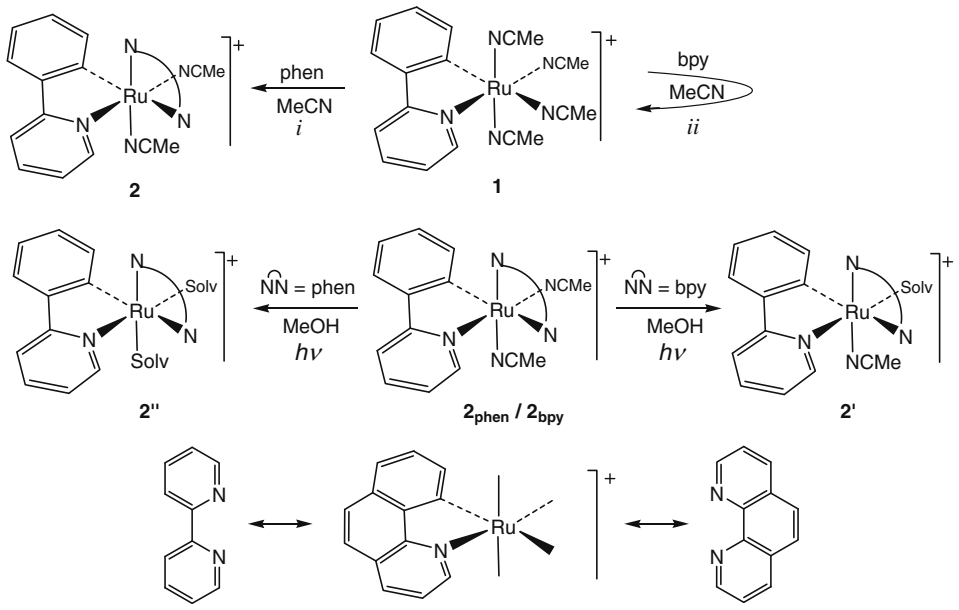

Scheme 1. Unusual properties of cycloruthenated complexes **1** and **2** [4] and cycloruthenated skeleton of benzo[*h*]quinoline (bottom) investigated in this work. See text for details.

Benzo[*h*]quinoline (bzqH) is known to form readily orthometalated complexes with various transition metals. The first preparation of palladium(II) complexes was reported in 1969 by Nonoyama et al. [8]. Ruthenium derivatives are however less common. The first complex described was the bis-metalacycle $[Ru(bzq)_2(CO)_2]$ [9], the CO ligands of which were later photosubstituted by pyridine or PPh_3 [10]. Mono-cyclometalated species $[RuCl(bzq)L_3]$ (L = CO, PPh_3) were described by Hiraki et al. [11]. The complex $[RuH(H_2)(bzq)(P^iPr_3)_2]$ was prepared from [Ru(COD)(COT)] (COD = 1,5-C_8H_{12}; COT = 1,3,5-C_8H_{10}) for studying hydrogen exchange processes [12]. An easy preparation of the neutral compound $[RuCl(\eta^6\text{-}C_6H_6)(bzq)]$ from $[RuCl(\mu\text{-}Cl)(\eta^6\text{-}C_6H_6)]_2$ and bzqH in methanol was reported very recently [13]. Related to our work, the complex $[Ru(bzq)(bpy)_2]PF_6$ (**6**) was first prepared by Reveco et al., from $[Ru(bpy)_2(MeOCH_2CH_2OMe)](PF_6)_2$ and bzqH, but the yield was just 8% [14]. In this paper, we describe a facile high-yield preparation of a series of ruthenium(II) complexes of benzo[*h*]quinoline and their physico-chemical properties including their activity as mediators in the electron exchange with glucose oxidase (GO).

2. Experimental

2.1. Syntheses

All experiments were performed under dry argon using Schlenk techniques. All solvents were dried and distilled under nitrogen prior to use. *N*,*N*-dimethylbenzylamine, 2-phenylpyridine, potassium hexafluorophosphate, tetra-*n*-butylammonium hexafluorophosphate, 2,2′-bipyridine, 1,10-phenanthroline, 1,3-cyclohexadiene, glucose oxidase from *Aspergillus niger* (type VII) were purchased from Sigma Aldrich Chemical and were used as received. Ruthenium trichloride was purchased from Strem Chemicals and converted into $[RuCl(\mu\text{-}Cl)(\eta^6\text{-}C_6H_6)]_2$ as described elsewhere [15]. The activity of glucose oxidase in terms of catalytically active FAD was determined spectrophotometrically using the extinction coefficient of $1.31 \times 10^4\ M^{-1}\ m^{-1}$ at 450 nm [16].

2.1.1. $[Ru(bzq)(NCMe)_4]PF_6$ (**3**)

To a suspension of $[RuCl(\mu\text{-}Cl)(\eta^6\text{-}C_6H_6)]_2$ (500 mg, 1.00 mmol), KPF_6 (736 mg, 4.00 mmol) and KOH (112 mg, 2.00 mmol) in 50 mL of acetonitrile was added 7,8-benzoquinoline (448 mg, 2.5 mmol). The mixture was heated at 40 °C for 60 h. The solvent was evaporated under vacuum, and the residue was dissolved in 10 mL of CH_2Cl_2. The solution was filtered through Al_2O_3, using first CH_2Cl_2, and then a 5:1 CH_2Cl_2/CH_3CN mixture as eluent. The bright yellow fraction was collected and evaporated to dryness. Crystallization from CH_2Cl_2:CH_3CN(5:1)/diethylether (slow diffusion) gave orange crystals, which were washed with diethylether and dried under vacuum (611 mg, 52%). ^1H NMR (δ, CD_3CN): 9.18 (dd, 1H, ^3J = 5.2 Hz, ^4J = 1.4 Hz), 8.26 (dd, 1H, ^3J = 8.1 Hz, ^4J = 1.35), 8.17 (dd, 1H, ^3J = 5.8 Hz, ^4J = 2.3 Hz), 7.83 (d, 1H, ^3J = 8.8 Hz), 7.67 (d, 1H, ^3J = 8.7 Hz), 7.53 (dd, 1H, ^3J = 8.0 Hz, ^4J = 5.38 Hz), 7.49 (d, 1H, ^3J = 4.0 Hz), 7.48 (s, 1H), 2.58 (s, 3H, $NCCH_3$), 1.96 (s, 3H, $NCCH_3$), 1.90 (s, 6H, $2NCCH_3$). ^{31}P NMR: −144 (hep, PF_6). MS-FAB$^+$: 444 (2%) $[M+H]^+$, 403 (25%) $[M+H-NCCH_3]^+$, 362 (5%) $[M+H-2NCCH_3]^+$, 321 (7%) $[M+H-3NCCH_3]^+$, 280 (4%) $[M+H-4NCCH_3]^+$. IR: 838 (s, PF_6), 2277 (m, $\nu_{N\equiv C}$). *Anal.* Calc. for $C_{21}H_{20}F_6N_5PRu$: C, 42.86; H, 3.43; N, 11.90. Found: C, 41.94; H, 3.48; N, 11.12%.

2.1.2. $[Ru(bzq)(bpy)(NCMe)_2]PF_6$ (**4**)

A solution of **3** (250 mg, 0.43 mmol) with 2,2′-bipyridine (132 mg, 0.85 mmol) in acetonitrile (30 mL) was stirred a room temperature for 48 h. The solvent was evaporated under vacuum, and the dark brown residue was dissolved in 10 mL of CH_2Cl_2. The solution was filtered through Al_2O_3 first using CH_2Cl_2, then a 10:3 CH_2Cl_2/NCMe mixture as eluent. The brown fraction was collected and evaporated to dryness under vacuum. Crystallization from CH_2Cl_2:CH_3CN (3:1)/diethylether (slow diffusion) gave dark brown crystals, which were washed with diethylether and dried under vacuum (171 mg, 60%). ^1H NMR (δ, CD_3CN): 9.47 (ddd, 1H, ^3J = 5.5 Hz, ^4J = 1.7 Hz, ^4J = 0.8 Hz), 8.48 (dt, 1H, ^3J = 8.0 Hz, ^4J = 1.1 Hz,), 8.44 (dd, 1H, ^3J = 6.9 Hz, ^4J = 1.1 Hz), 8.21 (td, 1H, ^3J = 7.7 Hz, ^4J = 0.5 Hz), 8.21 (dt, 1H, ^3J = 8.0 Hz, ^4J = 1.11 Hz), 8.05 (dd, 1H, ^3J = 8.0 Hz, ^4J = 1.4 Hz,), 7.91-7.86 (m, 2H), 7.74 (ddd,1H, ^3J = 5.8, Hz, ^4J = 1.7 Hz, ^4J = 0.8 Hz), 7.71-7.57 (m, 5H), 7.11 (dd, 1H, ^3J = 8.2 Hz, ^4J = 5.5 Hz), 6.84 (ddd, 1H, ^3J = 7.4, ^3J = 5.8 Hz, ^4J = 1.4), 2.25 (s, 3H, $NCCH_3$,), 2.12 (s, 3H, $NCCH_3$). ^{31}P NMR: −143.99 (hep, PF_6). MS-FAB$^+$: 663 (4%) $[M+H+PF_6]^+$, 517 (22%) $[M+H]^+$, 477 (19%) $[M+H-NCCH_3]^+$, 435 (72%) $[M+H-2NCCH_3]^+$, 279 (10%) $[M+H-2NCCH_3-bpy]^+$, 257 (7%) $[M+H-2NCCH_3-bzq]^+$.