Syntheses and properties of cyclometalated ruthenium(II) complexes with 1,10-phenanthroline and phenylphthalazine ligands

Abstract: Treatment of cis-[RuCl2(phen)]·2H2O (phen = 1,10-phenanthroline) with 1-(2,6-diisopropylphenoxy)-4-phenylphthalazine (HL1) or 1-(2,6-dimethylphenoxy)-4-phenylphthalazine (HL2) in the presence of AgPF6 afforded two cyclometalated ruthenium(II) complexes, [Ru(κ2-C,N-L1)(phen)](PF6) (1) and [Ru(κ2-C,N-L2)(phen)](PF6) (2), respectively. The two complexes have been characterized by UV–vis and luminescence spectroscopy. The structure of 1·1.5H2O has been determined by single-crystal X-ray diffraction.

Keywords: 1,10-phenanthroline; 1-phenoxy-4-phenylphthalazines; crystal structure; cyclometalated complex; phthalazine; ruthenium.

1 Introduction

In the past two decades, cycloruthenated complexes have been shown to be organometallic molecules useful for several interesting applications in various fields of chemistry, physics or biology owing to the strong σ-donor ability of the cyclometalating ligands [1–3]. For examples, they have been found to be important intermediates in the ortho functionalization of arenes via C–H activation [4], efficient dyes in dye-sensitized solar cells [5] and precatalysts for some certain processes, especially the asymmetric reduction of ketone and imines [6]. Cyclometalated ruthenium(II) complexes, [Ru(bpy)(C^N)]+ (C^N = cyclometalated bidentate ligand), bearing 2,2′-bipyridine analogous (N,C) bidentate ligands such as 2-phenylpyridine (Phpy) and its derivatives, 4-(2-pyridyl)benzaldehyde (Hpba), 2-phenylquinoline (PhQn) and so on therefore have been extensively studied. These cycloruthenated polypyridyl complexes have been used as active components in a variety of applications including supramolecular assembly, (photoinduced) electron-transfer reactions and photochemistry [7–9]. One the other hand, versatile phenylphthalazine-type ligands have only been employed in the synthesis of cyclometalated Ir(III) complexes, which exhibited unique phosphorescence properties [10–12]; with polymeric light-emitting devices doped with complex, tris(1-(2,6-dimethylphenoxy)-4-(4-chlorophenyl)phthalazine)-iridium(III), nearly 100% internal phosphorescence efficiency has been achieved [13]. Recently, we have reported the syntheses and phosphorescent properties of several heteroleptic ruthenium(II) polypyridine complexes with a series of substituted 2,2′-bipyridine ligands [14]. In this paper, we report the synthesis, structure and electronic properties of two cyclometalated ruthenium(II) complexes with 1,10-phenanthroline and phenylphthalazine-type (N,C) ligands.

2 Experimental section

2.1 General

All synthetic manipulations were carried out under dry nitrogen by standard Schlenk techniques. RuCl3·3H2O was used as purchased from Pressure Chemical Co. Ltd. cis-[RuCl2(phen)]·2H2O [15], 1-(2,6-diisopropylphenoxy)-4-phenylphthalazine (HL1) and 1-(2,6-dimethylphenoxy)-4-phenylphthalazine (HL2) [13] were prepared according to the literature methods. 1H NMR spectra were recorded on a Bruker ALX 400 spectrometer operating at 400 MHz and chemical shifts (δ, ppm) are reported with reference to SiMe4. Electronic absorption spectra were obtained on a Shimadzu UV-3000 spectrophotometer. Photoluminescence (PL) spectra were measured with a Shimadzu RF-5301PC fluorescence spectrophotometer. Positive-ion electrospray ionization mass spectra were recorded on a Perkin Elmer Sciex API 365 mass spectrometer. Elemental analyses were carried out using a Perkin-Elmer 2400 CHN analyzer.
2.2 General procedure for the preparation of the ruthenium complexes 1 and 2

cis-[RuCl₂(phen)]·2H₂O (0.62 g, 1.1 mmol), the phenylphthalazine ligand (1 equiv., 1.1 mmol) and AgPF₆ (0.56 g, 2.2 mmol) were added to ethylene glycol (20 mL), and the mixture was heated at 160°C for 2 h, during which the solution turned dark blue. The solution was stirred for additional 2 h and then cooled to room temperature. A black precipitate was obtained by filtration and recrystallized from CH₂Cl₂–hexane (1:1, v/v) to give a dark red crystalline product.

2.3 [Ru(κ²-C,N-L1)(phen)]²⁺(PF₆⁻) (1)

Yield: 0.67 g, 63% (based on ruthenium). - ¹H NMR (D₂[DMSO]): δ = 1.24 (d, J = 8.0 Hz, 12H), 2.92 (m, 2H), 6.53 (d, J = 7.6 Hz, 1H), 6.65 (d, J = 7.6 Hz, 1H), 6.91 (t, J = 7.2 Hz, 1H), 6.98 (d, J = 7.2 Hz, 1H), 7.03–7.11 (m, 4H), 7.41–7.52 (m, 6H), 7.66 (d, J = 7.2 Hz, 1H), 6.89 (t, J = 7.2 Hz, 1H), 6.98 (d, J = 8.4 Hz, 1H), 8.32 (m, 3H), 8.42 (m, 2H), 8.30 (m, 3H), 8.42 (m, 2H), 8.98 (d, J = 8.8 Hz, 1H). – MS (FAB): m/z = 826 [M–PF₆⁻]⁺. – Anal. for C₅₀H₄₀N₆F₆PRu: calcd. C 61.85, H 4.15, N 8.70%.

2.4 [Ru(κ²-C,N-L2)(phen)]²⁺(PF₆⁻) (2)

Yield: 0.56 g, 56% (based on ruthenium). - ¹H NMR (D₂[DMSO]): δ = 2.23 (s, 6H), 6.52 (d, J = 7.6 Hz, 1H), 6.65 (d, J = 7.6 Hz, 1H), 6.89 (t, J = 7.2 Hz, 1H), 6.98 (d, J = 7.2 Hz, 1H), 7.03–7.10 (m, 4H), 7.41–7.52 (m, 6H), 7.66 (d, J = 4.8 Hz, 1H), 7.96 (d, J = 8.4 Hz, 4H), 8.06 (d, J = 7.6 Hz, 2H), 8.13 (d, J = 4.8 Hz, 1H), 8.30 (m, 3H), 8.42 (m, 2H), 8.98 (d, J = 8.8 Hz, 1H). – MS (FAB): m/z = 770 [M–PF₆⁻]⁺. – Anal. for C₄₆H₃₁N₁₂F₄PRu: calcd. C 71.67, H 4.19, N 10.91; found C 71.63, H 4.15, N 10.93%.

2.5 X-ray crystallography

The crystallographic data and experimental details for [Ru(κ²-C,N-L1)(phen)]²⁺(PF₆⁻)·1.5H₂O (1·1.5H₂O) are summarized in Table 1. Intensity data were collected on a Bruker SMART APEX 2000 CCD diffractometer using graphite-monochromatized MoKα radiation (λ = 0.71073 Å) at T = 296(2) K. The collected frames were processed with the software SAINT [16]. The data were corrected for absorption using the program SADABS [17]. The structure was solved by Direct Methods and refined by full-matrix least squares on F² using the SHELXTL software package [18]. All non-hydrogen atoms were refined anisotropically. The positions of all hydrogen atoms were generated geometrically (C–H = 0.97 Å, and C–H = 0.93 Å), assigned isotropic displacement parameters and allowed to ride on their respective parent carbon atoms before the final cycle of least-squares refinement.

Cambridge Crystallographic Data Centre (CCDC) 1510576 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The CCDC via www.ccdc.cam.ac.uk/data_request/cif.

3 Results and discussion

Berlinguette et al. stated that the HOMO of a [Ru(N²⁺)(C=N)⁺] complex is localized on the Ru/C=N unit [19]. Therefore, extensive research has focused on the design of new HC=N ligands. According to a CCDC search, most of the HC=N ligands are 2-phenylpyridine and its derivatives [20, 21]. 4-Phenylphthalazine compounds...
have a structure similar to that of 2-phenylpyridine and could be easily synthesized and modified. As a result, we tried the reactions of two 4-phenylphthalazine compounds with cis-[RuCl(phen)] · 2H2O in the presence of AgPF6 in ethylene glycol. As is shown in Scheme 1, two cyclometalated ruthenium(II) complexes, [Ru(k2-C,N-L1)(phen)][PF6] (I) and [Ru(k2-C,N-L2)(phen)][PF6] (2), were obtained by the treatment of cis-[RuCl(phen)] · 2H2O with 1-(2,6-diisopropylphenoxy)-4-phenylphthalazine (HL1) or 1-(2,6-dimethylphenoxy)-4-phenylphthalazine (HL2), respectively, in moderate yields. The synthesis of the cationic complexes involved the use of AgPF6 to abstract chloride ions from the cis-[Ru(phen)2Cl2] · 2H2O precursor. The resulting intermediate [Ru(phen)2]2+ coordinated to the potential bidentate C^N ligand to give the cycloruthenated complexes.

Single crystals of [Ru(k2-C,N-L1)(phen)][PF6] · 1.5H2O (1 · 1.5H2O) were grown by vapor diffusion of hexane into a CH2Cl2 solution of the complex. Complex 1 · 1.5H2O crystallizes in the monoclinic space group C2/c with Z = 8. Figure 1 shows the structure of the [Ru(k2-C,N-L1)(phen)]2+ cation, and selected bond distances and angles are given in the figure caption. The structure exhibits no surprises, being similar to that of the analogous complex in which the metal center is replaced by iridium and the 4-phenyl moiety in L1 is substituted by 4-(4′-Cl-phenyl) [13]. The ruthenium atom lies in a distorted octahedral environment. The Ru–C(25) bond length of 1.989(2) Å is significantly shortened with respect to the average Ru–N length of 2.089(4) Å observed for the phen N(1), N(2), N(3), N(4) atoms, in good agreement with data for the complex bis(2,2′-bipyridyl)(4-nitro-2-(2-pyridyl)phenyl) ruthenium(II) [Ru–C 1.997(7) Å, av. Ru–N 2.080(5) Å] [19]. A tendency for increased ruthenium–nitrogen bond lengths in the trans position with respect to the Ru–C bond can be recognized [Ru–N(1) = 2.169(5) Å]. The increase of this Ru–N(1) bond length is indeed the most noticeable geometrical change introduced in the coordination sphere of the metal atom by the presence of a carbon atom, as also
observed for other [Ru(bpy)₂(C^N)]⁺ complexes [22]. The N(phen)–Ru–N(phen) bond angles of 78.0(2)° and 80.0(2)° in 1·1.5H₂O are near to the chelate angle N(5)–Ru–C(25) of 78.7(2)°.

The UV–vis absorption spectra of the new cycloruthenated complexes 1 and 2, together with the parent complex [Ru(bpy)₃](PF₆)₂, in CH₃CN at room temperature are shown in Fig. 2. At the first glance, both spectra for complexes 1 and 2 are grossly similar and reveal three intense transitions located at 214, 265 and 492 nm for the cyclometalated complex 1 with 2,6-diisopropylphenoxy substituents, and at 220, 266 and 495 nm for the cyclometalated complex 2 with 2,6-diisopropylphenoxy substituents. The first two bands are assigned to a typical spin-allowed 1π–π* transition of the ligands, and the third band is ascribed to the metal-to-ligand charge transfer (MLCT) transition. The two spectra are similar to that of [Ru(bpy)₃](PF₆)₂. It is interesting to note that there is a red-shift of about 40 nm (492 nm for 1, 495 nm for 2, 450 nm for [Ru(bpy)₃](PF₆)₂) observed for the low-lying transition depending on the presence of a Ru–N or Ru–C linkage. This considerable shift suggests that the low-energy transition is the main signature of the charge transfer arising between the ruthenium atom and phen or 4-phenylphthalazine ligand [22]. A previous study showed that the strong phosphorescence of iridium(III) complexes with 4-phenylphthalazine ligands is quenched by Hg²⁺, Cu²⁺ and Ag⁺ cations [11]. The room temperature PL spectra of the cyclometalated ruthenium(II) complexes 1, 2 and [Ru(bpy)₃](PF₆)₂ in CH₃CN solution are illustrated in Fig. 3. Complexes 1 and 2 both are weakly luminescent.

In summary, two new cyclometalated ruthenium(II) complexes, [Ru(κ²-C,N-L1)(phen)](PF₆) (1) and [Ru(κ²-C,N-L2)(phen)](PF₆) (2), have been synthesized by reactions of cis-[RuCl₂(phen)]·2H₂O with the 4-phenylphthalazine ligands in the presence of AgPF₆ in moderate yields. According to a CCDC search, most of the cycloruthenated complexes, [Ru(N^N)₂(C^N)]⁺, involve 2-phenylpyridine and its derivatives [7–9, 20, 21]. Isolation of the two phenylphthalazine-based ruthenium(II) complexes indicates that phenylphthalazine could also be cyclometalated by ruthenium(II). The two new complexes complement the limited list of examples of 4-phenylphthalazine-based transition metal complexes [11–13]. As single crystals for one of the complexes could be obtained, the results of an X-ray diffraction study now highlight specific features of the Ru–C and the trans-Ru–N bonds. An enhanced MLCT behavior is observed in the cyclometalated derivative with respect to the parent metal–bipyridine molecule. This information is of interest and importance for the design and synthesis of a new phenylphthalazine ruthenium(II) system.

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References