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Synthesis and characterization of Ru(II) and Ir(III) complexes that bear camphoric 1,3-diamine ligands

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ABSTRACT

Two rigid *N*-monosulfonylated 1,3-diamine ligands have been prepared starting from commercially available D-camphor through three steps. Their reactions with [Ru(η^6-arene)(μ-Cl)Cl]$_2$ (arene = *p*-cymene or $C_6H_5CO_2Et$) or [Ir(η^5-C_5Me_5)(μ-Cl)Cl]$_2$ afforded five new complexes. The structures of one monosulfonamide 1,3-diamine ligand and three organometallic complexes were confirmed by X-ray crystallography.

Introduction

In the last decades, bifunctional molecular catalysis based on metal-ligand cooperation has received considerable attention [1,2]. Currently, many half-sandwich-type bifunctional M/NH complexes, particularly Ru(II) and Ir(III) complexes, that bear chiral *N*-sulfonylated 1,2-diamine ligands such as 1,2-diphenylethylenediamine (dpen) and 1,2-cyclohexanediamine (cydn) have been reported and widely applied for asymmetric organic synthesis [3]. In contrast, complexes with 1,3-diamine ligands are relatively limited. It is well-established that 1,2-diamines exhibit cooperativity in chelating with transition metal atoms due to the formation of five-membered-ring complexes [2,3]. This cooperativity is weakened for 1,3-diamines because the six-membered-ring complexes formed by them are conformationally more flexible. Thus, for the design of new 1,3-diamine ligands, rigidifying the backbones should increase the stability of the corresponding complexes.

Rigid camphoric 1,3-diamine (**1**), which can be readily prepared from D-(+)-camphor [4], has been applied for asymmetric catalysis [5], the synthesis of functional Schiff-base metal complexes [4,6], the construction of supramolecular complexes, and the generation of *N*-heterocyclic carbenes [7,8]. It can also coordinate to Ni (II), Cu (II), Zn (II) and Pt (II) to give rise to discrete complexes [9–13]. We were interested in further modifying this versatile ligand by selectively sulfonylating the amino group linked to the secondary carbon atom. We envisioned that the introduction of the electron-withdrawing sulfonyl group might impose important effect on the property of the corresponding complexes. We thus synthesized compounds **2** and **3** (Fig. 1). In this paper, we describe the synthesis of five stable Ru(II) or Ir(III) complexes from these two ligands and the crystal structure of three of the new complexes.

Results and discussion

Synthesis of diamine ligands from D-camphor

As shown in Scheme 1, camphoric diamine (**1**) was prepared *via* Schmidt reaction from (+)-camphoric acid, which was obtained from the oxidation of D-(+)-camphor, according to reported procedure [4]. Monosulfonamides **2** and **3** were then synthesized by selective sulfamidation of **1** with tosyl chloride or pentafluorobenzenesulfonyl chloride in tetrahydrofuran using a modified procedure [5c] (Scheme 1).

The crystal structure of **2** was obtained and is provided in Fig. 2a. The related crystallographic data is summarized in Table 1. It can be seen that the cyclopentane ring of **2** possesses an envelope-like conformation with the C5 atom at the flap position and other four carbon atoms nearly in the same plane [14]. The sulfamide NH forms an intramolecular N–H···N hydrogen bond with the amine nitrogen with the NH···N distance being 2.32 Å.

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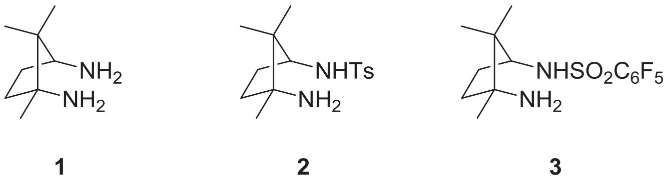


Fig. 1. Diamine ligands **1**–**3** derived from D-(+)-camphor.

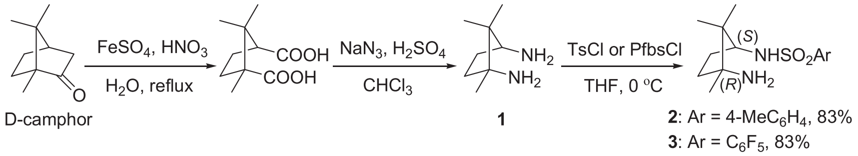
Synthesis of Ru(II) and Ir(III) complexes that bear a monosulfonyl diamine ligand

Ru(II) complexes RuCl[κ^2(*N*,*N*′)-(1*S*,3*R*)-$RSO_2NH\cap NH_2$](η^6-arene) **4a** and **4b** that bear a monosulfonyl diamine ligand were prepared as red solids by reacting [Ru(η^6-*p*-cymene)(μ-Cl)Cl]$_2$ with **2** or **3** in the presence of triethylamine in dichloromethane for 3 days at 30 °C in 87% and 84% isolated yields, respectively (Scheme 2). Complex **4c** was prepared in a procedure similar to that of **4a** by using [Ru(η^6-$C_6H_5CO_2Et$)(μ-Cl)Cl]$_2$ as a starting material (Scheme 2). For all the three reactions, only one diastereomer was obtained. The complexes have been characterized by ^{1}H and ^{13}C NMR and high resolution mass spectrometry (HRMS). The ^{1}H NMR spectra exhibited one set of signals, confirming the formation of only one diastereoisomer.

The reaction of [Ir(η^5-C_5Me_5)(μ-Cl)Cl]$_2$ with ligands **2** or **3** in the presence of triethylamine under similar conditions afforded **5a** and **5b** as yellowish solids in 70% and 73% isolated yields, respectively (Scheme 3). The two complexes were also characterized by ^{1}H and ^{13}C NMR spectroscopy and HRMS. The ^{1}H NMR spectra exhibited one set of signals, again confirming the formation of only one diastereoisomer.

*Crystal structures of Ru(II) complexes **4a** and Ir(III) complexes **5a** and **5b***

The crystal structures of **4a**, **5a** and 5**b** were obtained (Fig. 2b–d). Single crystal of **4a** was grown by slow evaporation of its methanol solution, while the crystals of **5a** and **5b** were grown by slow evaporation of their dichloromethane solution. The crystal data and structure refinements are summarized in Table 1. The bond lengths and bond angles of the cyclopentane ring in **2**, **4a**, **5a** and **5b** are collected in Table 2. Complexes **5a** and **5b** have two conformers in one unit cell. The structures of the two conformers are similar and thus only one of them is provided in Fig. 2 for both complexes. Compared with that of free ligand **2**, the conformation of the ligand in the complexes changed considerably. For all the three complexes, the sulfonyl group was orientated to the opposite direction of the complex core because of the chelation of the two nitrogen atoms to the metal atom. Thus, the benzene ring imposed a shielding effect on the two geminal methyl groups which caused their proton signals to shift upfield in the ^{1}H NMR spectra. It can be seen that, by comparing with the data of the free ligand, the chelation did not cause important change for the conformation of the cyclopentane ring of camphoric diamine, which should reflect the rigidity of this aliphatic ring.



Scheme 1. Synthesis of camphoric diamine ligands **1**–**3**.

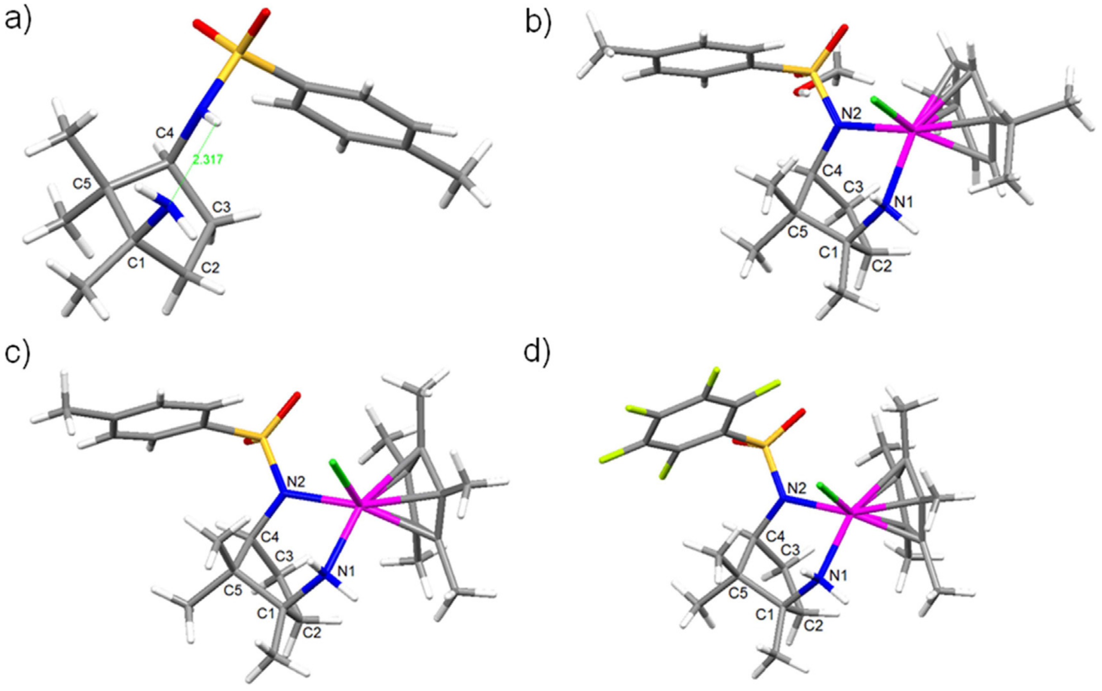


Fig. 2. X-ray crystal structures of a) ligand **2**, b) Ru(II) complex **4a**, in which methanol molecule is omitted for clarity, c) Ir(III) complex **5a**, and d) Ir(III) complex **5b**.