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Syntheses, structures and electrochemical properties of homoleptic ruthenium(III) and osmium(III) complexes bearing two tris(carbene)borate ligands

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ABSTRACT

Six-coordinate homoleptic ruthenium(III) and osmium(III) N-heterocyclic carbene complexes $[PhB(ImMe)_3]_2M(OTf)$ (M = Ru, **1a**; M = Os, **1b**) with two tris(N-heterocyclic carbene)borate ligands have been prepared and characterized by ESI-MS, elemental analyses, XPS, and single-crystal X-ray diffraction. X-ray diffraction shows that both complexes display octahedral configuration, in which the metal center is coordinated by two tridentate N-heterocyclic carbene ligands. Electrochemical properties of complexes **1a** and **1b** have been studied by cyclic voltammetry (CV) measurements, which reveal two reversible redox waves at 0.60, −0.63 V and 0.35, −0.86 V for **1a** and **1b**, respectively, indicating the strong donating nature of the tris(N-heterocyclic carbene)borate ligand.

The coordination and organometallic chemistry of N-heterocyclic carbenes (NHCs) has been of great interest in organometallic chemistry [1–4]. In the past two decades, monodentate NHCs have been extensively used as supporting ligands for organometallic catalysts [5]. Many polydentate N-heterocyclic carbenes have also been designed, and they allow preparation of organometallic compounds with a variety of geometries [6,7]. Among the polydentate N-heterocyclic carbenes, the tripodal tris(N-heterocyclic carbene)borate ligands (such as **A** and **B**, Chart 1), with a framework similar to that of the classic ligand tris(pyrazolyl)borate (Tp, **C**, Chart 1), have been of considerable interest due to their tripodal framework and chelating effect [8–26]. In contrast to the versatile coordination and organometallic chemistry of tris(pyrazolyl)borate [27,28], metal complexes with tridentate N-heterocyclic carbene ligands **A** and **B** have been limited to several metal ions.

Tris(3-alkylimidazol-2-ylidene)hydroborate $[HB(R\text{-}ImH)_3]$ (**A**, Chart 1) has been employed in the preparation of complexes of Fe(III) [8], Li(I) [9], Co(III) [10], Cu(I) [11,12], Ag(I), Au(I) [13], Mg(II), Fe(II) [14], Ni(II) [15], and Ca(II), Sr(II), Ba(II) [16]. Smith et al. have modified the tris(3-alkylimidazol-2-ylidene)hydroborate $[HB(R\text{-}ImH)_3]$ (**A**) to incorporate a phenyl group on the boron atom $[PhB(R\text{-}ImH)_3]$ (R = Me, ^{t}Bu, Mes **B**, Chart 1) and reported novel Co(II)-amido [17], Co(III)-imido [18], Mn(IV) [19], four-coordinate Fe(II) complex $PhB(MesIm)_3Fe{-}N{=}PPh_3$ [20], Fe(III)-imido [21], Fe-nitrido [22–25], and Fe(V)-nitrido [26] complexes, with interesting reactivities and properties. It is surprising that no ruthenium and osmium complex with the $Ph[B(R\text{-}ImH)_3]$ ligand has been reported yet. In comparison, the chemistry of Ru and Os complexes with tris(pyrazolyl)borate (Tp) ligand (**C**, Chart 1) has been extensively studied [27–34].

Herein we report the synthesis, structure, X-ray photoelectronic spectroscopy (XPS), and electrochemical properties of ruthenium(III) and osmium(III) complexes $[PhB(ImMe)_3]_2M(OTf)$ (M = Ru, **1a**; M = Os, **1b**) with two tris(carbene)borate ligands. To our knowledge, **1b** is the first Os(III)–NHC complex and **1a** is among a limited number of Ru(III)–NHC complexes reported in the literature [35].

The reaction of $LiPhB(MeIm)_3$, which was prepared in situ via the reaction of $[PhB(ImMe)_3](OTf)_2$ with 3.0 equals LDA, with the Ru(II) precursor $[Ru(COD)Cl_2]_n$ [36] resulted in the formation of a pale yellow solution. This air-sensitive solution was exposed to the air for several seconds with the color of the solution changing to blue, indicating the formation of a Ru(III) compound. $[PhB(ImMe)_3]_2Ru(OTf)$ (**1a**) was isolated from the solution (Scheme 1) [37]. However, the reaction of $LiPhB(MeIm)_3$ with the commercial $RuCl_3$ did not yield the same Ru(III) compound, and only an intractable product was formed. We have tried to isolate the expected Ru(II) complex before the air oxidation. However, no product could be obtained perhaps due to extreme air-sensitivity of this Ru(II) species.

A similar reaction of $LiPhB(MeIm)_3$ with $[Os(COD)Cl_2]_n$ was used to prepare the Os analog. However no obvious reaction was observed after 1 day of the reaction at any temperature between −20 and 60 °C. We then used $(Bu_4N)_2OsCl_6$ [38] as the starting material, leading to the formation of a purple solution (Scheme 1) [39]. The resulting solution was purified by column chromatography. Recrystallization from a mixture of CH_2Cl_2 and hexane gave a pure crystalline sample, which

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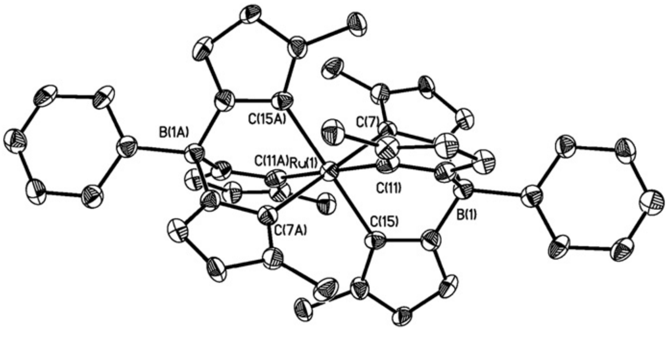

Fig. 1. ORTEP diagram of $[PhB(MeIm)_3]_2Ru(OTf)$ (**1a**). Thermal ellipsoids are shown at 30% probability. Hydrogen atoms, counterions and solvent have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru1–C7 = 2.103(4), Ru1–C11 = 2.041(5), Ru1–C15 = 2.075(4); C7–Ru1–C11 = 85.71(18), C7–Ru1–C15 = 83.41(16), C11–Ru1–C15 = 84.76(18).

was identified as $[PhB(ImMe)_3]_2Os(OTf)$ (**1b**). During the formation of **1b**, the starting Os(IV) was obviously reduced to Os(III).

Both complexes **1a** and **1b** are stable in solution and in the solid state. No decomposition was observed after standing in air for 3 months.

The X-ray crystal structures of **1a** and **1b** [40] reveal that they are unusual homoleptic Ru(III) [41–43] and Os(III) [41] complexes with two tridentate ligands (Figs. 1, 2). There are two crystallographically different molecules of **1a** and **1b** in the unsymmetrical units in their crystal structures. The metal atom in **1a** or **1b** is located on a crystallographic inversion center. The approximate S_6 geometry of these complexes is obvious if viewed along the B–M–B axis. The average metal–C bond lengths taken from the two crystallographically independent cations are 2.071 Å in **1a** and 2.077 Å in **1b**, respectively. Since no structural data was reported for the first Ru(III)–NHC complex $RuCl_2(PPh_3)[OCPh(CH_2\{1\text{-}C[NCHCHNBu^t]\})_2]$ [35] and no Os(III)–NHC complex is known, there is no reported Ru(III)/Os(III)–NHC bond length for comparison with those in **1a** and **1b**. Interestingly, the metal–NHC bond lengths in **1a** and **1b** are comparable with those reported for Ru(II) or Os(II)–NHC complexes [44–49].

Cyclic voltammetry (CV) studies have been performed on **1a** and **1b**, revealing two reversible redox waves (Fig. 3). A reversible wave with $E_{1/2}$ value at 0.60, 0.35 V vs Fc^+/Fc couple is attributed to the $Ru^{III/IV}$ and $Os^{III/IV}$ couple, respectively. Another reversible wave at −0.63, −0.86 V is attributed to the $Ru^{II/III}$ and $Os^{II/III}$ couple, respectively. Smith et al. [19] have pointed out that the tris(N-heterocyclic carbene)borate ligand is significantly more stabilizing of higher oxidation states of manganese complexes than other facially coordinating ligands, such as Tp*, Cp*, and Tp^{Me2}. The same result was also observed in our ruthenium and osmium complexes (Table 1). Earlier

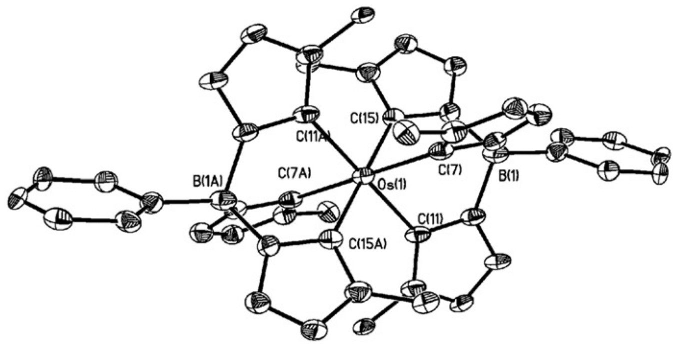

Fig. 2. ORTEP diagram of $[PhB(MeIm)_3]_2Os(OTf)$ (**1b**). Thermal ellipsoids are shown at 30% probability. Hydrogen atoms and counterions have been omitted for clarity. Selected bond lengths (Å) and angles (deg): Os1–C7 = 2.072(6), Os1–C11 = 2.081(5), Os1–C15 = 2.048(5); C7–Os1–C11 = 85.71(18), C7–Os1–C15 = 83.5(2), C11–Os1–C15 = 85.1(2).

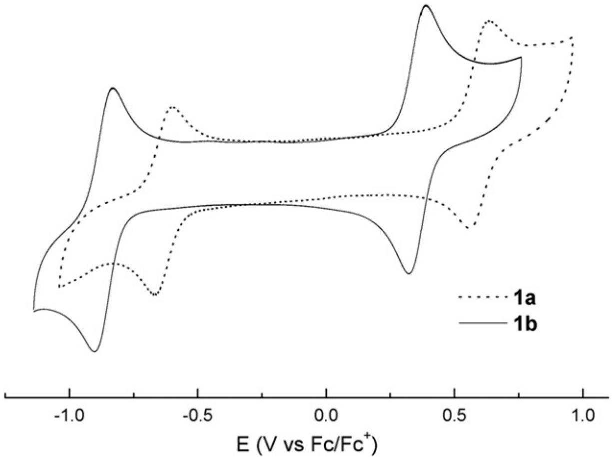

Fig. 3. Cyclic voltammograms of $[PhB(MeIm)_3]_2Ru(OTf)$ (**1a**) and $[PhB(MeIm)_3]_2Os(OTf)$ (**1b**) in MeCN/0.1 M NBu_4PF_6, glassy carbon electrode, scan rate 100 mV/s.

electrochemical studies on Cp_2Ru [41], $Cp^*{}_2Ru$ [51,52], Cp_2Os [41], $Cp^*{}_2Os$ [53] and Tp_2Ru [42,43] revealed that there is one reversible redox wave with a much more positive potential value compared to the $Ru^{II/III}$ and $Os^{II/III}$ couple in **1a** and **1b**. These CV measurement showed that both the oxidized and reduced species of **1a** and **1b** could exist. We have tried to use reductants such as sodium to reduce complexes **1a** and **b** in THF with the expectation to isolate Ru(II) and Os(II) species. A pale yellow or colorless solution formed from the reactions of **1a**, **b** with the reductant, respectively. Unfortunately, we could not isolate the expected products due to their extreme air-sensitivity. We have also attempted to oxidize complexes **1a** and **b** with the oxidants such as $(NH_4)_2Ce(NO_3)_6$, WCl_6, or NO^+PF_6. No product was isolated. It is noted that only six-coordinate homoleptic Fe(III) and Co(III) complexes were isolated from the reactions of Fe(II) or Co(II) precursor with tris(3-alkylimidazol-2-ylidene)hydroborate $[HB(R\text{-}ImH)_3]$ [8,10].

We also used XPS to probe the donating properties of carbene ligand in **1a** and **1b**. The bonding energies of Ru $3d_{5/2}$ and Os $4f_{7/2}$ of **1a**, **1b** and other related complexes are listed in Table 1. The binding energies of Ru $3d_{5/2}$ and Os $4f_{7/2}$ are 280.1 and 50.3 eV in complexes **1a** and **1b**, respectively. The binding energy of Ru $3d_{5/2}$ in **1a** (280.1 eV) is smaller than that of Ru(III) complex $[Ru(bpy)_2Cl]Cl$ (281.9 eV) [55], but very close to those of Ru(II) complexes for Cp_2Ru (280.3, 280.7 eV) [50,51] and $Cp^*{}_2Ru$ (279.7, 279.9 eV) [50,51]. Similarly, the binding energy of Os $4f_{7/2}$ in **1b** is close to those of Os(II) complexes Cp_2Os (50.6 eV) and $Cp^*{}_2Os$ (49.9 eV) [50]. The low electron binding energy in complexes **1a** and **1b** indicates that the metal centers are highly electron-rich due to the very strong electron-donating nature of the tris(carbene)borate ligand, which is in good agreement with the conclusions drawn from the electrochemical studies.

In conclusion, six-coordinate ruthenium(III) and osmium(III) complexes $[PhB(ImMe)_3]_2M(OTf)$ (M = Ru, **1a**; M = Os, **1b**) with two tris(N-heterocyclic carbene)borate ligands have been prepared and characterized. The isolation of these unusual Ru(III)–NHC and Os(III)–

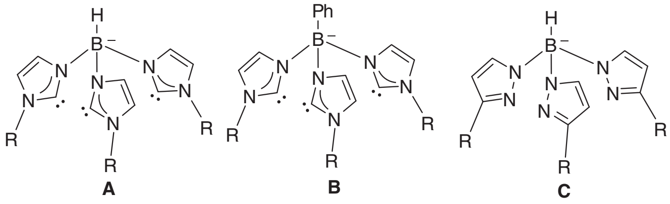

Chart 1. The tripodal borate ligands **A–C**.