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Half-sandwich Ru(II), Ir(III) and Rh(III) complexes with bridging or chelating N-heterocyclic bis-carbene ligand: Synthesis and characterization

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ABSTRACT

N-heterocyclic bis-carbene ligand (bis-NHC) which was derived from 1,1′-diisopropyl-3,3′-ethylenediimidazolium dibromide (**L·2HBr**) via silver carbene transfer method, reacted with $[(\eta^6\text{-}p\text{-cymene})\text{RuCl}_2]_2$ and $[\text{Cp}^*\text{MCl}_2]_2$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$, M = Ir, Rh) respectively, afforded complexes $[(\eta^6\text{-}p\text{-cymene})\text{RuCl}_2]_2(\text{L})$ (**1**), $[\text{Cp}^*\text{IrCl}_2]_2(\text{L})$ (**2**) and $[\text{Cp}^*\text{RhCl(L)}][\text{Cp}^*\text{RhCl}_3]$ (**3**). When $[\text{Cp}^*\text{IrCl}_2]_2$ was treated with 2 equiv AgOTf at first, and then reacted with bis-NHC ligand, $[\text{Cp}^*\text{IrCl(L)}]\text{OTf}$ (**4**) was obtained. The molecular structures of complexes **1**–**4** were determined by X-ray single crystal analysis, showing that **1** and **2** adopted bridging coordination mode, **3** and **4** adopted chelating coordination mode. All of these complexes were characterized by ^{1}H, ^{13}C NMR spectroscopy and element analysis.

1. Introduction

N-heterocyclic carbenes (NHCs) have emerged as an important class of ligands in organometallic chemistry because of their strong σ-donor electronic property which not only enhances the stability of complexes but also provides complexes with unexpected properties such as catalytic performance in C–C/C–N coupling reactions and olefin metatheses [1–11]. Transition-metal carbene complexes characterized by bischelate [5,10–19], pincer [10,20–29], or tripodal [5,30–32] coordination modes, especially bis-NHC Rh or Ir complexes, are versatile in the fields of asymmetric catalysis [2], transfer hydrogenation, hydroformylation of Olefins, hydrosilylation of terminal alkynes [5], C–H functionalization [27], hydrogenation of CO_2 to formic acid [33] etc.

Crabtree and coworkers [34] have reported that large reactivity differences and coordination preference of bis-NHC ligands were dependent on the length of linker chain and the steric size of the N-substituents. Besides, choice of counterion for the Ag–NHC intermediate also shows significant effect on coordination tendency of bis-NHC ligand [35]. Although a large number of transition-metal carbene complexes bearing bis-NHC ligand have been reported [36–43], to our knowledge there is limited research about the different coordination modes of bis-NHC metal complexes containing $(\eta^6\text{-}p\text{-cymene})$Ru(II), Cp*Ir(III) or Cp*Rh(III) fragments.

In order to study the coordination behavior of bis-NHC complex, we pay attention to bis-NHC ligand with $(\text{CH}_2)_2$ group as the linking chain and isopropyl as the N-substituent. We have studied the reactions of $[(\eta^6\text{-cymene})\text{RuCl}_2]_2$ and $[\text{Cp}^*\text{MCl}_2]_2$ (M = Ir, Rh) with bis-NHC ligand (ratio of metal/ligand = 2:1), and have successfully synthesized complexes **1**–**4**. We found significant differences on product geometry and stoichiometry when transmetalation to different metal sources. The products adopt (bis-NHC)Ru_2(II) (**1**) and (bis-NHC)Ir_2(III) (**2**) coordination mode, but chelating mode of Rh(III) (**3**) (Scheme 1). When half of the chloride were got rid of from $[\text{Cp}^*\text{IrCl}_2]_2$ primarily, it offered chelating coordination mode of Ir(III) complex (**4**) (Scheme 2). All of the products obtained can be used as precursor or model for catalytic application, the exploration is still in progress.

2. Results and discussion

2.1. Synthesis of ligand

The precursor 1,1′-diisopropyl-3,3′-ethylenediimidazolium dibromide (**L·2HBr**) was readily synthesized according to the procedure reported in literature [44] in high yield. The ligand is white and yellowish but very hygroscopic to air.

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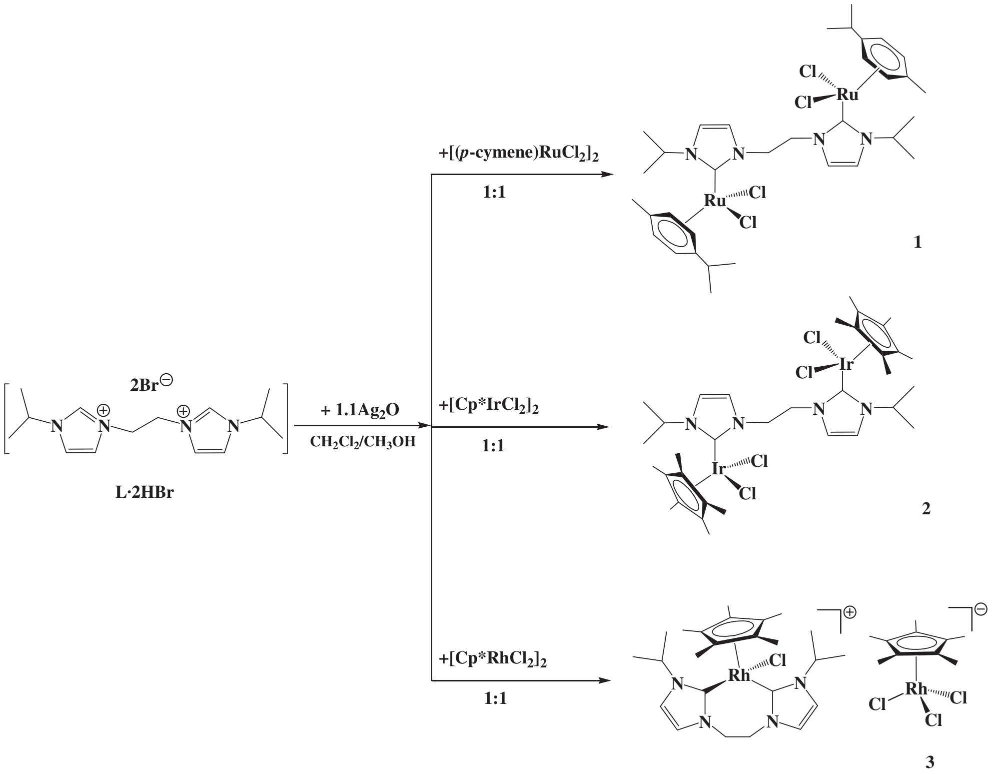


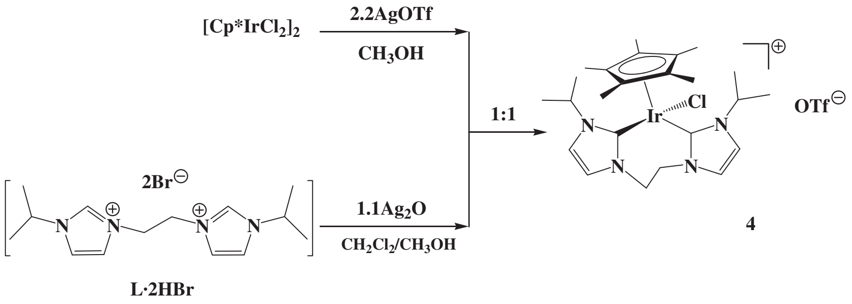
Scheme 1. Synthesis of **1**, **2** and **3**.

2.2. Transmetalation to half-sandwich Ru, Ir, and Rh complexes

We utilized a two-step silver carbene transfer method under mild condition [45]. Firstly, **L·2HBr** was treated with 1.1 equiv Ag_2O in a solution mixture of CH_2Cl_2 and CH_3OH, generating silver carbene intermediate in situ. Secondly, after filtration, the colorless filtrate continuously reacted with $[(\eta^6\text{-cymene})RuCl_2]_2$ or $[Cp^*MCl_2]_2$ (M = Ir, Rh) complexes (ratio of metal/ligand = 2:1) at room temperature, immediately produced products of **1**, **2** and **3** accordingly in good yields (Scheme 1). When 1.0 equiv $[Cp^*IrCl_2]_2$ reacted with 2.2 equiv AgOTf firstly, and then reacted with silver carbene intermediate, we got complex **4** (Scheme 2). Suitable single crystals for X-ray crystallography were obtained by the slow diffusion of hexane into a concentrated solution of them in CH_2Cl_2 respectively. The crystallographic data of them are summarized in Table 1. All of the complexes were fully characterized by ^{1}H, ^{13}C NMR spectra and elemental analyses.

An ORTEP drawing of complex **1** and selected bonds and angles are shown in Fig. 1. Complex **1** shows binuclear structure. The center metal Ru adopts a distorted octahedral geometry in which cymene group occupies three *fac* coordination sides. Ru–$C_{carbene}$ bond is nearly perpendicular to the planar Cl(1)–Ru(1)–Cl(2) with an angle of 89.7°. The length of Ru–$C_{carbene}$ bond is 2.08 Å, in the normal range of Ru–NHC bond [42,46]. The bond angle C_{cent}–Ru–$C_{carbene}$ (C_{cent} is the central point of the cymene group) is 128.3° with minimal repulsion between the cymene group and the imidazole ring. Both imidazole rings are parallel to each other. NMR spectra of **1** also confirmed this structure, which showed imidazole C–H signals at 8.14 and 7.11 ppm in ^{1}H NMR spectra and Ru–C signal at 171.7 ppm in ^{13}C NMR spectra. Compared to the analogous binuclear Ru carbene complex [42] reported by our group, it reveals that despite the change of the wingtip substituent from methyl to isopropyl, bis-NHC ligands adopt the same coordination fashion to the Ru fragment, offering products with similar configuration.

Wondered that whether the change of metal source would affect the configuration of products, we focus on the materials of $[Cp^*MCl_2]_2$ (M = Ir, Rh). Unexpectedly, under the same reaction ratio (metal/ligand = 2:1), bis-NHC ligand exhibited different



Scheme 2. Synthesis of **4**.