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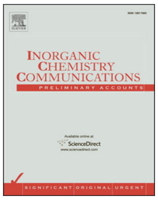

Short communication

Synthesis, characterization, and catalytic behavior of mono- and bimetallic ruthenium(II) and iridium(III) complexes supported by pyridine-functionalized *N*-heterocyclic carbene ligands

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ABSTRACT

We have prepared and characterized five unreported ruthenium(II) and iridium(III) complexes supported by pyridine-functionalized *N*-heterocyclic carbene ligands including a bimetallic iridium(III) complex. When activated, all complexes are active catalysts for the transfer hydrogenation of acetophenone.

Since Arduengo's 1991 report of an isolable, free *N*-heterocyclic carbene (NHC) [1], the coordination chemistry of NHCs has become an exceptionally fertile area of research and has been extensively reviewed [2–9]. In particular, chelating, functionalized NHC ligands [10,11] have been shown to effectively support a large number of catalytically active metal centers and circumvent catalyst decomposition by discouraging, for example, reductive elimination reactions between NHC ligands and hydrocarbyl, hydride, and acyl ligands [12]. Due, in part, to their facile preparation, pyridine-appended NHC ligands have become an active area of research. To date there have been numerous reports on the synthesis and catalytic behavior of various late transition metal centers supported by pyridine-functionalized NHCs [13–19]. Given the promising catalytic potential of these complexes, further exploration of pyridine-functionalized NHC ligand architectures is an important area of continued research.

Another burgeoning area of research in the field of organometallic synthesis and catalysis has been the development of bimetallic catalyst systems [20–22]. Bimetallic complexes are of interest for diverse purposes: from elucidating the mechanisms of metalloenzymes [23] to rate enhancements of industrially relevant catalytic processes due to cooperation between metal centers [24–26] and chemiluminescence [27]. Compared to more traditional organometallic ligands, chelating bimetallic NHC ligand architectures [28–35] and, in particular, bimetallic donor-functionalized NHC ligands [36–43] are less developed. In light of the apparent utility of bimetallic catalysts and the strong catalytic track record of metal complexes supported by donor-functionalized NHCs, further development of bimetallic complexes supported by donor-functionalized NHCs is warranted.

Catalytic transfer hydrogenation of carbonyl compounds and imines is an industrially important reaction [44,45] and a good test case for catalytic activity since the reaction proceeds under benign conditions ($T_{rxn} \leq 82$ °C, iPrOH as hydrogen source). Furthermore, the catalytic cycle of transfer hydrogenation shares elementary steps with other industrially relevant catalytic processes (e.g. dehydrogenation of alcohols). Thus, a metal complex that exhibits catalytic activity for transfer hydrogenation may be a promising catalyst for other important reactions.

Noyori and co-workers showed that a ligand-appended electrophile can enhance the rate of transfer hydrogenation by facilitating the migratory insertion of hydride to a metal-bound carbonyl compound [46]. We hypothesized that the second metal center of a bimetallic transition metal complex may play the role of secondary electrophile in a manner similar to Noyori's "N-H effect" and yield

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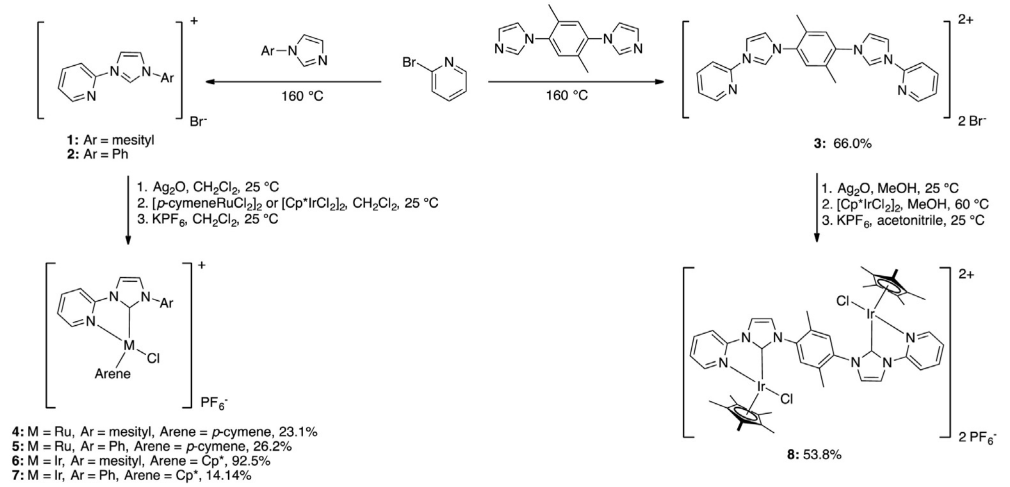

Scheme 1. Synthesis of mono- and bisimidazolium ligand precursors (**1–3**) and complexes **4–8**.

similar rate enhancements for catalytic transfer hydrogenation. Thus, we set out to prepare bimetallic complexes supported by pyridine-functionalized NHC ligands. Herein we describe the synthesis and characterization of several previously unreported monometallic iridium(III) and ruthenium(II) complexes supported by pyridine-functionalized NHC ligands, an analogous unreported bimetallic iridium(III) complex, and the results of catalytic transfer hydrogenation trials using these complexes as precatalysts.

The mono- and bisimidazolium ligand precursors (**1–3;** Scheme 1) were prepared according to the method reported by Crabtree et al. in which the arylimidazole (**1,2**) or arylbisimidazole (**3**) was allowed to react with 2-bromopyridine at 160 °C under neat conditions [47].

Compounds **1** [48] and **2** [49] have been prepared and characterized previously while, to our knowledge, **3** has not been reported. The corresponding, air-stable metal complexes (**4–8**) were prepared via transmetalation from the in situ-formed Ag(I)—Br complexes and either [Cp*IrCl$_2$]$_2$ or [*p*-cymeneRuCl$_2$]$_2$ followed by anion exchange with KPF$_6$. The monometallic complexes (**4–7**) were readily prepared at room temperature using dichloromethane as solvent, while, due to low solubility in dichloromethane, the bisimidazolium

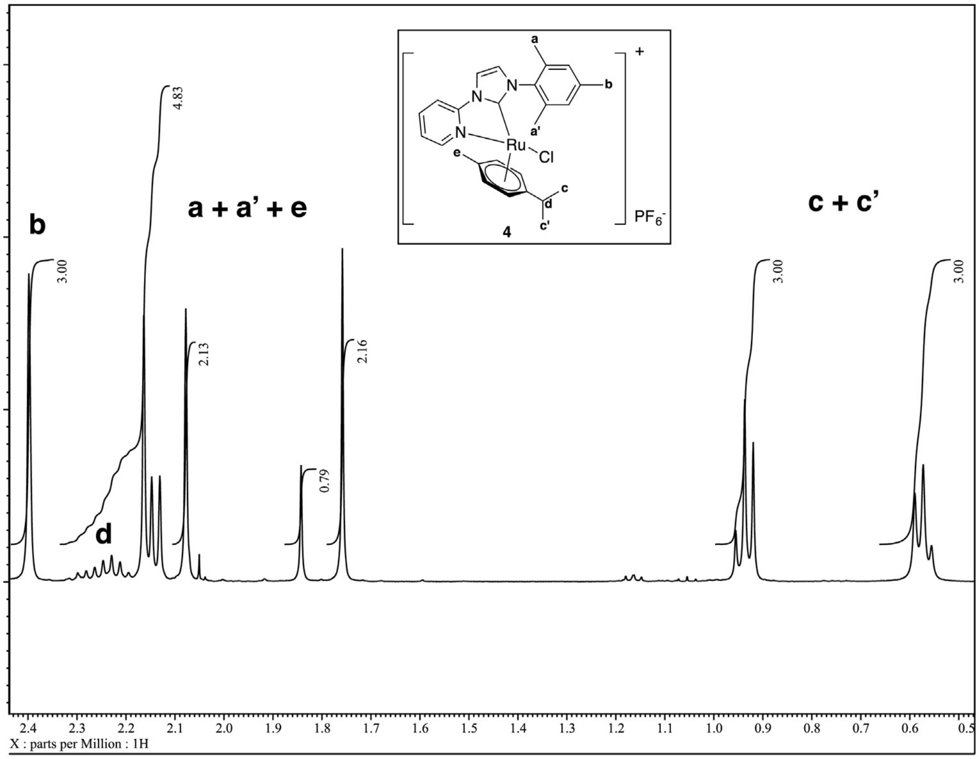

Fig. 1. Alkyl region of ^{1}H NMR (400 MHz, d_6-DMSO) for **4**.