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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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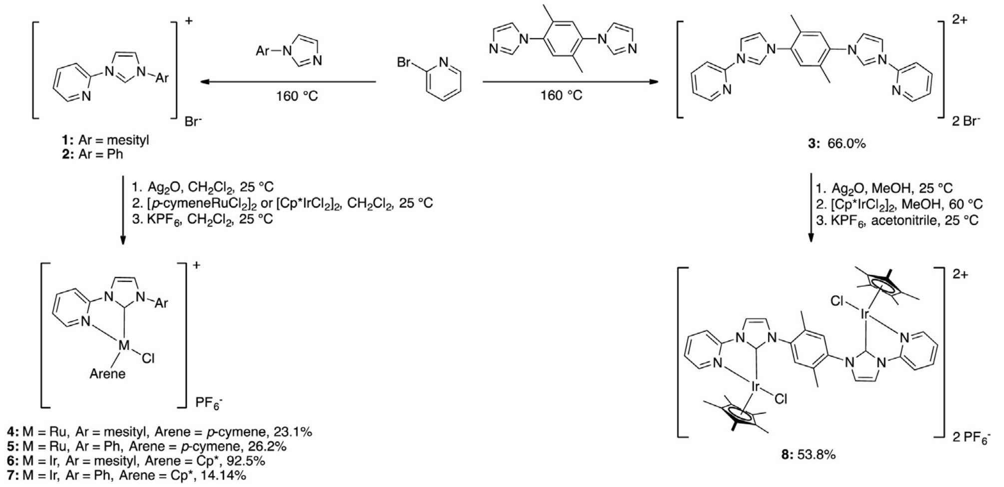


Scheme 1. Synthesis of mono- and bisimidazolium ligand precursors (**1**–**3**) and complexes **4**–**8**.

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-cymene$RuCl_2$]$_2$ 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

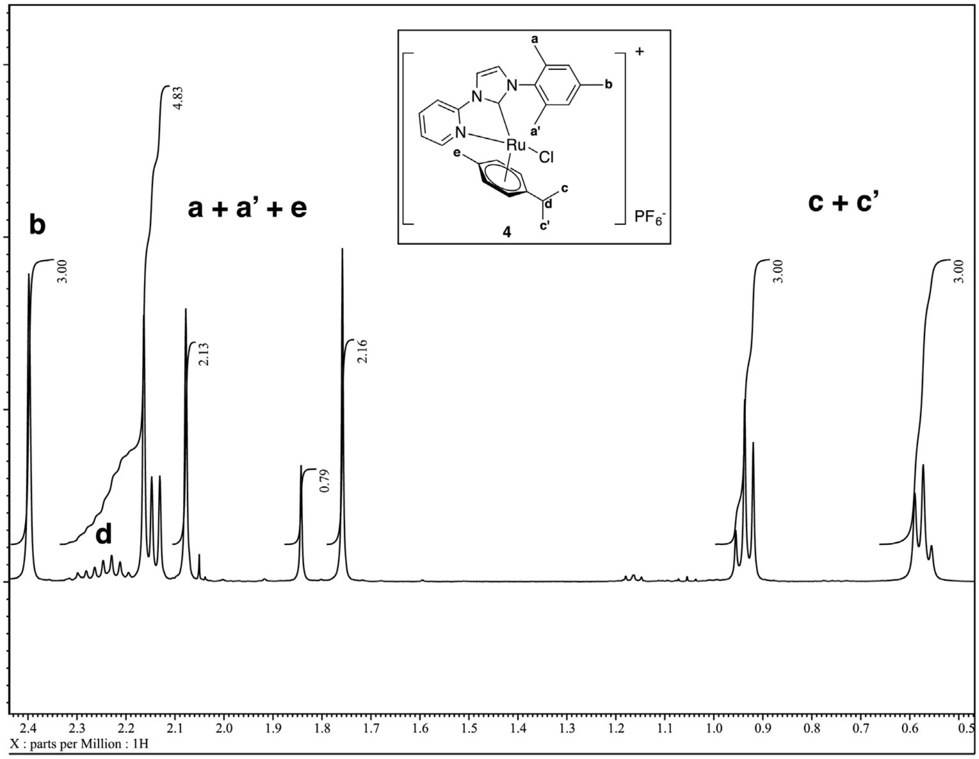
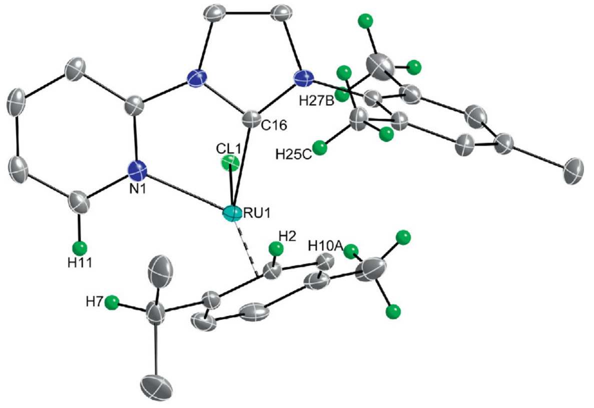


Fig. 1. Alkyl region of ^{1}H NMR (400 MHz, d_6-DMSO) for **4**.



4

Ru(1)-cent	1.7214(15) Å
Ru(1)-C(16)	2.029(3) Å
Ru(1)-Cl(1)	2.4615(7) Å
Ru(1)-N(1)	2.098(3) Å
Cl(1)-H(10A)	2.99(25) Å
Cl(1)-H(27B)	2.67(21) Å
H(7)-H(11)	2.54(37) Å
H(25C)-H(2)	2.314(0) Å
C(16)-Ru(1)-Cl(1)	85.32(9)°
C(16)-Ru(1)-N(1)	76.49(12)°

Fig. 2. ORTEP diagram of **4**. Thermal ellipsoids are shown at the 35% probability level. PF_6^- counterions and non-interacting hydrogen atoms have been omitted for clarity.

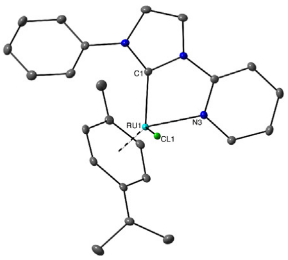
salt (**3**) was metalated at 60 °C in methanol and the anion exchange was conducted in acetonitrile to yield **8**. We have prepared several other pyridine-functionalized, arene-linked bisimidazolium salts including the benzene-linked analog of **3**, however, the 2,5-dimethylbenzene-linked salt was chosen for this study because it was more soluble in methanol than analogous compounds. Possibly due to greater air/moisture sensitivity under the comparatively harsh reaction conditions (i.e. protic solvent, elevated temperature) attempts to isolate the analogous bimetallic ruthenium(II) compound have thus far been unsuccessful.

The ^{1}H NMR spectra of compounds **4** and **6** revealed hindered rotation about the N—C_{mes} bond as evidenced by separate signals for the *ortho*-methyl groups and *meta*-hydrogens of the mesityl ring. This is consistent with the solid-state structure of these two compounds in which one side of the mesityl group is proximal to a metal bound chloride while the other is distal. For compound **4** in particular, the coordination environment around the metal center appears somewhat distorted and the rotation around several C—C bonds appears to be hindered due to steric congestion. For example, the difference in Cl—Ru-centroid angle between **4** and **5** is 2.21° while the difference in the Cl—Ir-centroid angles for **6** and **7** is only 0.27° thus indicating greater distortion in the case of the ruthenium(II) complexes possibly as a result of the bulky *p*-cymene ligand. Indeed, the entire alkyl region of the ^{1}H NMR spectrum for **4** is quite complicated (Fig. 1) presumably due to hindered rotation of the *p*-cymene ring, and also the C—C bonds connected to methyl groups **a**, **a′**, **c**, **c′**, and **e**. For example, whereas the signal for the isopropyl methyl groups appear as a 6H doublet for compound **5**, in compound **4** the signals for **c** and **c′** appear as broad multiplets at 0.94 ppm and 0.57 ppm, indicating that the protons on methyl groups **c** and **c′** are not equivalent on the NMR timescale. The signals for protons of methyl groups labeled **a**, **a′**, and **e** and the methine proton **d** are likewise complex and poorly resolved despite the fact that the integration of this region matches well with the expected value of 10H. In the solid-state structure of **4** (Fig. 2), the distance between hydrogen atoms of methyl groups **a**, **a′**, and **e**, methine hydrogen **d** and their nearest non-bonded neighbor are all within or near the sum of the van der Waals radii which indicates significant steric congestion consistent with the complicated ^{1}H NMR spectrum.

The ^{1}H NMR spectrum of compound **5**, which bears an *N*-phenyl group, suggests decreased steric congestion in the coordination sphere as the signals corresponding to the isopropyl group attached to *p*-cymene display first order splitting indicating free rotation of the isopropyl group and methyl group. Likewise, the ^{1}H NMR spectrum for compound **7** was consistent with free rotation about the N—C_{phenyl} bond and of the Cp* as indicated by a singlet at 1.39 ppm corresponding to the methyl groups of the Cp* moiety. The ^{1}H NMR spectrum of compound **8** was consistent with the highly symmetrical solid-state structure of this compound with a relatively uncongested coordination sphere about each iridium center; the aromatic protons of the 2,5-dimethylbenzene linker appeared as a 2H singlet at 7.92 ppm and the methyl protons of the linker appeared as a 6H singlet at 2.44 ppm, while the Cp* methyl protons appeared as a 30H singlet at 1.45 ppm.

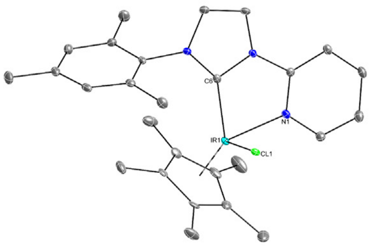
The solid-state structures of compounds **4**–**8** were determined via X-ray crystallography (Figs. 2–4). Compounds **4** and **5** exhibited structural parameters similar to a *N*-3-butenyl pyridine-NHC ruthenium(II) complex reported by Saha and co-workers [50]: the Ru—C_{NHC} bond distance was within 0.02 Å, the Ru—N_{pyr} distance was within 0.01 Å. However, the Ru—Cl distances in compounds **5** and **6** were 0.2 Å greater than those for the compound reported by Saha. This difference is likely due to the greater steric demand of the *N*-mesityl and *N*-phenyl substituents compared to the *N*-3-butenyl analog. Compounds **6**–**8** revealed similar solid-state structures to the related pyrimidine compounds reported by Crabtree and co-workers [51]. Specifically, the Ir-cent, Ir—N_{pyr}, and Ir—C_{NHC} distances for **6** were all within 0.02 Å of those reported for the analogous mesityl-appended pyrimidine complex, and the C_{NHC}—Ir—Cl (88.43(7)° for **6** vs. 86.98(19)°) and C_{NHC}—Ir—N_{pyr} (76.91(9)° for **6** vs. 76.7(3)°) bond angles were similar. Compound **8** revealed a highly symmetric *anti* arrangement of iridium metal centers in the solid state consistent with the ^{1}H NMR spectrum (vide supra).

Compounds **4**–**8** were evaluated for activity as transfer hydrogenation catalysts. Under air-free conditions, upon activation with KOH and KPF_6, each complex showed activity for catalytic transfer hydrogenation of acetophenone to form 1-phenylethanol (Table 1). Compounds **4**–**6** exhibited similar activities to the pyrimidine analogs reported by Crabtree and co-workers [51] reaching ≥92.0% conversion and ≥88 turnovers (TON) in 4 h. In the case of the ruthenium complexes **4** and **5**, the phenyl-appended compound **5** exhibited a higher activity at $t = 1$ h (entries 2 vs. 4, Table 1); this may be due to the lower steric demand of the phenyl moiety compared to the mesityl group. Curiously, the opposite trend was observed for the analogous iridium compounds (entries 6 vs. 8, Table 1) in which the mesityl-appended complex (**6**) exhibited twice the turnover frequency of **7** (TOF = 86 h^{-1} vs. 38 h^{-1}). One possible explanation for this observation is that the presumed 16 electron phenyl-appended catalytic intermediate may undergo *ortho*-metalation of the *N*-phenyl moiety leading to catalyst deactivation. This would not be surprising in light of the propensity of electron deficient Ir(III)-centers to participate in C—H activation [52]. As noted earlier, we had hoped that bimetallic complex **8** would exhibit superior activity in transfer hydrogenation to its monometallic analogs. We were disappointed to find that this was not the case with **8** exhibiting only ca. 20% of the activity of **6** (entries 10 vs. 6, Table 1) and ca. 45% of the activity of **7** (entries 10 vs. 8, Table 1). Two possible factors may contribute to the low



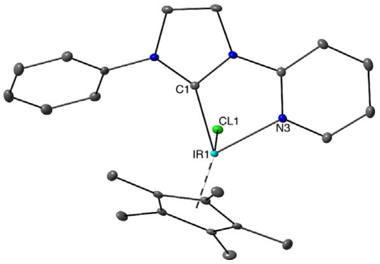
5

Ru(1)-cent	1.7155(8) Å	C(1)-Ru(1)-Cl(1)	85.14(5)°
Ru(1)-C(1)	2.0145(19) Å	C(1)-Ru(1)-N(1)	76.65(7)°
Ru(1)-Cl(1)	2.4397(4) Å		
Ru(1)-N(1)	2.1055(16) Å		



6

Ir(1)-cent	1.8255(12) Å	C(6)-Ir(1)-Cl(1)	85.32(9)°
Ir(1)-C(6)	2.024(2) Å	C(6)-Ir(1)-N(1)	76.91(9)°
Ir(1)-Cl(1)	2.4103(5)Å		
Ir(1)-N(1)	2.108(2) Å		



7

Ir(1)-cent	1.8221(10) Å	C(1)-Ir(1)-Cl(1)	87.09(6)°
Ir(1)-C(1)	2.018(2) Å	C(1)-Ir(1)-N(3)	76.75(7)°
Ir(1)-Cl(1)	2.4172(5) Å		
Ir(1)-N(3)	2.1047(17) Å		

Fig. 3. ORTEP diagrams of **5**–**7**. Thermal ellipsoids are shown at the 35% probability level. Hydrogen atoms and PF_6^- counterions have been omitted for clarity.

activity of the catalyst derived from **8**: (1) the high steric demand of the 2,5-dimethylbenzene linker makes it likely that the Ir(III) centers remain isolated from one another and are thus incapable of cooperation in the catalytic cycle, and (2) the presumed 16 electron intermediate generated from **8** may undergo *ortho*-metalation via C—H activation thereby leading to catalyst deactivation. Future work will focus on investigating the nature of the active species and interrogating the possibility of deleterious C—H activation and further developing bimetallic complexes incorporating aliphatic linkers which may lead to greater conformational flexibility, circumvent *ortho*-metalation, and increase catalytic activity.

We have synthesized and characterized five previously unreported ruthenium(II) and iridium(III) complexes supported by pyridine-functionalized NHC ligands including a novel bisimidazolium salt (**3**) and the corresponding bimetallic complex (**8**). Each of the compounds has shown activity for catalytic transfer hydrogenation upon activation with KOH and KPF_6. We plan to explore different linker architectures for pyridine-functionalized bisimidazolium compounds and less sterically demanding ancillary ligands, expand the scope of bimetallic coordination complexes supported by pyridine-functionalized NHCs to other late metal centers, and evaluate the catalytic potential of these new complexes for transfer hydrogenation and other organic transformations.

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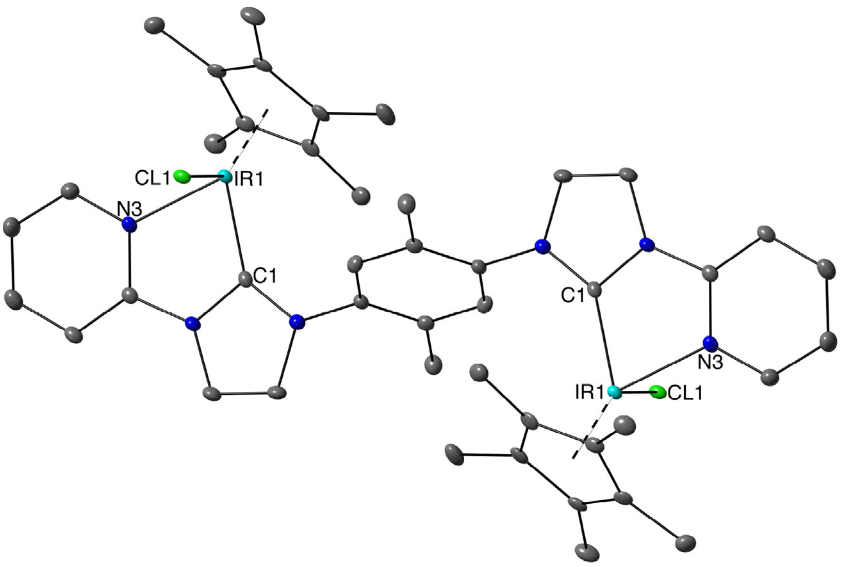
Appendix A. Supplementary material

Procedures and characterization data for the compounds **3**–**8**, procedural details for catalytic trials, and X-ray crystallography procedures and data are available as electronic supplementary material. Full cifs for each structure are also available free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures. CCDC 1540972, 1540970, 1540973, 1540971, and 1540969 contains the supplementary crystallographic data for **4**, **5**, **6**, **7**, and **8**, respectively, for this paper. Supplementary data



8	
Ir(1)-cent	1.8245(14) Å
Ir(1)-C(1)	2.012(3) Å
Ir(1)-Cl(1)	2.4148(7) Å
Ir(1)-N(3)	2.120(3) Å
C(1)-Ir(1)-Cl(1)	88.26(9)°
C(1)-Ir(1)-N(3)	76.48(11)°

Fig. 4. ORTEP diagram of **8**. Thermal ellipsoids are shown at the 35% probability level. Hydrogen atoms and PF_6^- counterion have been omitted for clarity.

Table 1
Results of catalytic transfer hydrogenation trials using **4**–**8**/KOH/KPF_6.

Entry[a]	Catalyst	Time (minutes)	% conversion[b]	TON[c]	TOF (h^{-1})[d]
1	**4**	30	33.3	35	71
2	**4**	60	54.5	58	58
3	**4**	240	92.0	88	44
4	**5**	60	79.1	84	84
5	**5**	240	95.5	101	25
6	**6**	30	81.3	86	86
7	**6**	240	98.9	105	26
8	**7**	30	35.3	38	38
9	**7**	240	76.5	81	20
10	**8**[e]	30	16.1	17	17
11	**8**[e]	240	48.9	52	13
12	**8**[e]	1440	95.9	102	4

[a] General conditions: Catalyst (16 μmol), KOH (0.2 mmol), and KPF_6 (30 μmol) were dissolved in 10 mL of iPrOH at 82 °C and acetophenone (1.7 mmol) was added.

[b] Determined via gas chromatography.

[c] mol product/mol metal (metal = Ru or Ir).

[d] TON/time.

[e] 8 μmol of compound **8**.

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