

Functionalization of an iridium–diamidocarbene complex by ligand-based reactions with titanocene and zirconocene sources



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This paper is dedicated to Professor Malcolm L. H. Green, a long-time friend and a pioneer in the exploratory chemistry of metallocenes and other organometallic compounds.

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ABSTRACT

A (^tBu-DAC)Ir(COD)Cl complex (^tBu-DAC = 1,3-bis(N-*tert*-butyl)diamidocarbene, COD = 1,5-cyclooctadiene) reacts with titanocene(II) and zirconocene(II) sources to form heterobimetallic complexes by metallocene coordination at the remote oxalamide binding site. Structural and spectroscopic data reveal the formation of a doubly-reduced [^tBu-DAC]²⁻ ligand upon metallocene complexation. The metallocene-substituted complexes catalyze benzaldehyde hydrosilylation at rates over an order of magnitude faster than those observed with the parent iridium complex.

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1. Introduction

The rate and selectivity of organometallic reactions can be dramatically influenced by the electronic environment of the metal center. Traditionally, to gain mechanistic insight on ligand effects for a metal-mediated reaction, a series of independently-synthesized ligands and their corresponding metal complexes must be prepared. An alternative strategy uses a remote ligand functionalization to “switch” the electronic properties of a complex [1]. This late-stage modification allows for the rapid synthesis of a series of complexes from a common precursor, and reactivity differences between these complexes provide insight into the electronic preferences for a reaction.

N-heterocyclic carbenes (NHCs) are versatile ligands for a wide range of metal-catalyzed transformations [2]. While variation of NHC steric properties can be readily achieved, it remains difficult to significantly alter their electronic properties [3]. The late-stage functionalization of NHC ligands is of interest as a strategy for the convenient synthesis of NHCs with diverse electronic properties. Recent reports have utilized chemical [4], electrochemical [5], or photochemical [6] stimuli to tune NHC donor properties;

however, studies comparing the reactivity of these switchable complexes remain rare.

Herein, we report electronic modification of an iridium–diamidocarbene complex by ligand-based reactions with titanocene(II) and zirconocene(II) sources. Upon metallocene binding, three resonance contributors can be envisioned depending on the extent to which the metallocene reduces the diamidocarbene ligand (A–C, Fig. 1) [7]. A combination of X-ray crystallographic, UV–Vis and NMR spectroscopic data suggests that the diamidocarbene ligand is doubly reduced upon interaction with the Cp₂Ti or Cp₂Zr fragments, and this ligand reduction renders the carbene donor more electron rich. Iridium-catalyzed hydrosilylation is accelerated by over an order of magnitude for the metallocene-substituted complexes, demonstrating that ligand-based modification alters electronic properties, and therefore catalytic activity, of these complexes.

2. Results and discussion

The recently reported 1,3-bis(N-*tert*-butyl)diamidocarbene (^tBu-DAC) [8] ligand platform was selected for remote functionalization studies due to the presence of both a carbene donor and a secondary α-dicarbonyl functional group. Treatment of [Ir(COD)Cl]₂ with 2 equivalents of ^tBu-DAC in toluene generated

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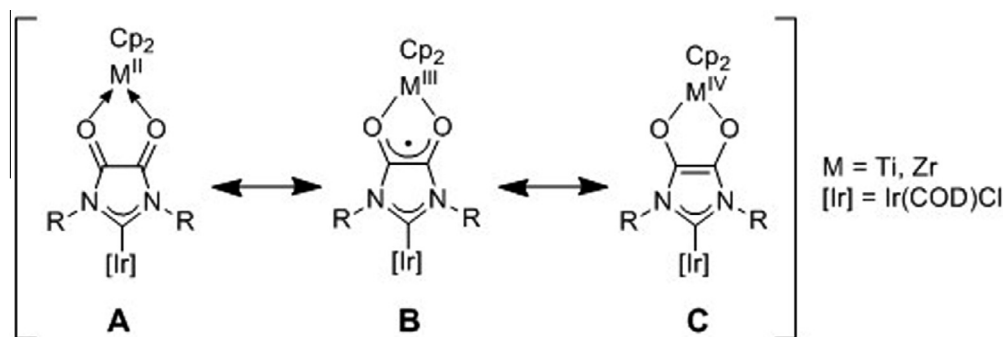
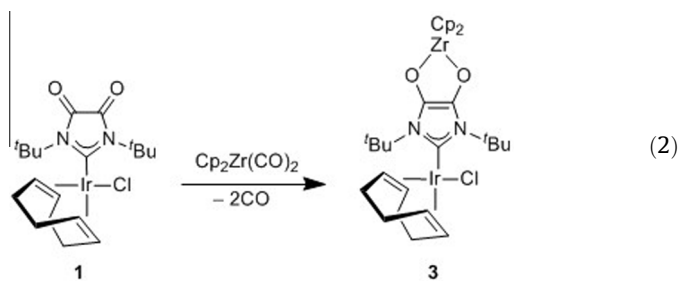
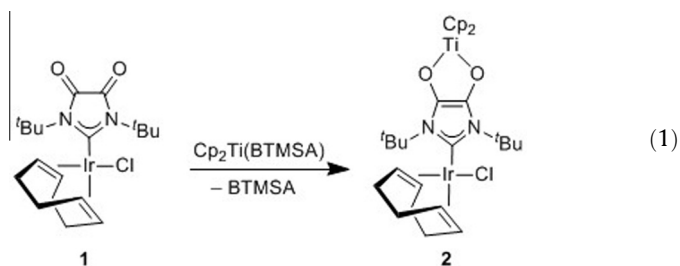


Fig. 1. Three possible resonance contributors for the metallocene–diamidocarbene platform.

(^tBu-DAC)Ir(COD)Cl (**1**), which was isolated as a yellow-green powder in 83% yield. The blue titanocene adduct (Cp₂Ti-^tBu-DAC)Ir(COD)Cl (**2**) was generated by treatment of **1** with bis(cyclopentadienyl)titanium–bis(trimethylsilyl)acetylene [9] in THF, and was isolated in 90% yield (Eq. (1)). Lastly, the orange zirconocene derivative (Cp₂Zr-^tBu-DAC)Ir(COD)Cl (**3**, Eq. (2)) was prepared by addition of bis(cyclopentadienyl)zirconium dicarbonyl [10] to **1** in toluene (95% isolated yield).



X-ray crystallographic characterization of **1–3** allowed for solid-state structural comparisons (Figs. 2–4). All three complexes feature the expected square-planar geometry of a d⁸ iridium complex. Complexes **2** and **3** contain the Cp₂M (M = Ti, Zr) fragment bound to the α-dicarbonyl site of the ^tBu-DAC ligand.

A comparison of selected bond lengths of **1–3** (Fig. 5) indicates that metallocene coordination causes elongation of the C_{amide}–O bond length of the ^tBu-DAC ligand (C_{amide}–O (avg) of 1.198(11) Å for **1**, 1.313(3) Å for **2**, and 1.331(3) Å for **3**). In contrast, the C_{amide}–C_{amide} bond length is substantially contracted upon metallocene binding (1.505(19), 1.373(5), and 1.377(5) Å for **1**, **2**, and **3**, respectively). The bond distances of **2** and **3** are consistent with a dominant contribution from a [^tBu-DAC]²⁻ ene-diolate resonance form (C, Fig. 1) [11]. The Ir–C_{carbene} bond length of **1** is quite short (1.964(13) Å), which can be attributed to strong π-backbonding from iridium to the diamidocarbene ligand [12]. The Ir–C_{carbene} distance is increased for derivatives **2** and **3** (2.056(4) and 2.068(3) Å, respectively), suggesting that the π-acceptor properties of ^tBu-DAC are diminished upon derivatization with the Cp₂Ti and Cp₂Zr fragments.

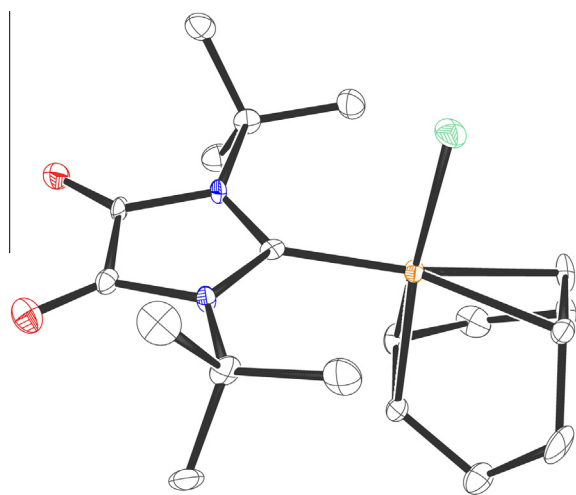


Fig. 2. ORTEP diagram of **1**, with hydrogen atoms omitted for clarity and thermal ellipsoids shown at 50%.

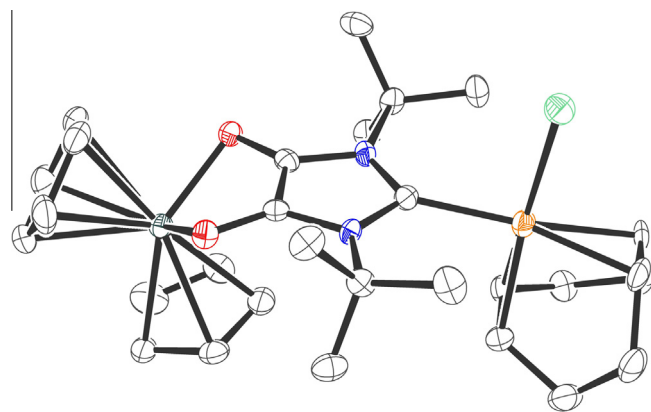


Fig. 3. ORTEP diagram of **2**, with hydrogen atoms omitted for clarity and thermal ellipsoids shown at 50%.

UV–Vis spectra of **1–3** in THF are presented in Fig. 6. Intense low-energy transitions are observed for **2** and **3** at 580 nm ($\epsilon_{\max} = 15,100 \text{ M}^{-1} \text{ cm}^{-1}$) and 415 nm ($\epsilon_{\max} = 14,200 \text{ M}^{-1} \text{ cm}^{-1}$), respectively. The intensity of these absorptions is consistent with their assignment as ligand-to-metal charge-transfer (LMCT) transitions from the electron rich [^tBu-DAC]²⁻ ligand to the d⁰ titanium and zirconium centers of **2** and **3** [13]. This LMCT transition occurs at a longer wavelength for **2** than for **3** due to the greater electrophilicity of titanium relative to zirconium [14].

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