

## Synthesis of Rhodium and Iridium Complexes Supported by Bis(indolylphosphino)silyl Pincer Ligand: Competitive N–H and C–H Bond Activation by an Ir(I) Species

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### Reading Guide

1. Read the first paragraph in the **Introduction** (“Reactivity involving...” p. 2768 to “...existing methodologies.” p. 2769). You should be able to
  - a. understand why metal-mediated N-H bond cleavage via oxidative addition is important to the field of organometallic chemistry
  - b. understand which challenges are associated with N-H bond activation
  - c. note the route the authors have chosen to study N-H bond activation
2. Briefly read the third and fourth paragraphs in the **Introduction** (“Starting in the early 2000s...” p. 2769 to “...toward N-H reductive elimination.” p. 2770). You should be able to
  - a. note previous synthetic examples in which N-H bond activation was successful
  - b. identify products of N-H oxidative addition in **Scheme 2A-C**
  - c. note the use of pincer ligands in bond activation
  - d. identify the pincer ligands used in **Scheme 2A-C**
3. Read the fifth and sixth paragraphs in the **Introduction** (“As these studies have highlighted...” to “...species with C-H and N-H bonds.” p. 2770). You should be able to
  - a. note the use of pincer ligands in bond activation
  - b. identify the pincer ligands proposed in **Scheme 2D**
  - c. understand the route the authors have chosen to study N-H bond activation
4. Read **Synthesis of (iPr-PSiP<sup>Ind</sup>)MH(Cl) (M = Rh, Ir) Precursor Complexes** (p. 2770). You should be able to
  - a. identify complexes **1** and **2** as precursor complexes for salt metathesis
5. Read the first and third paragraphs in **Synthesis of Anilido, Alkylamido, Hydrazido, and Amidate Hydride Complexes by Salt Metathesis and Protonolysis Routes** (“The synthesis of Rh and Ir...” p. 2770 to “...at the anilido nitrogen is planar.” p. 2771 and “In an effort to extend...” to “...are exceedingly rare.” p.2772). You should be able to
  - a. identify the anilide and amide ligands used along with the corresponding hydride complexes **3a-5c** formed via salt metathesis in **Scheme 3**
  - b. contrast the reactivity between Ir and Rh complexes
  - c. identify the coordination geometry around the metal centers for complexes **4a** and **4b** in **Figure 2** and **Table 1**
6. Read the fourth paragraph in **Synthesis of Anilido, Alkylamido, Hydrazido, and Amidate Hydride Complexes by Salt Metathesis and Protonolysis Routes** (“The reactivity of alkylamido...” p. 2772 to “...initial salt metathesis reaction.” p. 2773). You

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should be able to

- a. note the formation of byproducts when using alkylamide ligands in the synthesis of hydride complexes via salt metathesis
  - b. identify the associated reaction pathways in **Scheme 4**
7. Briefly read **Synthesis of (<sup>i</sup>Pr-PSiP<sup>Ind</sup>)M<sup>I</sup> Species and Evidence of sp<sup>2</sup>-C-H Bond Activation** (pp. 2774-75). You should be able to
- a. note the work performed by the authors to form coordinately unsaturated complexes **8a** and **9a** as suitable precursors to the target complexes via N-H oxidative addition
  - b. note the difficulty in obtaining the precursor complexes
  - c. identify the formation of byproducts from competing pathways, including C-H bond activation, in **Scheme 6**
8. Read **Investigation of N-H Bond Oxidative Addition by (<sup>i</sup>Pr-PSiP<sup>Ind</sup>)M<sup>I</sup> (M = Rh, Ir)** (pp. 2775-76). You should be able to
- a. note the difficulty in obtaining the targeted complexes from N-H oxidative addition on the precursor complexes
  - b. note the presence of competing pathways