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

Helia Hollenhorst, Robert McDonald, Michael Ferguson, and Laura Turculet*
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Note: The Covalent Bond Classification (CBC) method is used to assign ligand functions (X, L, Z).
http://www.columbia.edu/cu/chemistry/groups/parkin/cbc.htm

For a complex in the neutral form $MX_xL_lZ_z$

Electron count	*EN*	*m + 2l + x*
Valence number	*VN*	*x + 2z*
Ligand bond number	*LBN*	*l + x + z*
d^n metal configuration		*m – valence number*

1. Why is the study of metal-mediated N-H bond cleavage via oxidative addition important to the field of organometallic chemistry?

2. Which competing pathways to N-H oxidative addition are typically observed when reacting primary amines in the formation of amido hydride complexes?

3. Give the structures of the N-H oxidative addition products shown in Scheme 2A, 2B, and 2C.

4. What are pincer ligands? Why are they useful?

5. Consider the pincer ligands mentioned in this work.
   a. Give the structure of the pincer ligand previously used by Goldman, Hartwig and coworkers and shown in Scheme 2A. Which XLZ ligand functions are present?

   b. Give the structure of the pincer ligand used in this work and shown in Scheme 3. Which XLZ ligand functions are present?

6. Compounds **1** and **2** are prepared in this work as precursor complexes for salt metathesis. Write the MLXZ notation and determine the valence number, ligand bond number, electron count, and d^n configuration for complex **1** or **2**, as shown in equation 1.

Compound	MLXZ	Valence Number	Ligand Bond Number	Electron Count	d^n

7. Scheme 3 provides a list of anilide and amide ligands used in the formation of anilido and amido hydride complexes (**3a**-**5c**) via salt metathesis.
   a. Give their general formula.
   b. What does the suffix *-ide/-o* indicate?

8. Consider the percent yields reported in Scheme 3 for the formation of anilido hydride complexes (**3a**-**4d**) via salt metathesis.
    a. What is the trend between Rh (**3a-c**) and Ir (**4a-c**) complexes?
    b. Which competing pathway do the authors suspect in the formation of complexes **3a-c**?

9. What is the geometry of complexes **4a-b**, as indicated in Figure 2 and Table 1?

10. Write the MLXZ notation and determine the valence number, ligand bond number, electron count, and d^n configuration for complexes **2** and **5d'** shown in Scheme 4.

Compounds	MLXZ	Valence Number	Ligand Bond Number	Electron Count	d^n

11. Which organometallic reaction steps(s) are proposed in the formation of **5d'** from **2** in Scheme 4? How does each step affect the valence number and electron count for the complex?

12. What is the coordination mode of the three phosphine ligands in complex **10**, as shown in Figure 4 and Scheme 6?

13. Table S1 of the Supplemental Information provides ^{1}H NMR data for the iridium amidate complexes **7b** and **7c** (see structures given in Scheme 3). Propose an explanation for the upfield shift observed between compound **7b** and **7c**.

Compound		^{1}H NMR (N*H*), ppm, benzene-d_6
(^{i}Pr-PSiP^{Ind})IrH[NH(CO)Ph]	**7b**	5.90
(^{i}Pr-PSiP^{Ind})IrH[NH(CO)Me]	**7c**	4.65