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Reading Guide for “Synthesis, Electrochemistry, and Reactivity of Half-Sandwich Ruthenium Complexes Bearing Metallocene-Based Bisphosphines” Shaw, A.P.; Norton, J.R.; Bucella, D.; Sites, L.A.; Kleinbach, S.S.; Jarem, D.A.; Bocage, K.M.; Nataro, C. *Organometallics* **2009**, 28, 3804-3814.

This reading guide focuses on the synthesis, properties, and electrochemistry of (Cp/Cp*)Ru complexes bearing several metallocene-based bisphosphines. The X-ray crystallography structures are not emphasized.

1. Read the **Introduction**. After reading this section, you should be able to:
 - a. Describe how metallocene-based bisphosphines have been used in previous coupling reactions and how these ligands present unique steric and electronic properties.
 - b. Recognize that analogues of 1,1'-bis(diphenylphosphino)ferrocene (dppf) have been explored and have shown similar catalytic properties and improved yields for coupling reactions.
 - c. Describe the investigations that were performed to study the Ru complexes, and understand the purpose for each investigation.
2. Briefly read the **Synthesis of the Complexes** and examine **Scheme 1, 2, and 3**.
 - a. Be able to understand what each metallocene-based bisphosphine ligand abbreviation stands for in complexes **1a-1i** and **2a-2h**. Make sure to know what the metal and the R group are in each ligand.
 - b. Understand the effect that different metallocene-based bisphosphine ligands have on the synthesis of the Ru complexes.
 - c. For Scheme 3 recognize that **6j[PF₆]₂** is a precursor and more easily manipulated than **1i** and **1j[PF₆]**.
3. Read **Electrochemistry** and examine **Table 3** and **Table 4**.
 - a. Be able to assign E₁ and E₂ to each respective metal. Note how the authors assigned E₁ and E₂ based on the observed potentials.
 - b. Note the oxidations that occur for complexes with ferrocene-based bisphosphine ligands, whereas complexes with Ru and Os-based metallocene bisphosphine ligands only undergo one oxidation. Be able to know which metal is being oxidized.
 - c. Consider the potentials given in both Table 3 and 4 and be able to explain how these potentials correlate to properties such as sensitivity to the nature of the PR₂ groups and/or identity of the metal in the bisphosphine ligands, and Cp/Cp* or hydride/chloride ligands electron donor abilities.
4. Read **Reactivity of the Hydrides with Iminium Cations** and examine **Table 6**.
 - a. Understand how CpRu(P-P)H complexes can be used to catalyze the ionic hydrogenation of iminium cations.

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- b. Consider why the CpRu(P-P)H complexes in this study are generally poor hydride donors. Consider the effect of the bisphosphines bite angles and of the ease of oxidation at the Ru center on the rate of hydride transfer (as shown in the study done by Guan and coworkers).
5. Read **Protonation of the Hydride Complexes**.
 - a. In equation (4), identify the kinetic and thermodynamic products. Note the term isomerization and know what it means.
 - b. Note how the dihydride product obtained here differs in conformation from a dihydride product typically expected in a hydrogenation reaction.
 - c. **3j²⁺** and **4j²⁺** were analyzed by ¹H NMR. Understand the difference in the number of resonance peaks provided for each compound, suggesting that either a dihydrogen or a dihydride complex was formed. Propose reasons for this difference.
 - d. Understand how the authors used the T₁ (min) of the ¹H NMR to distinguish between the dihydrogen and dihydride complexes.
 - e. Upon protonation, **2j[PF₆]** provides a dihydrogen complex, **3j[PF₆][BF₄]**, that is unusually stable for many hours at room temperature but eventually converts to the dihydride complex **4j[PF₆][BF₄]**. Use the authors' observations on the complexes respective acidity and your knowledge of equilibria to explain this phenomenon.
6. Read the **Conclusion**.
 - a. Focus on the results pertaining to what is highlighted in this reading guide. Be able to summarize how these results correlate to the authors' initial goals and motivations.