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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.

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1. What motivations did the authors have for using half-sandwich ruthenium complexes bearing metallocene-based bisphosphines?
2. Given these motivations, what did the authors do in this study?
3. Consider the complex **1e**.
 - a. Draw the **1e** complex, making sure to include the full structure of the metallocene-based bisphosphine ligand.
 - b. Give the full name of the metallocene-based bisphosphine ligand.
4. Consider the reaction of **6j**[PF₆]₂ to **2j**[PF₆].
Use the CBC method to count electrons in both complexes. Be sure to list the classification (i.e. ML₁X_xZ_z^{+/-Q}), valence number, ligand bond number, electron number, and dⁿ count.

	6j [PF ₆] ₂	2j [PF ₆]
Classification		
Equivalent Neutral Class		
Valence Number		
Ligand Bond Number		
Electron Number		
dⁿ Count		

5. Complexes **1a-1e** were prepared by reacting CpRu(PPh₃)₂Cl with metallocene-based bisphosphine ligands. Propose a reasonable explanation as to why the dtbpf ligand did not work for this synthesis, while other ligands did..
6. Consider the redox potentials measured for the chloride complexes **1a-1h**.
 - a. How did the authors assign the potentials to each metal?
 - b. What was the effect of changing from a Cp to a Cp* ligand on the Ru(III/II) potential? Explain.

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- c. What was the effect of changing the metal and/or phosphine substituents in the metallocene-based bisphosphine ligand on the Ru(III/II) potential?
7. Consider the redox potentials reported for the hydride complexes **2a-2j**.
 - a. Which complexes showed irreversible oxidations?
 - b. Why do $18e^-$ metal hydrides often undergo oxidation, but not the reversible reduction reaction?
 - c. How does the Ru(III/II) potential in a hydride complex compare to its chloride analog? Explain.
8. What was the purpose of using iminium cations in this experiment?
9. Upon protonation, most hydride complexes give a dihydrogen complex that isomerizes to a *trans*-dihydride. In this study, however, **2j**[PF₆] forms a dihydrogen complex, **3j**[PF₆][BF₄], that is stable for several hours at room temperature.
 - a. Explain why **3j**[PF₆][BF₄] eventually isomerizes into **4j**[PF₆][BF₄].
 - b. Explain how the difference in acidity between **3j**[PF₆][BF₄] and **4j**[PF₆][BF₄] can be used to predict the equilibrium position between the two isomers.
 - c. What type of reaction is taking place in equation 4? Which dihydride conformation (cis or trans) would you normally expect to form from the dihydrogen sigma complex?
 - d. Explain how the authors distinguished between the dihydrogen and dihydride complexes using ¹H NMR.