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Design, synthesis, and carbon-heteroatom coupling reactions of organometallic nickel (IV) complexes

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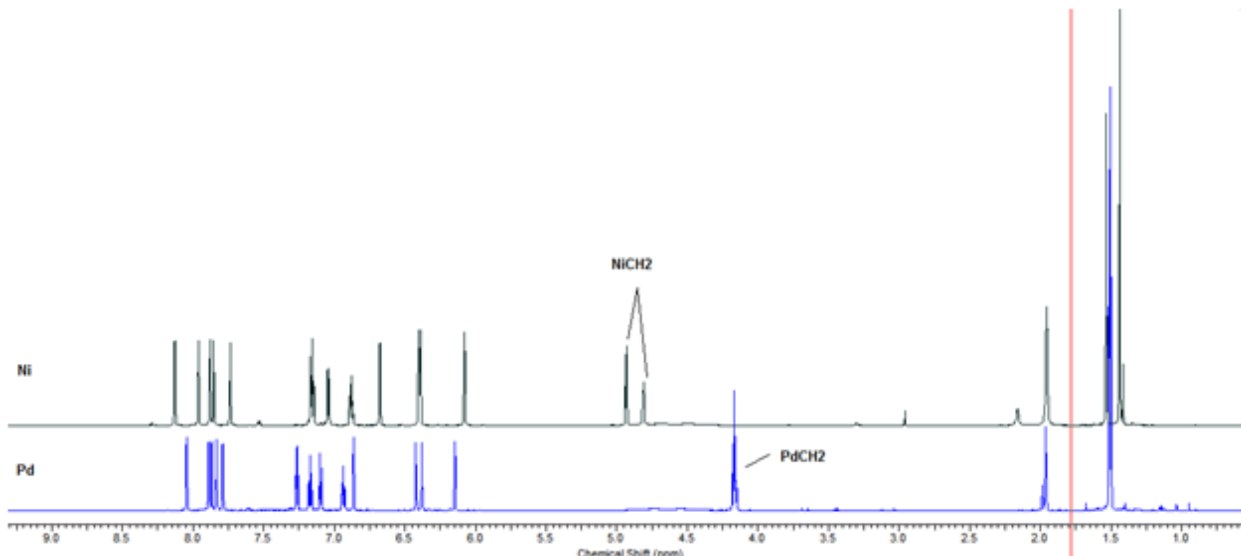
1. The following questions examine the issue of how these complexes presented in the article were designed, specifically the characteristics of the metal and the oxidant.
 - a. What motivations did the authors have for using nickel in their experiments?
 - b. Do you agree with the author's reasoning for switching from Pd to Ni? Use the website www.webelements.com to obtain the concentration in ppb by atoms in the Earth's crustal rocks of the metals nickel, palladium, and platinum. Given this information, as well as additional information you are able to find, do you support the author's claims on the importance of investigating nickel? Be sure to explain your reasoning using information from your sources.
 - c. Look up the cost of oxidant used in the transformation shown in Fig. 3A, available from Acros Chemical. Report the cost per gram and per mol. Compare this to the cost of iodobenzene diacetate, available from Oakwood Chemical.
 - d. This paper examines a stoichiometric oxidation but suggests that the ultimate goal would be to design a catalytic process. In designing an economical catalytic transformation that involves an oxidant, the cost of the oxidant can be more significant than the cost of the metal used in the catalyst. Explain why this is.
 - e. What type of reaction(s) are the authors trying to catalyze using their nickel complexes? Why is this reaction important?
2. In this paper the oxidation state of the metal is important. What ways are oxidation states represented in chemical formulas? What style is used to indicate oxidation state in this paper?
3. Consider the carbon heteroatom coupling reaction in Fig. 1B on page 1219.
 - a. Give the molecular geometries for complex **1** and complex **4**.
 - b. Use the CBC method to count the valence electrons in complexes **1** and **4**. Be sure to list the classification (i.e. ML_nX_m), valence number, ligand bond number, electron number, and d^n count.
 - c. What type of reaction occurs when proceeding from complex **1** to complex **4** via reaction pathway b?
 - d. What type of reaction occurs to yield the product **3** from **4**?

4. The formation of benzocyclobutane **3** from compound **1** is shown in Fig. 1B. Use this figure and your chemical knowledge to answer the following questions.
 - a. What does it mean that the compound was characterized *in situ*?
 - b. Using the oxidant S-(trifluoromethyl)dibenzothiophenium triflate (TDTT) the authors observe the formation of an intermediate compound (**4**). What spectroscopic evidence was used to support the formation of **4**?
 - c. Why did the authors suggest that using TDTT as an oxidant would permit the observation of intermediate **4** whereas the use of NFTPT, PhI(OAc)₂, or PhICl₂ as oxidants did not permit the observation of intermediate **2**?

5. This question explores the d-orbital splitting diagrams for several oxidation states of nickel, and how these electron arrangements affect their properties.
 - a. Assume that the redox reactions of [(bpy)Ni^{II}(CH₂CMe₂-o-C₆H₄)] shown in Fig. 1 occur at the metal center. Scanning in a positive direction is an oxidation and scanning in a negative direction is a reduction. What is the redox reaction that happens at each of the four large bumps in the cyclic voltammogram (Fig. 1A)?
 - b. Draw the d-orbital splitting according to the crystal field of the complex, one for Ni(II), Ni(III), and Ni(IV) then fill in the electron populations for the nickel d-orbitals for each oxidation state. What is the electronic spin total (S) of each complex? (Assume that the coordination number increases by one for each one electron oxidation.)
 - c. According to Fig. 1A the electrochemical oxidation of nickel occurs via two 1 electron oxidations. What evidence suggests that the observable intermediate **4** is the result of a two electron reduction and contains a Ni(IV) center instead of a Ni(III) center? What other experimental techniques could be used to identify the presence of a Ni(III) center?
 - d. Why is Ni(III) not observed during the chemical oxidation of **1** ?

6. Analyze the ¹H NMR spectra in the supporting information (Fig. S1, Page S5) to explore the relationship between ¹H NMR chemical shifts and the nature of the metal centers in compounds **1** and **4**.
 - a. What happens to the chemical shift of the ¹H NMR resonances of the methylene (CH₂) group of (bpy)Ni^{II}(CH₂CMe₂-o-C₆H₄)(**1**) upon reaction with S-(trifluoromethyl)dibenzothiophenium triflate to form (bpy)Ni^{IV}(CH₂CMe₂-o-C₆H₄)(CF₃)(OTf)(**4**)?
 - b. Based on your answer above, why does the chemical shift of these resonances move in this direction?
 - c. The ¹H NMR resonance of each set of methylene protons (CH₂) of (bpy)Ni^{II}(CH₂CMe₂-o-C₆H₄) changes from one resonance to two resonances upon reaction with-(trifluoromethyl)dibenzothiophenium triflate to yield (bpy)Ni^{II}(CH₂CMe₂-o-C₆H₄)(OTf)(CF₃). Provide an explanation for phenomenon.

7. Stacked ^1H NMR spectra of $\text{TpNi}^{\text{IV}}(\text{CH}_2\text{CMe}_2\text{-}o\text{-C}_6\text{H}_4)(\text{CF}_3)$ (**8**) (top) and a related compound $\text{TpPd}^{\text{IV}}(\text{CH}_2\text{CMe}_2\text{-}o\text{-C}_6\text{H}_4)(\text{CF}_3)$ (bottom) are shown below. What can be inferred about the electron density of Ni vs Pd by comparing the chemical shifts of their respective CH_2 resonances?



8. Use the table below to explore the relationship between ^{19}F NMR chemical shifts and the nature of the metal centers in these compounds.

| $(\text{py})_3\text{CH}$ complexes | ^{19}F NMR (Ni- CF_3) |
|--|--|
| (6) $[(\text{py}_3\text{CH})\text{Ni}^{\text{IV}}(\text{CH}_2\text{CMe}_2\text{-}o\text{-C}_6\text{H}_4)(\text{CF}_3)]\text{OTf}$ | -13.12 |
| (7) $(\text{py}_3\text{CH})\text{Ni}^{\text{II}}(\text{C}_6\text{H}_4\text{-}o\text{-CMe}_2\text{CH}_2\text{OAc})(\text{CF}_3)$ | -22.45 |
| Tp Complexes | |
| (8) $\text{TpNi}^{\text{IV}}(\text{CH}_2\text{CMe}_2\text{-}o\text{-C}_6\text{H}_4)(\text{CF}_3)$ | -16.11 |
| (9b) $\text{TpNi}^{\text{II}}(\text{C}_6\text{H}_4\text{-}o\text{-CMe}_2\text{CH}_2\text{OPh})$ | -20.52 |

- What is the general trend one observes when Ni^{IV} is converted to Ni^{II} ?
 - What can be inferred from the ^{19}F NMR data (shown above) in regards to the relative electron density of the Ni^{II} and Ni^{IV} metal centers?
9. Consider the ligand environments around nickel in complexes **4** (Fig. 1), **6** (Fig. 2A), and **8** (Fig. 3A).
- What are the similarities between these complexes?
 - What are the differences between these complexes?
 - Which of these complexes is the *least* stable? Explain how you know this.
 - How did the changes to the ligand environment affect the stability of the complexes?

10. The reaction in Fig. 3B shows a transformation of complex **8** to complex **9**. The authors propose an S_N2 mechanism for this reaction.
- Draw a mechanism, including any transition states or intermediates. (You may abbreviate the ligands.) Note that one of the arms of the hydrotris(pyrazolyl)borate ligands is not coordinated in the product.
 - What experimental evidence supports the S_N2 mechanism?
11. The authors cite reference 39 as the source of the nucleophilicity parameters (n_x) used in the plot in Fig. 4. The values of n_x were derived from measuring rates of S_N2 reactions between an electrophile (methyl iodide) and a corresponding nucleophile.
- Write the equation in reference 39 for how the n_x values were experimentally determined. Interpret the equation in words.
 - Use reference 39 to look up the values for n for PhO^- and PhS^- . Why is n for PhS^- higher for than PhO^- ?
 - If reference 39 had contained data for benzyl iodide as an electrophile, would the authors have used those values of n_x instead of the ones derived from methyl iodide as the electrophile? Explain.

12. Examine in more detail the features of the cyclic voltammogram and what they tell us about the metal center.

- What might the difference in shapes for the two waves in the cyclic voltammogram of $(\text{bpy})\text{Ni}^{\text{II}}(\text{CH}_2\text{CMe}_2\text{-}o\text{-C}_6\text{H}_4)$ in Fig. 1A mean?
- The voltammogram was recorded at 100mV/s. When the scan is run slower the peak on the right broadens and when the scan is run faster the peak on the right sharpens. Is the difference in peak shapes due to slow electron transfer or is it due to instability of the oxidized product? What other observations support your answer?
- Apply the answers from parts a and b to interpret the cyclic voltammograms for $[(\text{Tp})\text{Ni}^{\text{II}}(\text{CH}_2\text{CMe}_2\text{-}o\text{-C}_6\text{H}_4)]$ and $[(\text{Tp})\text{Pd}^{\text{II}}(\text{CH}_2\text{CMe}_2\text{-}o\text{-C}_6\text{H}_4)]$ shown below. What are the differences in the shapes of the voltammograms for Ni (black) versus Pd (blue)? How does one interpret the reason for these differences?

