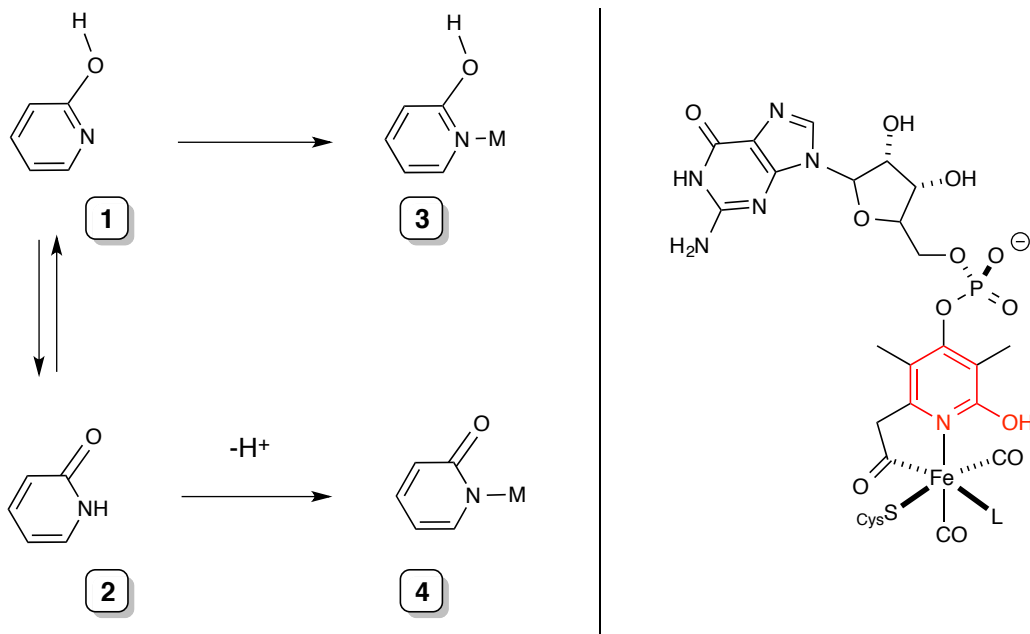


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Background

Proton-responsive ligands are an important class of ligands that can change their bonding character to a metal upon introduction/removal of a proton or tautomerization. Nature takes advantage of this feature in the FeGP cofactor of [Fe]-hydrogenase (Scheme 1, right),¹ where the 2-hydroxypyridine moiety (highlighted in red) supports the Fe ion, facilitates H₂ cleavage, and engages in hydrogen bonding. However, 2-hydroxypyridine (**1**) has 2-pyridone (**2**) as a tautomer. Each of these molecules can bind to a metal center through the nitrogen as shown in **3** and **4**, respectively. How do **1** and **2** affect the *d*-electron count at the metal center? How do they influence the overall electron number of the complex? By the end of this exercise you should be able to discuss how proton-responsive ligands can impact the bonding in metal complexes when protonated or deprotonated.

Scheme 1



Worked Example

In Scheme 2 is a Ru-based compound featuring the 2-hydroxypyridine moiety embedded in a larger heterocycle. How do we count the electrons for species **5** and **6**? Carbonyl is classified as an L-type ligand. The tridentate ligand going in-and-out of the plane of the page is known as a terpyridine (tpy) ligand. As the name suggests each connection point is analogous to an individual pyridine, which means each pyridine is a L-type ligand and tpy overall is L₃. These ligands are common to both **5** and **6**. The remaining ligand, based on bipyridine (denoted bpy' and bpy'' for **5** and **6**) adopts a tautomer similar to 2-

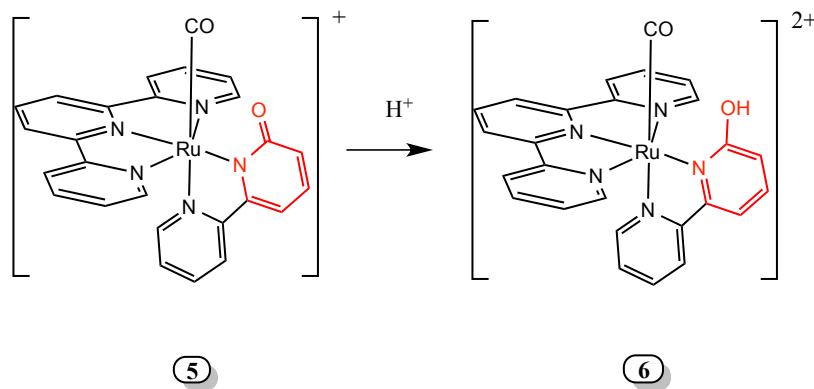
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pyridone in **5** and 2-hydroxypyridine in **6**. When you break the M–N bonds in **5** to create a neutral ligand, the black ring in bpy' looks like pyridine (L-type) but the red ring, with only two bonds to N, is X-type. Thus, the total classification is ML_5X^+ or ML_4X_2 as a neutral species. This informs us that the valence number is 2, the *d*-count is 6, and the electron number is 18. In **6**, breaking the Ru–N bond in the red ring results in a ligand that looks like pyridine (L-type) and therefore bpy'' is an L_2 ligand. However, they arrived at **6** by protonating **5** so the overall charge increased to 2+ and therefore the compound is ML_6^{2+} . This converts to ML_4X_2 in the neutral form, giving the same electron counts. A summary of the ligand types are provided in Table 1.

Table 1. Electron count summary for species **5** and **6**.

Ligand	Classification
CO	L
tpy	L_3
bpy'	LX
bpy''	L_2

Scheme 2



In-Class Exercise

Apply your new knowledge of classifying tautomeric ligands to classify and count electrons for the species in Scheme 3. Does the metal undergo redox chemistry? Is the metal-ligand bonding constant throughout the proton cascade? These complexes are all related to hydroboration catalysts enabled by proton-responsive ligands that were recently reported by the Szymczak group.³

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Scheme 3

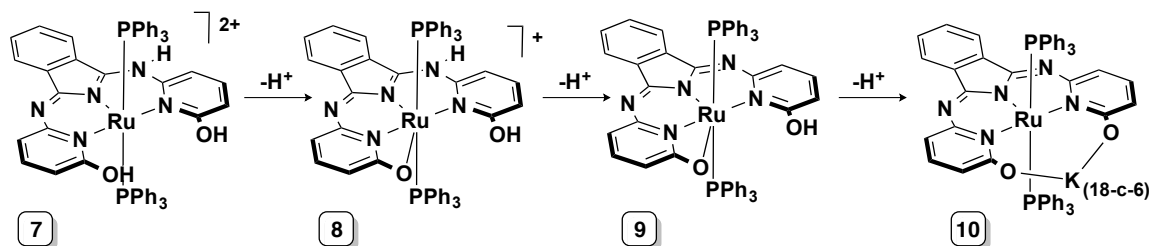


Table 2. Electron counts for compounds 7–10. Show all work to support your answers in the space provided.

Compound	d^n	electron number
7		
8		
9		
10		

Does the metal undergo redox chemistry due to changes in ligand protonation?

Does the metal-ligand bonding change throughout the proton cascade?

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