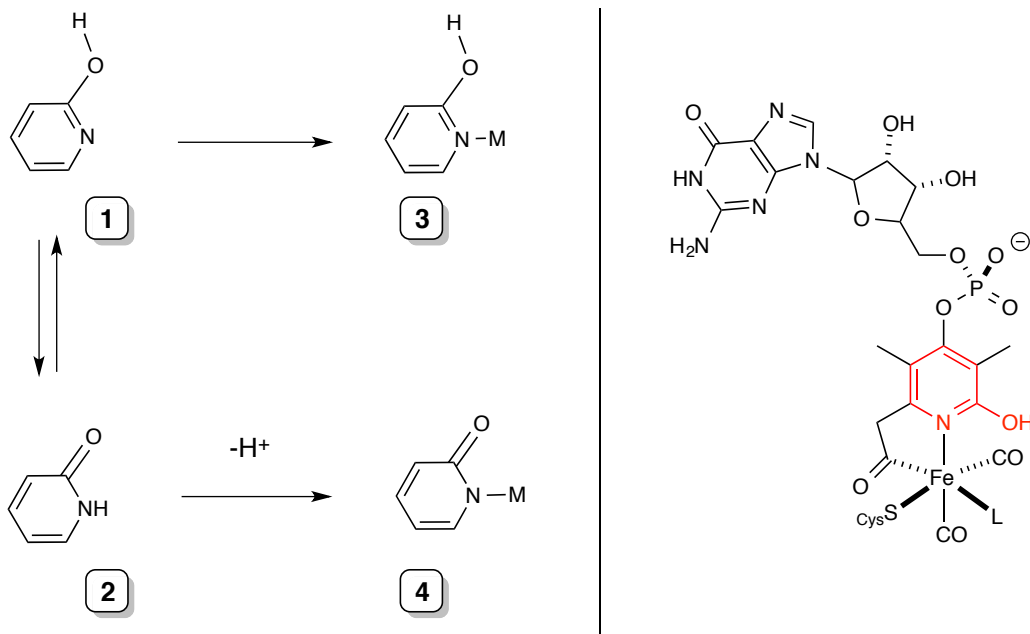


Created by Mary Grellier, University of Toulouse (mary.grellier@icc-toulouse.fr), Elizabeth A. Jensen, Aquinas College (jenseeli@aquinas.edu), Richard L. Lord, Grand Valley State University (lordri@gvsu.edu), Kari L. Stone, Benedictine University (kstone@ben.edu), Nathaniel K. Szymczak, University of Michigan (nszym@umich.edu), and Santiago Toledo, St. Edward's University (stoledoc@stedwards.edu) and posted on VIPEr (www.ionicvipr.org) on June 30, 2016. Copyright 2016. This work is licensed under the Creative Commons Attribution-NonCommercial-ShareAlike 4.0 License. To view a copy of this license visit <https://creativecommons.org/licenses/by-nc-sa/4.0/>.

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 count 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 counted as a neutral, two-electron donor. 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 that this is an overall neutral, six-electron donor. These ligands are common to both **5** and **6**. The remaining ligand, based on bipyridine (denoted bpy⁺) adopts a tautomer similar to 2-

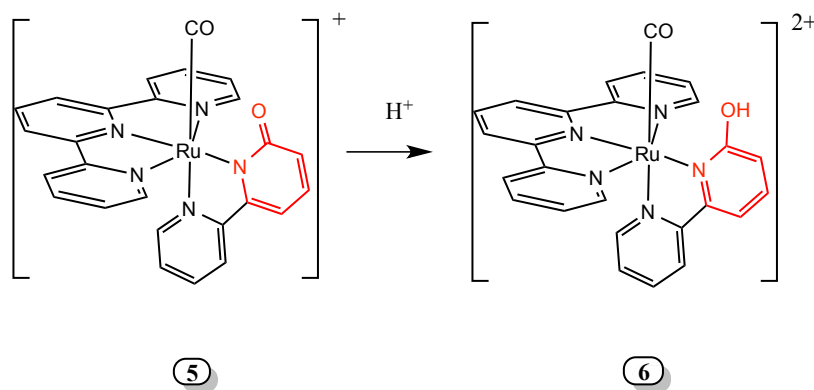
Created by Mary Grellier, University of Toulouse (mary.grellier@lcc-toulouse.fr), Elizabeth A. Jensen, Aquinas College (jenseeli@aquinas.edu), Richard L. Lord, Grand Valley State University (lordri@gvsu.edu), Kari L. Stone, Benedictine University (kstone@ben.edu), Nathaniel K. Szymczak, University of Michigan (nszym@umich.edu), and Santiago Toledo, St. Edward's University (stoledoc@stedwards.edu) and posted on VIPEr (www.ionicvipr.org) on June 30, 2016. Copyright 2016. This work is licensed under the Creative Commons Attribution-NonCommercial-ShareAlike 4.0 License. To view a copy of this license visit <https://creativecommons.org/licenses/by-nc-sa/4.0/>.

pyridone in **5** and 2-hydroxypyridine in **6**. When you break the M–N bonds in **5**, the black ring in bpy' looks like pyridine (2 e⁻, neutral) but the red ring, with only two bonds to N, would be a 2 e⁻, anionic donor. Thus, knowing that the complex has an overall 1+ charge one can infer that the Ru is a 2+ ion with a d⁶ electron count. Summing these up, **5** should be an 18-electron complex. In **6**, breaking the Ru–N bond in the red ring results in a ligand that looks like pyridine and implies that this ring is a neutral, two-electron donor. However, they arrived at **6** by protonating **5** so the overall charge increased to 2+ and therefore the Ru oxidation state, and overall electron count, does not change. This counting is summarized in Table 1.

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

5			6		
L	e ⁻ count	charge	L	e ⁻ count	charge
CO	2	0	CO	2	0
tpy	6	0	tpy	6	0
bpy'	4	1-	bpy'	4	0
Ru	d ⁶	2+	Ru	d ⁶	2+
overall	18	1+	overall	18	2+

Scheme 2



In-Class Exercise

Apply your new knowledge of classifying tautomeric ligands to complete Table 2 for the compounds shown 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

Created by Mary Grellier, University of Toulouse (mary.grellier@icc-toulouse.fr), Elizabeth A. Jensen, Aquinas College (jenseeli@aquinas.edu), Richard L. Lord, Grand Valley State University (lordri@gvsu.edu), Kari L. Stone, Benedictine University (kstone@ben.edu), Nathaniel K. Szymczak, University of Michigan (nszym@umich.edu), and Santiago Toledo, St. Edward's University (stoledoc@stedwards.edu) and posted on VIPEr (www.ionicvipr.org) on June 30, 2016. Copyright 2016. This work is licensed under the Creative Commons Attribution-NonCommercial-ShareAlike 4.0 License. To view a copy of this license visit <https://creativecommons.org/licenses/by-nc-sa/4.0/>.

Scheme 3

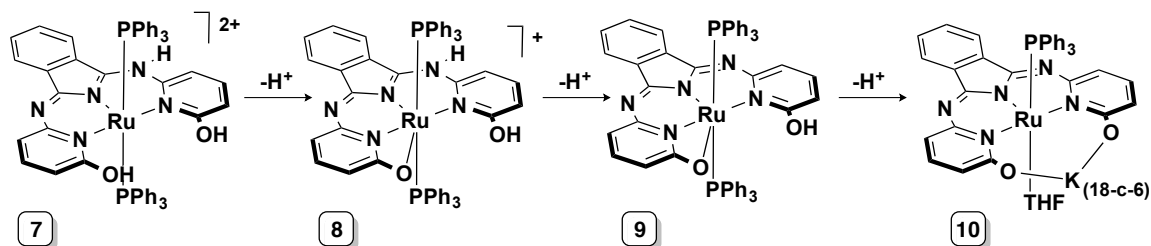


Table 2. Electron counts for compounds 7–10. Show all work to support your answers in the space provided.

Compound	<i>d</i> -electron count	overall e ⁻ count
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?

Created by Mary Grellier, University of Toulouse (mary.grellier@lcc-toulouse.fr), Elizabeth A. Jensen, Aquinas College (jenseeli@aquinas.edu), Richard L. Lord, Grand Valley State University (lordri@gvsu.edu), Kari L. Stone, Benedictine University (kstone@ben.edu), Nathaniel K. Szymczak, University of Michigan (nszym@umich.edu), and Santiago Toledo, St. Edward's University (stoledoc@stedwards.edu) and posted on VIPEr (www.ionicvipr.org) on June 30, 2016. Copyright 2016. This work is licensed under the Creative Commons Attribution-NonCommercial-ShareAlike 4.0 License. To view a copy of this license visit <https://creativecommons.org/licenses/by-nc-sa/4.0/>.

References

1. Moore, C. M.; Dahl, E. W.; Szymczak, N. K. *Curr. Opin. Chem. Biol.* **2015**, *25*, 9-17 (doi: 10.1016/j.cbpa.2014.11.012).
2. Tomon, T.; Koizumi, T.; Tanaka, K. *Eur. J. Inorg. Chem.* **2005**, 285-293 (doi: 10.1002/ejic.200400522).
3. Geri, J. B.; Szymczak, N. K. *J. Am. Chem. Soc.* **2015**, *137*, 12808-12814 (doi: 10.1021/jacs.5b08406).