

UNIVERSITY OF RHODE ISLAND
Department of Chemistry
VIRTUAL SEMINAR

3:00 PM, Monday, March 1, 2021
Please email blucht@uri.edu for link

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***“Consequences of Proton
Tautomerism in Organotransition
Metal Chemistry”***

HOST
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Consequences of Proton Tautomerism in Organotransition Metal Chemistry

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This seminar explores the importance of proton tautomerism in organotransition metal chemistry. For example, using a doubly protic bis-pyrazolato-pyridine pincer ligand, an octahedral Ir^{III}-H has been synthesized from an Ir^I starting material. This hydride was generated by adding sufficient electron density to the metal center such that it became the thermodynamically preferred site of protonation. It was observed via UV-Vis spectroscopy that this octahedral Ir^{III}-H establishes an equilibrium with a ligand protonated Ir^I. A consequence of this tautomerism is that this mixture evolves H₂ in a dinuclear reductive elimination reaction (generating an Ir^{II}-Ir^{II} dimer). This case study highlights how proton tautomerism can facilitate access to new reaction pathways for organotransition metal compounds.

These lessons have been applied towards the design of an Ir-based model of the extradiol catechol dioxygenases. This model compound reacts with O₂, ultimately resulting in the selective oxygenation of the aminophenolate ligand. The product of this oxygenation reaction is the first crystallographically characterized transition metal orthoester. We suggest that this outcome was made possible by proton tautomerism.



Jonathan L. Kuo, Ph.D.

Jonathan L. Kuo, Ph.D. is a National Institutes of Health sponsored Postdoctoral Fellow at the University of Pennsylvania. Previously, he earned his doctorate from Columbia University and his B.S. from the University of California, Los Angeles. Jonathan is interested in developing transition metal catalyzed processes that approach perfect atom economy. Examples include oxidations which use O₂, or reductions which use H₂. Many of these transformations involve a careful consideration of how to choreograph the movement of protons and electrons around a transition metal ion in a controlled fashion.