

Title: Catalytic Reductive O-Atom Transfer Methods via P(III)/P(V)=O Redox Cycling

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Abstract:

Despite well-known thermodynamic and kinetic challenges associated with phosphine oxide reduction, recent developments have demonstrated the viability of the P(III)⇌P(V)=O redox couple to drive O-atom transfer reactions in a catalytic way.¹ In this presentation, recent developments in the use of small-ring phosphacycles as catalysts for a diverse range of synthetic O-atom transfer reactions will be described.² Synthetic reactions focusing on carbon-heteroatom bond forming methods will be highlighted. Physical and mechanistic studies will be described to illustrate important design principles in organophosphorus redox catalysis.

References and Notes:

1. Lipshultz, J.M.; Li, G.; Radosevich, A.T. “Main Group Redox Catalysis of Organopnictogens: Vertical Periodic Trends and Emerging Opportunities in Group 15.” *J. Am. Chem. Soc.* **2021**, *143*, 1699–1721.
2. Li, G.; Nykaza, T.V.; Cooper, J.C.; Ramirez, A.; Luzung, M.R.; Radosevich, A.T. “An Improved P(III)/P(V)=O-Catalyzed Reductive C–N Coupling of Nitroaromatics and Boronic Acids by Mechanistic Differentiation of Rate- and Product-Determining Steps.” *J. Am. Chem. Soc.* **2020**, *142*, 6786–6799

Bio-Sketch of Speaker

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PROFESSIONAL APPOINTMENTS

Aug. 2016 – present	MIT, Associate Professor
Jul. 2016	Pennsylvania State University, Associate Professor
Jul. 2010 – Jun. 2016	Pennsylvania State University, Assistant Professor

EDUCATION

Nov. 2007 – May 2010	MIT, NIH Postdoctoral Fellow with Prof. Daniel G. Nocera
Sep. 2002 – Oct. 2007	UC Berkeley, Ph.D. Research with Prof. F. Dean Toste
Sep. 1998 – May 2002	Univ. of Notre Dame, B.S. Research with Prof. Olaf Wiest

AWARDS

2018 Camille and Henry Dreyfus Environmental Chemistry Mentor
2015 Amgen Young Investigators' Award
2015 Thieme Chemistry Journal Award
2014 Alfred P. Sloan Research Fellowship in Chemistry
2014 CAREER Award – National Science Foundation

REPRESENTATIVE PUBLICATIONS

Lipshultz, J.M.; Radosevich, A.T. “Uniting Amide Synthesis and Activation by P^{III}/P^V-Catalyzed Serial Condensation: Three-Component Assembly of 2-Amidopyridines.” *J. Am. Chem. Soc.* **2021**, *143*, 14487–14494.

Li, G.; Miller, S.P.; Radosevich, A.T. “P^{III}/P^V=O-Catalyzed Intermolecular N–N Bond Formation: Cross-Selective Reductive Coupling of Nitroarenes and Anilines.” *J. Am. Chem. Soc.* **2021**, *143*, 14464–14469.

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Li, G.; Nykaza, T.V.; Cooper, J.C.; Ramirez, A.; Luzung, M.R.; Radosevich, A.T. “An Improved P(III)/P(V)=O-Catalyzed Reductive C–N Coupling of Nitroaromatics and Boronic Acids by Mechanistic Differentiation of Rate- and Product-Determining Steps.” *J. Am. Chem. Soc.* **2020**, *142*, 6786–6799.

Nykaza, T.V.; Li, G.; Yang, J.; Luzung, M.R.; Radosevich, A.T. “P^{III}/P^V=O-Catalyzed Cascade Synthesis of N-Functionalized Azaheterocycles.” *Angew. Chem. Int. Ed.* **2020**, *59*, 4505–4510.