Ti-Catalyzed Oxidative Amination Reactions: A Platform For Reaction Discovery

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Titanium is an ideal metal for green and sustainable catalysis—it is the 2^{nd} most earthabundant transition metal, and the byproducts of Ti reactions (TiO₂) are nontoxic. However, a significant challenge of utilizing early transition metals for catalytic redox processes is that they typically do not undergo facile oxidation state changes because of the thermodynamic stability of their high oxidation states. Several years ago our group discovered that Ti imidos (L_nTi=NR) can catalyze oxidative nitrene transfer reactions from diazenes via a Ti^{II}/Ti^{IV} redox couple. We are using this new mode of reactivity to develop a large suite of practical synthetic methods. In this talk, our latest synthetic and mechanistic discoveries related to Ti nitrene transfer catalysis and other amination reactions will be discussed, including new computational catalyst design strategies for selective construction of pyrroles via [2+2+1] cycloaddition of alkynes with Ti nitrenes and alkynes, as well as new methods for catalytic oxidative amination, N-N oxidative coupling of pyrazoles, and more.



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Ian Tonks is the Lloyd H. Reyerson professor at the University of Minnesota – Twin Cities, and associate editor for the ACS journal *Organometallics*. He received his B.A. in Chemistry from Columbia University in 2006 and performed undergraduate research with Prof. Ged Parkin. He earned his Ph.D. in 2012 from the California Institute of Technology, where he worked with Prof. John Bercaw on olefin polymerization catalysis and early transition metal-ligand multiply bonded complexes. After postdoctoral research with Prof. Clark Landis at the University of Wisconsin – Madison, he began his independent career at the University of Minnesota in 2013. His current research interests are focused on the development of earth



abundant, sustainable catalytic methods using early transition metals, and also on catalytic strategies for incorporation of CO₂ into polymers. Prof. Tonks' work has rbeen recognized with an Outstanding New Investigator Award from the National Institutes of Health, an Alfred P. Sloan Fellowship, a Department of Energy CAREER award, and the ACS *Organometallics* Distinguished Author Award, among others. Additionally, Prof. Tonks' service toward improving academic safety culture was recently recognized with the 2021 ACS Division of Chemical Health and Safety Graduate Faculty Safety Award.