Developments in Photocatalytic Hydrophosphination

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Abstract: An important challenge for chemists is increasingly efficient routes to element–carbon bonds, as characterized by energetic costs and atom economy, among other factors. An atom-economical route to metal-catalyzed element–carbon bond formation is the addition of an E–H bond across an unsaturated substrate, generally termed heterofunctionalization. For hydrophosphination or P–C bond formation, challenges in substrate scope, selectivity, and catalyst have loomed. Starting from poor initial hydrophosphination catalysis with zirconium compounds of the type $(N_3N)ZrX$ ($N_3N = N(CH_2CH_2NSiMe_3)_3^{3-}$; X = anionic ligand), a family of earth abundant, highly active, and selective catalysts have been discovered and investigated. Surprisingly, photolysis is a critical factor in activity for these catalysts. The arc of catalysis moves from zirconium to iron chemistry that informs most recent discoveries in simple copper catalysts that may be the most active known. For example, bis(acetylacetonato)copper(II) is an active catalyst for the hydrophosphination of alkenes and alkynes with primary and secondary phosphines. Under thermal conditions, the activity of $Cu(acac)_2$ is comparable to some of the best literature catalysts. However, under ambient temperature irradiation centered at 365 nm, the conversions are remarkable with some reactions complete in minutes. The photocatalytic conditions are critical, and comparison to literature catalysts has been made where $Cu(acac)_2$ is still superior in activity. Nevertheless, this simple, inexpensive catalyst is highly effective, placing hydrophosphination in the hands of many more synthetic chemists.

Biography: Rory Waterman is currently Professor of Chemistry at the University of Vermont (UVM). After earning a Ph. D. in 2004 with the late Gregory Hillhouse, and a Miller Postdoctoral Fellowship at the University of California, Berkley, with Don Tilley, he started at UVM in 2006 as an assistant professor, was promoted to associate professor with tenure in 2012, and was promoted full professor in 2016. His work has garnered recognition including a Sloan Fellowship, Cottrell Scholar Award, Humboldt Fellowship, Fellow of the Royal Society of Chemistry, Fellow of the American Chemical Society, and most recently, a Fellow of the American Association for the Advancement of Science (AAAS). His research interests span syntenic and catalytic inorganic and organometallic chemistry with applications in materials and energy as well as issues in professional development an inclusion in the sciences.