

Seminarios itinerantes

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University of Virginia

29 de Mayo a 2 de Junio 2017

Transition metal catalyzed hydroarylation of olefins: New catalysts for alkyl and alkenyl arenes

Lunes, 29 de Mayo, Universidad de Oviedo

11:00 h, Facultad de química (japm@uniovi.es)

Martes, 30 de Mayo, CINQUIMA, Universidad de Valladolid

12:00 h, Sala de conferencias del edificio QUIFIMA (espinet@qi.uva.es)

Miércoles, 31 de Mayo, Universidad de Alcalá de Henares

12:00 h, Aula de grados, edificio de farmacia (juanc.flores@uah.es)

Jueves, 1 de Junio, IIQ, CSIC – Universidad de Sevilla

12:00 h, Salón de actos del IIQ (campora@iiq.csic.es)

Viernes, 2 de Junio, CIQSO, Universidad de Huelva

12:30 h, Sala de conferencias (perez@dqcm.uhu.es)

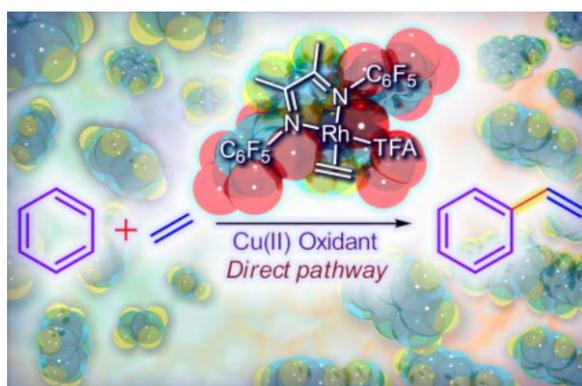
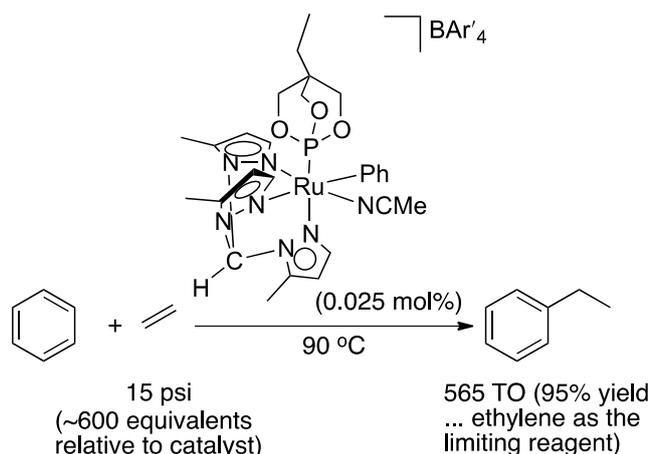
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The selective catalytic functionalization of C–H bonds of hydrocarbons remains one of the foremost challenges facing synthetic chemists. Processes that convert C–H bonds of simple hydrocarbons into new C–C bonds are particularly important. For example, alkyl and alkenyl arenes are currently produced on a scale of billions of pounds per year, and the addition of aromatic C–H bonds across olefin C=C bonds, olefin hydroarylation, provides an atom economical reaction with broad potential including applications in both commodity scale processes as well as fine chemical synthesis. Current industrial catalysts (e.g., Friedel-Crafts catalysis or zeolites) for arene alkylation are based on acid-mediated olefin activation. New catalysts that operate by an entirely different pathway that involves transition metal-mediated C–H activation followed by olefin insertion into metal-aryl bonds offer new opportunities.

The Gunnoe group has been studying olefin hydroarylation (to produce alkyl aromatics) and oxidative olefin hydroarylation (to produce alkenyl aromatics) catalyzed by well-defined homogeneous catalysts based on Ru, Rh and Pt. The goal is to combine understanding of transition metal mediated C–H activation and controlled olefin insertion to design novel catalytic routes for important classes of chemicals. For TpRu(L)(NCMe)Ph (Tp = hydridotris(pyrazolyl)borate; L = CO, PMe_3 , $\text{P(OCH}_2)_3\text{CEt}$, P(N-pyrrolyl)_3 , etc.) catalyst precursors, which provide a range steric and electronic profiles, the impact of the donor ability of the ligand "L" on the rate of stoichiometric benzene C–H activation has been elucidated. Importantly, these studies have led to an understanding of the primary catalyst deactivation pathway and a prediction that replacing anionic Tp ligands with charge-neutral tris(pyrazolyl)alkane ligands would provide increased catalyst longevity. In fact, using $[(\text{HC}(\text{pz}'_3)\text{Ru}(\text{P(OCH}_2)_3\text{CEt})(\text{NCMe)Ph})][\text{BAR}'_4]$ [$\text{HC}(\text{pz}'_3)$ = tris(3,5-dimethylpyrazolyl)methane] as catalyst precursor gives > 500 turnover numbers (TONs) of ethylbenzene formation (~95% yield) while the corresponding $\text{TpRu}(\text{P(OCH}_2)_3\text{CEt})(\text{NCMe)Ph}$ complex gives 20 TONs under the same conditions.



and yields $\geq 95\%$. Turnover numbers > 800 have been demonstrated with catalyst stability up to 96 hours.

In an effort directed toward alkenyl arene synthesis, catalysts based on d^8 transition metals have been pursued. Detailed studies of Pt(II) complexes supported by chelating bipyridyl ligands revealed a strategy for the direct formation of vinyl arenes; however, catalyst decomposition to Pt(s) is problematic. It was hypothesized that Rh(I) complexes could be effective catalysts. Recently, it was reported that $(^{\text{F}}\text{DAB})\text{Rh}(\text{TFA})(\eta^2\text{-C}_2\text{H}_4)$ [$^{\text{F}}\text{DAB}$ = *N,N'*-bis(pentafluorophenyl)-2,3-dimethyl-1,4-diaza-1,3-butadiene; TFA = trifluoroacetate] converts benzene, ethylene and Cu(II) acetate to styrene, Cu(I) acetate, and acetic acid with high selectivity



Brent GUNNOE received his B.A. from West Virginia University in 1993, where he was a Presidential Scholar and was awarded the Outstanding Junior (1992) and Senior (1993) Chemistry Student. After obtaining a Ph. D. from the University of North Carolina (1997) under the direction of Professor Joseph Templeton and serving as a postdoctoral researcher at the University of Virginia (1997-1999) with Professor Dean Harman, Gunnoe began his independent career as an Assistant Professor at North Carolina State University. In 2008 he moved to the University of Virginia as Professor of Chemistry. He is co-author of three book chapters, three patents and greater than 130 referred journal publications, and he has delivered over 125 invited lectures. He was the recipient of a National Science Foundation CAREER Award, the Sigma Xi Faculty Research Award, an Alfred P. Sloan Research Fellowship and the LeRoy and Elva Martin Award for Teaching Excellence. From 2009-

2015, Gunnoe served as the Director of the Center for Catalytic Hydrocarbon Functionalization (CCHF), an Energy Frontier Research Center funded by the United States Department of Energy. He currently serves as Associate Editor for *ACS Catalysis*.