**Dinitrogen binding and catalytic functionalization by organometallic actinide complexes**

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Chemists have spent more than a century trying to make catalysts that can convert atmospheric dinitrogen to ammonia, or to directly to amines under mild conditions. Hundreds of d-block complexes are now known to bind N2, and a few catalysts for N2 conversion to ammonia or tris(silyl)amine have been developed.

The binding of dinitrogen to any f-block metal cation is still extremely rare, but studies of the binding of traditionally inert small molecules such as N2 are an important contribution to the fundamental understanding of bonding and electronic structure for these large, relativistic metals.

We will discuss the development of our understanding of N2 binding organometallic f-block complexes over the years, our recent development of the first molecular f-block complexes that can catalyse the reduction and functionalisation of dinitrogen; and the use of structural control by the ligand framework to enables the first catalytic conversion of dinitrogen into a secondary silylamine by any metal.

1. Metallacyclic actinide catalysts for dinitrogen conversion to ammonia and secondary amines. P. L. Arnold, T. Ochiai, F. Y. T. Lam, R. P. Kelly, M. L. Seymour, L. Maron, *Nature Chem.* **2020**, *12*, 654-659. doi:10.1038/s41557-020-0457-9.
2. Dinuclear uranium complexation and manipulation using robust tetraaryloxides. J. A. L. Wells, M. L. Seymour, M. Suvova, P. L. Arnold, *Dalton Trans.* **2016**, *45*, 16026-16032. doi:10.1039/C6DT02630C.
3. Small molecule activation by uranium tris(aryloxides): Experimental and computational studies of binding of N2, coupling of CO, and deoxygenation insertion of CO2 under ambient conditions. S. M. Mansell, N. Kaltsoyannis, P. L. Arnold, *J. Am. Chem. Soc.* **2011**, *133*, 9036-9051. doi:10.1021/ja2019492.