John Arnold, Professor

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Education

Ph.D: University of California, San Diego, 9/82 - 12/86, with Professor T. Don Tilley. *Thesis*: Synthesis, Structure and Reactivity of Silyl Derivatives of Tantalum and Niobium.

B.Sc: Applied Chemistry, Salford University, Salford, U.K., 9/79 - 6/82, First Class Honors.

Academic Carrier Director	Berkeley Center for Green Chemistry, 2010-present
Associate Editor for the Americas	Dalton Transactions, 2002-present
Professor	University of California, Berkeley, 6/00 – present
Vice Chair	Chemistry Department, 7/95-6/99
Associate Professor	University of California, Berkeley, 7/95 –6/00
Associate Scientist	Lawrence Berkeley National Laboratory, 1991 - present
Assistant Professor	University of California, Berkeley, 7/89 -6/95
Royal Society Research Fellow	Imperial College, London, 10/88-6/89

Awards and Honors

College of Chemistry Teaching Award, 2007, 1994; Fellow of the Royal Society of Chemistry, 2002; Sloan Research Fellowship; 1993-95, Royal Society 1983 University Research Fellow, 1988-89; SERC Postdoctoral Fellowship, 1988; Undergraduate Prizes, Salford University, 1981, 1982.

Total Publications

166 refereed articles, h-index: 47

Research Interests

Work in my group is focused on chemical questions relating to energy and the environment, from the perspective of inorganic and organometallic reactivity. The last three years has seen the group expand into fuel cell chemistry, which has become a major focus area in our research. We are continuing our long-standing interest in early transition metal chemistry, with a new focus on catalysis, and are building our efforts in actinide chemistry.

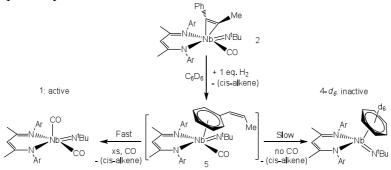
Catalytic Hydrogenation with Early Transition Metal Imido Complexes: Unusual Structural and Mechanistic Findings

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Early-transition-metal hydrogenation catalysts have received less attention than comparable late-transition-metal systems, particularly since the discovery of Wilkinson's catalyst. This emphasis on late-transition-metal systems has been largely driven by practical concerns including functional-group tolerance and ease of handling. Further examination of early-transition-metal systems is particularly attractive from two viewpoints: 1) the identification and elucidation of unusual mechanisms of dihydrogen activation and 2) the application of the intrinsic properties of early transition metals, in particular high-valent complexes, to the selective hydrogenation of alkynes to Z alkenes. This transformation is typically accomplished by Lindlar's catalyst, and is practically difficult to employ and suffers, particularly in the case of conjugated aromatic systems, from E/Z isomerization and overhydrogenation.

This presentation describes the recent results of two attempts to develop new chemistry with early transition metals from group 5. First, the discovery of a Nb(III)-mediated catalytic hydrogenation of internal alkynes to Z-alkenes is reported. The mechanistic proposal involves initial reduction of the alkyne by the Nb(III) complex (BDI)Nb(N'Bu)(CO)₂ to provide a Nb(V) metallacyclopropene, itself capable of σ -bond metathesis reactivity with H₂. The resulting alkenyl hydride species then undergoes reductive elimination to provide the Z-alkene product and regenerate a metal complex in the Nb(III) oxidation state. Support for the proposed mechanism is derived from *i*) the dependence of product selectivity on the relative concentrations of CO and H₂, *ii*) the isolation of complexes closely related to those proposed to lie on the catalytic cycle, *iii*) H/D crossover experiments, and *iv*) DFT studies on multiple possible reaction pathways.



Second, we report the synthesis of the cationic vanadium bisimido complex [V(NtBu)2(PMe3)3][Al-(PFTB)4] and its application to the selective catalytic hydrogenation of alkynes to Z alkenes.

$$R_{1} = Me, R_{2} = P1, 24 n, 100\%$$

$$R_{1} = R_{2} = Et; 72 h, 62\%$$

$$R_{1} = R_{2} = T1; 24 n, 100\%$$

$$R_{1} = R_{2} = TR; 72 h, 62\%$$

$$R_{1} = R_{2} = TR; 72 h, 10\%$$
(1)
$$R_{1} = H; R_{2} = H; 72 h, 52\%$$

$$R_{1} = Ph, R_{2} = H; 72 h, 10\%$$