



An enigmatic trailblazer on the frontier of discovery: Richard A. Andersen

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We are honored to serve as guest editors for this virtual, special issue, encompassing contributions to both *ChemComm* and *Dalton Transactions*, in celebration of the impact that Richard “Dick” Andersen has had on inorganic and organometallic chemistry, on the occasion of his 75th birthday. This impact is reflected in his many and diverse contributions to chemistry and his mentorship, which has had a profound influence on numerous former coworkers. We have the privilege of being Dick’s colleagues at UC Berkeley and are grateful to him for sage advice across many years of mutual engagement and interaction.

Even casual acquaintances are struck by two of the hallmarks of Dick’s character – his infectious enthusiasm for chemistry, and his critical thinking. These characteristics carry over to his research, where his intense focus and interactive nature have enabled many important contributions to f-element and transition-metal chemistry, partly through collaborative projects. His strong dedication to teaching, and his diverse interests in chemical research, are reflected in the contributions found in this issue.

Dick Andersen was born in Oklahoma but grew up in the small town of Yankton, South Dakota, the only child of a truck driver and school teacher. His early education was unremarkable but his high school chemistry

teacher, Alfred Halsted, impressed upon him the connections between chemistry and everyday life. During his undergraduate education at the University of South Dakota, Dick’s interest in chemistry was reignited by an inspirational teacher, Norman Miller, who had just arrived from DuPont Central Research and taught inorganic chemistry from Cotton and Wilkinson’s first (1962) edition of “*Advanced Inorganic Chemistry*”. Dick was fascinated by the properties of transition-metal complexes, and even at this early stage in his education resolved to work with Geoffrey Wilkinson at Imperial College, London. In fact, Dick found his way to Imperial in 1974 as a postdoctoral fellow, but his graduate studies were conducted at the University of Wyoming with the legendary organometallic chemist Geoffrey Coates, who had recently moved from the University of Durham. Dick was Coates’ last student, and in his time in Laramie, Coates completed the 3rd edition of his seminal book “*Organometallic Compounds*”, coauthored with Wade and Green. Dick credits Coates with providing him the basic training to function in a laboratory, apply the scientific method, and write manuscripts. Dick’s time in Coates’ lab was extremely productive, and produced many fundamental organometallic and alkoxide compounds of beryllium.

On 17 October 1973, the day it was announced that Geoff Wilkinson and E. O. Fischer would share the Nobel Prize in Chemistry, Wilkinson sent a letter to

Dick indicating his intention to hire him as a postdoc. Dick’s time in London was formative in cementing his primary interests and research philosophies, and in striking life-long friendships with coworkers Ernesto Carmona and Roberto Sanchez-Delgado. He also honed his mentoring skills during this time, working with undergraduates Peter Edwards (now at Cardiff University) and Richard Jones (now at University of Texas). Dick’s research in the Wilkinson group was profoundly influential, in mapping out new routes to a range of transition-metal alkyl complexes at a time when such compounds were the topic of considerable interest.

Dick Andersen began his career at Berkeley in 1976, and following Geoff Wilkinson’s advice of “don’t repeat your PhD thesis over and over again” he established new research directions in (1) the organometallic chemistry of metal–metal multiply bonded compounds and (2) f-metal chemistry. The first area, defining ligand substitution patterns in quadruply-bonded Mo₂ complexes, involved work by Vera Mainz and Greg Girolami. The latter area, which was to become a long-standing focus of Dick’s affiliation with the actinide program at Lawrence Berkeley National Laboratory (LBNL), began with use of the sterically bulky amido ligand –N(SiMe₃)₂ to stabilize low-valent and low-coordinate f- and d-metal centers with the help of early coworkers Howard Turner (an undergraduate), Steve Simpson (a postdoc)

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and Roy Planalp (a grad student). A key compound resulting from this work, synthesized by Dick himself, is the now commonly employed U(III) starting compound $U[N(SiMe_3)_2]_3$. In work started by Don Tilley and continued with Jim Boncella, divalent lanthanide amido complexes of Eu and Yb were prepared and explored. Around this time, John Robbins, a graduate student working with the late Jim Smart, was utilizing the new Threlkel-Bercaw synthesis of pentamethylcyclopentadiene to prepare decamethylmetallocenes of the first-row d-metals, and it seemed that a similar approach might give a monomeric, 4f metal metallocene. Thus began Dick's long fascination with decamethyltitanocene, $Yb(C_5Me_5)_2$, and its unusual properties, including its bent structure (from work by Carol Burns and collaborator Arnie Haaland and Jennifer Green) and its coordination of non-traditional ligands such as dimethylacetylene and $MeBe(C_5Me_5)$. In collaboration with Hans Brintzinger, Dick showed that under pressure $Yb(C_5Me_5)_2$ binds carbon monoxide, and an interpretation of the infrared data, with collaborators Laurent Maron and Odile Eisenstein, showed that the resulting complex is different from analogues involving Eu, Sm, Ca and Sr, in that it forms a non-traditional O-bonded CO complex. An especially intriguing ytterbocene complex is $(C_5Me_5)_2Yb(2,2'$ -bipyridine), first prepared by Don Tilley in 1978 but not published until 23 years later. This delay reflects Dick's commitment to developing a thorough understanding of chemical phenomena before publishing; although the X-ray structure and considerable characterization data were obtained early on, the bizarre electronic properties defied satisfactory explanation. In particular, the magnetism of this complex was difficult to understand in the context of simple bonding models; it is neither diamagnetic like the analogous bis(pyridine adduct) nor a trivalent paramagnet with a bipyridyl radical anion. This system, investigated by a succession of coworkers including Dave Berg, Madeleine Schultz, Marc Walter and Greg Nocton, was eventually explained by

Corwin Booth, a collaborator at LBNL, by the Kondo model for correlated electron behavior and a multi-configurational ground state. It is now widely appreciated that his model applies to a number of other complexes involving metals in this region of the periodic table. Dick's interest in alkyl complexes, with diverse metal centers from beryllium to uranium, have continued as can be seen (for example) in work published with Steve Stultz, Phil Matsunaga, Mike Smith, Wayne Lukens, Chad Sofield, and Marc Weydert (the latter co-advised with colleague Robert Bergman).

Dick's passionate and infectious enthusiasm for chemistry and discovery make him a great collaborator, and he has benefited from several cooperative research endeavors throughout his career. A conversation with Jean-Marie Basset in 1999 initiated an interest in surface organometallic chemistry with lanthanide hydrides, and corresponding molecular models. With Evan Werkema, Dick produced the monomeric hydride $(1,2,4\text{-}t\text{-Bu}_3C_5H_2)_2CeH$, which is a rare monomeric lanthanide hydride that represents a model for a surface-bound species. This hydride reacts with a range of CH_3X molecules by way of C–H activation and the formation of transient cerium-carbenoid intermediates, a reaction pathway that was elucidated with calculations by Dick's longtime collaborators in computational chemistry, Odile Eisenstein and Laurent Maron. More recent work on the grafting of lanthanide species onto silica, in collaborative work with Christophe Coperet, has led to his current obsession with solid-state NMR spectroscopy and specifically use of information contained from the chemical shift anisotropy. His strong involvement in collaborative science is reflected in the many Visiting Professorships he has been invited to across the world, including stints in Sevilla, Lyon, Montpellier, New South Wales, Australia, and Zürich, and as a Humboldt Professor in various locations in Germany.

One of Dick's important collaborators has been his colleague Bob Bergman. A number of former Berkeley PhD students have had the good fortune to have both

as mentors, including John Hartwig, Pat Holland, and Kris McNeill. A common theme in this chemistry was metal–ligand multiple bonding, a strong interest that has defined a number of Dick's studies in d- and f-block chemistry. Exemplary further systems include the uranium imido complex $(C_5H_4Me)_3UNPh$, first prepared by John Brennan, and decamethyltitanocene imidos, oxos, and sulfidos, investigated by Mitch Smith, Guofu Zi, Zach Sweeney and Jennifer Polse (the latter two being co-advised by Bergman).

We are very pleased to see the many, varied contributions to this special issue honoring Dick Andersen and his influence on our field. His high scientific standards and colorful means of expression have guided and inspired generations of researchers passing through Berkeley, many of whom were not formally defined as coworkers. He is respected as a faculty member who readily contributes time and energy as an eager consultant and sounding board, and students relate to him because of his youthful passion for chemistry, and because throughout his career he has maintained his own synthetic projects at the bench. Appropriately, one of the contributions to this dedicated issue, by Dick's former student Joanne Stewart and coauthors, focuses on his legendary skills as a teacher and mentor. A particular passion of Dick's has been the Berkeley course in synthetic inorganic chemistry, Chemistry 108. A large number of talented undergraduates have learned synthetic chemistry as a result of Dick's hands-on approach to this course and many have gone on to exploit these skills in their subsequent careers.

Dick Andersen is truly one of the remarkable figures in inorganic chemistry, whose enigmatic and colorful personality lends a unique flair to his science. Not surprisingly, Dick is a big fan of Bob Dylan, the 2016 Nobel laureate in Literature, and one of Dick's favorite Dylan lyrics perhaps also captures his independent spirit: "...to be on your own, with no direction home, a complete unknown, like a rolling stone" (Highway 61 Revisited, cut 1). Happy birthday, Dick!