

American Chemical Society

National Awards Nomination Packet

F. Albert Cotton Award in Synthetic Inorganic Chemistry:2018 for: Richard Adams

Received: 10/25/2016

Cycle Year: 1

"For pioneering contributions of the syntheses, structures and reactivity of polynuclear metal carbonyl complexes."

NOMINATOR:

Tobin Marks
Northwestern Univ
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Evanston, IL 60208-3113
UNITED STATES

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Fax: (847)491-2990
Email: t-marks@northwestern.eduXXX

- Have you discussed this award nomination with the nominee? Yes

NOMINEE:

Richard Adams
Univ of South Carolina
631 Sumter St Gsrc
Columbia, SC 29208-0001
UNITED STATES

Tel: (803)782-2896
Email: adamsrd@mailbox.sc.eduXXX

ACS Current Member: Yes
Years of Service: 49
Date of birth: 01/01/1947
Present Position: Professor
Industry: Academia

CODE OF CONDUCT:

- To the best of my knowledge, including past and present circumstances, the nominee:
 1. Employs and requires good safety protocols and practices in his/her laboratory and/or work environment;
 2. Upholds the highest ethical standards in his/her laboratory and/or work environment; and
 3. Otherwise engages in conduct that is consistent with both the objects of the American Chemical Society as stated in Article II Section 1 of its Constitution and the Chemical Professional Code of Conduct.

Code of Conduct Answer: Yes

SUPPORTER 1

Francois Gabbai
Texas A&M Univ
PO Box 30012
College Station, TX 77842-3012
UNITED STATES

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SUPPORTER 2

Gregory Robinson
Univ of Georgia
1001 Cedar St
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October 25, 2016

Nomination Letter for Richard D. Adams

Dear F. Albert Cotton Award in Synthetic Inorganic Chemistry Selection Committee,

Alignment of the work for the Purpose of the Award.

Richard D. Adams is one of the world leaders in research on the synthesis of multimetallic carbonyl cluster complexes.

Significance. Adams has synthesized and structurally characterized a range of new organometallic cluster complexes and studied their ability to perform multicenter organic transformations. He was the first to elucidate the mechanism of aromatic binuclear CH bond activation, *Angew. Chem.*, **2016**, 55 (4), 1324 – 1327. He was the first to provide unambiguous evidence that intact cluster complexes can produce catalysis in solution.

Highlights of some of Adams' most important work are summarized below.

Binuclear Aromatic CH Bond Activation. Adams et al. have prepared the first binuclear complex, $\text{Re}_2(\text{CO})_8(\mu\text{-H})(\mu\text{-Ph})$, **1** that contains a bridging hydride and bridging phenyl ligand. It reversibly adds and eliminates benzene at room temperature and they have established the first *binuclear* mechanism for CH bond-making/bond-breaking by using DFT computational analyses. Compound **1** reacts with naphthalene and anilines by aromatic CH activation.

Oxidative Additions of Organo-gold Complexes to Metal carbonyl Cluster Complexes. Adams has recently discovered the first examples of the oxidative addition of organogold complexes, such as $\text{RAu}(\text{PPh}_3)$, $\text{R} = \text{CH}_3$, Ph , and C_{10}H_9 (pyrenyl), to metal cluster complexes such as $\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$ and $[\text{Ir}_4(\text{CO})_{11}\text{Br}]^-$ to yield complexes containing $\text{Au}(\text{PPh}_3)$ groups and terminal or bridging R groups, e.g. $\text{Os}_3(\text{CO})_{10}[\mu\text{-Au}(\text{PPh}_3)](\mu\text{-Ph})$. The unusual bridging R groups undergo facile multicenter ligand transformations (*Organometallics* **2012**, 31, 2961).

Transition Metal - Main Group Bimetallic Clusters.

Tin, germanium and bismuth are widely used as modifiers in heterogeneous catalysis. Adams et al. have recently prepared a range of new transition metal complexes containing tin, germanium and bismuth ligands. For example, they have made the first rhodium-tin cluster complex $\text{Rh}_3(\text{CO})_3(\mu\text{-SnPh}_2)_3(\text{SnPh}_3)_3(\mu_3\text{-SnPh})_2$ from the reaction of Ph_3SnH with $\text{Rh}_4(\text{CO})_{12}$. This complex contains an *unprecedented* eight tin ligands including three terminal SnPh_3 groups. Adams et al. have shown that the phenyl groups can be cleaved from GePh_3 ligands and this elimination was shown to occur at a single metal site in a triiridium complex, *Organometallics* **2012**, 31, 2621. He has shown that iridium-bismuth complexes are precursors for excellent catalysts for the selective oxidation of picoline to Niacin (Vitamin B₃), *ACS Catal.*, **2013**, 3, 3106.

Bimetallics for Hydrogen Activation.

Adams et al. have prepared a series of *highly* unsaturated platinum-rhenium carbonyl cluster complexes by using the sterically-encumbered P^tBu_3 ligand. The complex $\text{Pt}_3\text{Re}_2(\text{CO})_6(\text{P}^t\text{Bu}_3)_3$, **2** which is unsaturated by the amount of **10** valence electrons, adds three equivalents of H_2 at room temperature to form the hexahydrido complex $\text{Pt}_3\text{Re}_2(\text{CO})_6(\text{P}^t\text{Bu}_3)_3(\mu\text{-H})_6$, **3**. The reaction formally adds six electrons to the cluster. The metal cluster in **3** is structurally similar to **2**, but it contains six hydrido ligands, one bridging each of the six Re-Pt bonds (*Acct. Chem. Res.*, **2009**,

42, 409). The Adams group has also synthesized the new tetranuclear platinum-rhenium complex $\text{Pt}_2\text{Re}_2(\text{CO})_7(\text{PBUt}_3)_2(\mu\text{-H})_2$, **4** which is deficient by six electrons. Compound **4** adds hydrogen at 25 °C to yield the tetrahydrido complex $\text{Pt}_2\text{Re}_2(\text{CO})_7(\text{PBUt}_3)_2(\mu\text{-H})_4$, **5**. Most interestingly, this hydrogen addition is reversed when **5** is heated.

Activation of a Metal-Hydride Complex by Platinum.

Adams has demonstrated a novel activation of a metal-hydride complex for an alkyne insertion reaction. Addition of $\text{Pt}(\text{PBUt}_3)_2$ to $\text{HOs}(\text{CO})_4(\text{SnPh}_3)$ yielded the activated complex $(\text{PBUt}_3)\text{Pt}(\mu\text{-H})\text{Os}(\text{CO})_4(\text{SnPh}_3)$ that readily inserts PhC_2H into the Os-H bond to yield the bimetallic alkenyl complex, $(\text{PBUt}_3)\text{Pt}[\mu\text{-C}(\text{Ph})\text{CH}_2]\text{Os}(\text{CO})_4(\text{SnPh}_3)$. This insertion reaction does not occur in the absence of the platinum complex, *J. Am. Chem. Soc.*, **2007**, 129, 7545.

Metallation of Polyynes and its Effect on Electrocommunication.

Polyalkynes have been suggested for possible use as “*molecular wires*” for the construction of new nanoscale electronic devices. Adams was the first to demonstrate that chains of osmium atoms could be aligned along ferrocenylpolyynes chains and he showed that the metal atoms induce rehybridization along the carbon chains which enhances electro-communication through the π -bonds along the carbon chain, see *Organometallics* **2002**, 21, 2970.

Impact on the Discipline:

Adams has discovered and developed a range of new methods for the synthesis of polynuclear organometallic complexes. He has shown how metal atoms work cooperatively to achieve multi-center rearrangements of hydrocarbons which is fundamental to understanding multicenter organometallic chemistry and its applications to heterogeneous catalysis.

Benefits to Society:

Adams has shown that heteronuclear metal cluster complexes can be deposited and activated on supports and serve as efficient catalysts for organic transformations (*Phil. Trans. R Soc. A* **2010**, 368 1473). Supported metal clusters are widely used by the chemical industry as catalysts, ranging from petroleum reforming of fuels to the synthesis of commodity chemicals, specialty chemicals and drugs.

Sincerely,



Tobin J. Marks
 Vladimir N. Ipatieff Professor of Catalytic Chemistry
 Professor of Materials Science and Engineering
 Northwestern University
<http://chemgroups.northwestern.edu/marks/>

NAME: Richard D. Adams

ADDRESS: Department of Chemistry and Biochemistry
University of South Carolina
631 Sumter St.
Columbia, SC 29208

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Email: Adamsrd@mailbox.chem.sc.edu

EDUCATION:

Pennsylvania State University, State College, PA, B.S., 1969
Massachusetts Institute of Technology, Cambridge, MA, Ph. D., 1973, Inorganic Chemistry, Thesis Title: Studies of Bridge-Terminal Coordination Rearrangements in Organometallic Compounds. Ph. D. Supervisor: F. Albert Cotton

EXPERIENCE:

Assistant Professor - SUNY at Buffalo, 1973-1975
Assistant Professor - Yale University, 1975-1980
Associate Professor - Yale University, 1980-1984
Professor - University of South Carolina, 1984-2005
Visiting Professor - Institut le Bel, Université Louis Pasteur, FRANCE, 1993
Visiting Professor - National Science Council of Taiwan, TAIWAN, 1994
Visiting Professor - Ecole National Supérieur Chimie de Paris, Paris, FRANCE, 1999
Arthur S. Williams Professor of Chemistry, Univ. of South Carolina, 1995 – 2006
Director, USC NanoCenter, Univ. of South Carolina, 2001 – 2005
Carolina Distinguished Professor 2006 - present

PROFESSIONAL ORGANIZATIONS:

American Chemical Society
Fellow of American Association for the Advancement of Science
Material Research Society

PUBLICATIONS:

Author and Coauthor of over 580 research publications.

Coeditor and coauthor of the text "Catalysis by Di- and Polynuclear Metal Cluster Complexes" with F. A. Cotton, Wiley, 1998.

Editor, "50th Anniversary of the Discovery of Ferrocene", Volumes 637-639 of the Journal of Organometallic Chemistry, Elsevier, Amsterdam, 2001.

Coeditor and coauthor of the text "The Chemistry of Metal Cluster Complexes" with H. D. Kaesz and D. F. Shriver, VCH Publishers, 1990.

Editor, Volume 10, Comprehensive Organometallic Chemistry II, 1982 - 1994, Abel, E., Stone, F. G. A, and Wilkinson, G., Exec. Ed., Elsevier, Oxford, 1995.

AWARDS and HONORARIA:

Fellow of Alfred P. Sloan Foundation, 1979-81

Recipient of Russell Award for Research in Science and Engineering from the University of South Carolina, 1989.

Chairman, Gordon Conference on Inorganic Chemistry, 1991.

Recipient of 1999 ACS National Award in Inorganic Chemistry.

Recipient of 1999 Charles H. Herty Medal of the Georgia Section of the American Chemical Society.

Recipient of 1999 Charles H. Stone Award of the Carolina-Piedmont Section of the American Chemical Society.

Visiting Professor of the Institut Universitaire de France, 2000.

U. S. Senior Scientist Award of the Alexander von Humboldt Foundation, Germany, 2000.

Pioneer Award from the American Institute of Chemists, 2000.

Outstanding Academic Chemist Award, South Carolina Section of the American Chemical Society, 2001.

Southern Chemist Award of American Chemical Society, Memphis Section of the American Chemical Society, 2001.

South Carolina Governor's Award for Excellence in Science – 2003

Fellow of the American Association for the Advancement of Science – 2003

Henry J. Albert Award, International Precious Metals Institute, 2005.

Carolina Trustee Professor, University of South Carolina, 2005.

Chini Memorial Award Lectureship of the Italian Chemical Society, 2007.

ACS National Award for Distinguished Service in the Advancement of Inorganic Chemistry, 2010.

Distinguished Scientist Award of the Southeastern Universities Research Association (SURA), 2011.

European Academy of Sciences and Arts - Member of Natural Sciences Section, 2011.

Florida Award of the Florida Section of the ACS, 2016.

SUPERVISOR: for over 40 Ph.D. degrees and 3 M. S. degrees.

LECTURES – Over 200 research lectures at major universities in last 30 years

EDITORIAL POSITIONS:

1. Coeditor Editor of the Journal of Cluster Science, 1992 - present.

2. American Regional Editor of the Journal of Organometallic Chemistry, 1998 - present.

RESEARCH INTERESTS:

1. The Organometallic Chemistry and Catalytic Properties of Heterometallic Cluster Compounds and Multimetallic Nanoparticles
2. Activation of H₂ and C- H Bonds by Electronically Unsaturated Polynuclear Metal Complexes

1. R. D. Adams, V. Rassolov and Y. O. Wong, Binuclear Aromatic C-H Bond Activation at a Dirhenium Site, *Angew. Chem. int. Ed.* **2016**, 55 (4), 1324 – 1327, <http://dx.doi.org/10.1002/anie.201508540>.
2. R. D. Adams, V. Rassolov and Y. O. Wong, Facile C-H Bond Formation by Reductive-Elimination at a Dinuclear Metal Site, *Angew. Chem. int. Ed.* **2014**, 53, 11006 – 11009, DOI: [10.1002/anie.201406219](http://dx.doi.org/10.1002/anie.201406219).
3. R. D. Adams, V. Rassolov and Q. Zhang, Unsaturated Triosmium Carbonyl Cluster Complexes with Bridging Aryl Ligands: Structures, Bonding and Transformations, *Organometallics*, **2013**, 32, 6368 – 6378.
4. R. D. Adams, M. Chen, G. Elpitiya, M. E. Potter, R. Raja, Iridium-Bismuth Cluster Complexes yield Bimetallic Nano-Catalysts for the Direct Oxidation of 3-Picoline to Niacin, *ACS Catal.*, **2013**, 3, 3106–3110.
5. R. D. Adams, F. Fang, Q. Zhang, M. B. Hall, E. Trufan, α -Cleavage of Phenyl Groups from GePh₃ Ligands in Iridium Carbonyl Cluster Complexes. A Mechanism and its Role in the Synthesis of Bridging Germylene Ligands, *Organometallics*, **2012**, 31, 2621 - 2630.
6. R. D. Adams and M. Chen, Synthesis and Structures of Iridium-Gold Carbonyl Cluster Compounds Containing Methyl and σ -Aryl Ligands, *Organometallics*, **2012**, 31, 6457 - 6465.
7. R. D. Adams, M. Chen, E. Trufan and Q. Zhang, A New Method for Introducing Tin ligands into Tetrairidium Dodecacarbonyl, *Organometallics*, **2011**, 30, 661-664.
8. R. D. Adams, W. C. Pearl, Jr., Y. Wong, Q. Zhang, M. B. Hall and J. R. Walensky, A Tetrahena-heterocycle from the Palladium-Catalyzed Dimerization of Re₂(CO)₈(μ -SbPh₂)(μ -H) exhibits an Unusual Host-Guest Behavior, *J. Am. Chem. Soc.*, **2011**, 133, 12994-12997.
9. R. D. Adams, Q. Zhang, X. Yang, Two Dimensional Bimetallic Carbonyl Cluster Complexes with New Properties and Reactivities, *J. Am. Chem. Soc.*, **2011**, 133, 15950 - 15953.
10. R. D. Adams and M. Chen, Transmetalation Reactions yield new Tetra- and Penta-iridium Carbonyl Complexes Containing σ -Bonded Phenyl Rings, *Organometallics*, **2011**, 30, 5867 - 5872.
11. R. D. Adams and E. Trufan, Ruthenium-Tin Cluster Complexes and their Applications as Bimetallic Nanoscale Heterogeneous Hydrogenation Catalysts, *Phil. Trans Royal. Soc.* **2010**, 368, 1473-1493.
12. R. D. Adams, B. Captain, Unusual Structures and Reactivity of Mixed Metal Cluster Complexes Containing the Palladium/Platinum Tri-*t*-butylphosphine Grouping, *Acc. Chem. Res.* **2009**, 42, 409-418.
13. R. D. Adams, E. Trufan, Diruthenium-tin Complexes from the Reaction of Ph₂SnH₂ with Ru(CO)₅ and their Reactions with Bis(*tri-t*-butylphosphine)platinum, *Organometallics*, **2008**, 27, 4108-4115.
14. R. D. Adams, E. M. Boswell, B. Captain, A. B. Hungria, P. A. Midgley, R. Raja, J. M. Thomas, Bimetallic Ru-Sn Nanoparticle Catalysts for the Solvent-free, Selective Hydrogenation of 1,5,9-Cyclododecatriene to Cyclododecene, *Angew. Chem. int. Ed.*, **2007**, 46, 8182-8185.

15. R. D. Adams, B. Captain, C. Beddie and M. B. Hall, Photo-reversible Multiple Additions of Hydrogen to a Highly Unsaturated Platinum-Rhenium Cluster Complex, *J. Am. Chem. Soc.*, **2007**, *129*, 986-1000.
16. R. D. Adams, B. Captain, Mark D. Smith, C. Beddie and M. B. Hall, Unsaturated Platinum-Rhenium Cluster Complexes. Synthesis, Structures and Reactivity, *J. Am. Chem. Soc.* **2007**, *129*, 5981-5991.
17. R. D. Adams, B. Captain, E. Trufan and L. Zhu, The Activation of Metal Hydride Complexes by Tri-*t*-butylphosphine-Platinum and -Palladium Groups, *J. Am. Chem. Soc.* **2007**, *129*, 7545-7556.
18. R. D. Adams, B. Captain and L. Zhu, Facile Activation of Hydrogen by an Unsaturated Platinum-Osmium Cluster Complex, *J. Am. Chem. Soc.* **2007**, *129*, 2454-2455.
19. R. D. Adams, B. Captain, W. Fu, P. J. Pellechia and M. D. Smith, A Novel Dynamical Rearrangement of a Metal Cluster in a Process that Closely Resembles the Hopping Mechanism of Adatom Diffusion on Metal Surfaces, *Angew. Chem. int. Ed.*, **2002**, *41*, 1951-1953.
20. R. D. Adams, T. S. Barnard, Z. Li, W. Wu and J. Yamamoto, The Catalytic Hydrogenation of Diphenylacetylene by a Layer Segregated Platinum-Ruthenium Cluster Complex, *J. Am. Chem. Soc.*, **1994**, *116*, 9103-9113.

François P. Gabbaï
Arthur E. Martell Chair of Chemistry

Selection Committee

October 21, 2015

F. Albert Cotton Award In Synthetic Inorganic Chemistry
American Chemical Society

Dear Selection Committee,

I have always admired Rick Adams for his studies of metal carbonyl cluster complexes, and it is a pleasure for me to submit this letter in support of his nomination for the above mentioned award. Over the past few years, Rick's efforts have been focused on the synthesis and structural characterization of polynuclear metal carbonyl cluster complexes with the goal to understanding multicenter ligand coordination and reactivity, particularly with regard to the activation of small molecules. He has prepared a remarkable series of novel unsaturated platinum-rhenium complexes that activate several equivalents of hydrogen, in some cases reversibly, under mild conditions, even at room temperature. After several fascinating papers in this topic, Rick has been able to extend his approach to the activation of C-Hs bond. I am making particular reference to a 2016 *Angew. Chem.* paper in which he shows that aromatic C-H bonds undergo activation at the core of a unique dirhenium complex. Aided by computations, Rick has proposed a compelling mechanism which suggests that the generation of the reactive "reduced" dirhenium complex occurs in concert with the oxidative addition step. This recent paper builds on my favorite of Rick's recent contributions, namely, his elegant demonstration in a 2014 *Angew. Chem.* paper that such complexes also support reductive C-H bond formation. I also note that the addition and elimination steps that these complexes can sustain bode well for application in catalysis.

In addition to his many excellent contributions to the homogeneous chemistry of bi- and poly-nuclear species, Rick has also kept an astute eye for opportunities in nanomaterial synthesis. He has prepared a series of ruthenium-tin compounds that have been shown to serve as precursors to new nanoscale heterogeneous catalysts that exhibit extraordinary activity and selectivity for olefin hydrogenation reactions. In a 2013 *ACS Catal.* paper, he has shown that decomposition of a high nuclearity iridium-bismuth cluster complex can be used to generate a bimetallic Bi/Ir nanocatalyst which promotes the selective oxidation of picoline to nicotinic acid. Materials prepared from separate components were notably inferior, underscoring the value and uniqueness of the mixed-metal cluster approach designed by the candidate.

Altogether, Rick's work has provided a much deeper understanding of the assembly processes, the structures, bonding, molecular dynamics and reactivity of polynuclear metal complexes and he has demonstrated that they have applications to real world problems. Given his seminal contribution to these areas, Rick is an exceptional and compelling candidate for this award. His nomination has my wholehearted and unequivocal support.

Sincerely,

A handwritten signature in black ink, appearing to read "F. Gabbaï".

François Gabbaï

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13 October 2016

Selection Committee
ACS Award in Inorganic Chemistry
American Chemical Society

Dear Selection Committee:

I am pleased to enthusiastically support the nomination of Dr. Richard (Rick) D. Adams, Carolina Distinguished Professor of Chemistry at the University of South Carolina, for the 2018 F. Albert Cotton Award in Synthetic Inorganic Chemistry.

Rick built a highly successful career on the studies of the synthesis and reactivity of transition metal carbonyl cluster complexes. His studies of multicenter reactivity were predicated on his clever synthesis of a range of new polynuclear metal carbonyl cluster complexes. He synthesized a variety of novel tri-osmium cluster complexes containing hydrocarbonyl ligands and studied the nature of multicenter C-H bond activation processes exhibited by them (*Organometallics* **2013**, 32, 6368). Recently, he synthesized some novel di-rhenium complexes containing both bridging aryl and bridging hydride ligands (*Angew. Chem.*, **2016**, 55, 1324), that perform the activation and reductive elimination of C-H bonds in aromatic compounds—including benzene itself even at room temperature!

Rick has also prepared some remarkable highly unsaturated platinum-rhenium cluster complexes that can activate up to three equivalents of hydrogen per cluster at room temperature. Indeed, he prepared a range of ruthenium-tin complexes that were shown to be precursors to a bimetallic “nanocatalysts” that exhibit remarkable selectivity for the hydrogenation of polyolefins (*Phil. Trans. R Soc. A* **2010**, 368, 1473).

The stated purpose of the F. Albert Cotton Award in Synthetic Inorganic Chemistry is “To recognize distinguished work in synthetic inorganic chemistry”. Indeed, the Cotton Award places a particular emphasis on “creativity and imagination”. When I read one of Rick’s papers wherein he has prepared (yet) another amazing molecule I am filled with a sense of wonder and a compelling question comes to mind: “Just how did he synthesize that compound?” This is, perhaps, the greatest compliment a synthetic inorganic chemist can receive. Professor Rick Adams, one of the most prolific and creative synthetic inorganic chemists of our time, is richly deserving of the prestigious Cotton Award in Synthetic Inorganic Chemistry.

Sincerely,

Gregory H. Robinson

(Total Words: 321)