

Seminarios itinerantes

# Karsten MEYER

Friedrich - Alexander Universtät Erlangen - Nürnberg 15 a 25 de Febrero 2016

# From nuclear fuels to CO<sub>2</sub> functionalization and H<sub>2</sub>O splitting catalysis at reactive uranium complexes

- Chemistry between phobia and enthusiasm -

Lunes, 15 de Febrero, **Universidad de Alcalá de Henares** 12:00 h, Aula 14, Facultad de Farmacia (manuel.gomez@uah.es)

Martes, 16 de Febrero, **CINQUIMA**, **Universidad de Valladolid** 16:30 h, Sala de conferencias del edificio QUIFIMA (albeniz@qi.uva.es)

Jueves, 18 de Febrero, ISQCH, CSIC – Universidad de Zaragoza 9:30 h, Sala de Grados de la Facultad de Ciencias (sola@unizar.es)

Viernes, 19 de Febrero, Universitat Rovira i Virgili, Tarragona 10:00 h, Facultad de Ciencias (carmen.claver@urv.cat)

Lunes, 22 de Febrero, Universitat Jaume I, Castellón 11:00 h, Seminario Edificio de Investigación I (eperis@uji.es)

Martes, 23 de Febrero, IIQ, CSIC – Universidad de Sevilla 12:00 h, Salón de actos del IIQ (sconejero@iiq.csic.es)

Jueves, 25 de Febrero, CIQSO, Universidad de Huelva 12:00 h, Salón de actos del CIQSO (trodri@dqcm.uhu.es)



Grupo Especializado de Química Organometálica de la Real Sociedad Española de Química



Uranium and, its in traces existing heavier neighbor, plutonium, are the heaviest naturally occurring elements, and they share one common thing with each other: they undeniably have the worst reputation of all elements of the periodic table.

In this lecture, a general introduction is given on how radioactivity of naturally abundant and man-made elements, e.g. in plutoniumpowered cardiac pacemakers and satellites, impact our modern life. A brief tour through basic inorganic chemistry shows how pitchblende is transformed into nuclear fuels, how organometallic chemists have discovered the element for basic chemical research, and how this field has sparked new discoveries of current interest ever since. In our efforts to activate small molecules of industrial and biological importance, we have turned our attention to coordinatively unsaturated, reactive uranium coordination complexes. For example, the chelating triazacyclononane (tacn), single N, and arene-anchored tris(aryloxide) ligands, (ArO)<sub>3</sub>tacn<sup>3-</sup>,  $(ArO)_3N^{3-}$ , and  $(ArO)_3mes^{3-}$  have provided access to reactive coordination compounds of uranium in oxidation states II, III, IV, V,



Fusion heat powered red-hot glowing 100 Watt  $^{238}\text{PuO}_2$  heat source used in the 1970s space missions. The source is about 250 g and about 3 cm in diameter.

Photo: Courtesy of Dr. David L. Clark, LANL

and VI with tailorable steric and electronic profiles. These complexes display a pronounced selectivity and reactivity in reactions with carbon dioxide, related small heteroallene molecules (COS and CS<sub>2</sub>), and H<sub>2</sub>O. In this seminar, our work on CO<sub>2</sub> activation, including unprecedented coordination modes, reductive cleavage, insertion, and functionalization reactions is reported. Most recently, the stoichiometric and catalytic "disproportionation" of CO<sub>2</sub> to CO and CO<sub>3</sub><sup>2–</sup> *via* reductive cleavage of CO<sub>2</sub> was accomplished. The molecular and electronic structure of a new oxidation state in U coordination chemistry is reported; namely U(II), with a  $5f^4$  quintet ground state. In K(2.2.2-crypt)[((<sup>Ad,Me</sup>ArO)<sub>3</sub>mes)U], the electron-rich U(II) center is supported by  $\delta$  backbonding.

Finally, a rare U(IV) hydroxo complex,  $[((^{Ad,Me}ArO)_3mes)U(OH)]$ , with a terminal OH functionality was synthesized by selective oxidation of the U(III) complex  $[((^{Ad,Me}ArO)_3mes)U]$  with H<sub>2</sub>O. Comprehensive electrochemical studies revealed that the U(III) complex can be regenerated in a catalytic cycle combining chemical and electrochemical reaction steps to produce H<sub>2</sub> from water. Thus, trivalent  $[(^{Ad,Me}ArO)_3Mes)U]$  was found to be the first molecular uranium catalyst for electrocatalytic H<sub>2</sub> production. Utilization of  $[(^{Ad,Me}ArO)_3Mes)U]$  during H<sub>2</sub>O electrolysis lowered the overpotential by 0.5 V, increased the steady-state electrolysis current by a factor of 10, and lowered the faradaic resistance of the reaction by three orders of magnitude.

# Leading References:

D.P. Halter, F.W. Heinemann, J. Bachmann and K. Meyer in Nature 2016, DOI:10.1038/nature16530.

H.S. LaPierre, F.W. Heinemann, W. Hieringer and K. Meyer in Angew. Chem. Int. Ed. 2014, 53, 7158.

A.-C. Schmidt, F.W. Heinemann, W.W. Lukens and K. Meyer in J. Am. Chem. Soc. 2014, 136, 11980.

S. Franke, F. W. Heinemann and K. Meyer in Chem. Sci. 2014, 5, 942.

O. P. Lam, S. Franke, F. W. Heinemann and K. Meyer in *J. Am. Chem. Soc.* **2012**, *134*, 16877.

A.-C. Schmidt, A. Scheurer, F.W. Heinemann and K. Meyer in *Chem. Commun.* **2012**, 48, 8634.

S.J. Zuend, O.P.Lam, F.W. Heinemann and K. Meyer in Angew. Chem., Int. Ed. 2011, 50, 10626.

O.P. Lam, F.W. Heinemann and K. Meyer in Angew. Chem., Int. Ed. 2011, 50, 5965.

O. P. Lam, S.C. Bart, F.W. Heinemann and K. Meyer in Chem. Commun. 2010,46, 3137.

A.R. Fox, S.C. Bart, K. Meyer and C.C. Cummins in Nature 2008, 455, 341.

S.C. Bart, F.W. Heinemann, E. Bill, N.M. Edelstein and K. Meyer in J. Am. Chem. Soc. 2008, 130, 12536.

I. Castro-Rodriguez and K. Meyer in J. Am. Chem. Soc. 2005, 127, 11242.

I. Castro-Rodriguez, H. Nakai, L. Zakharov, A.L. Rheingold and K. Meyer in Science 2004, 305, 1757.



Grupo Especializado de Química Organometálica de la Real Sociedad Española de Química





Karsten MEYER (born May 17th, 1968) studied chemistry (October 1989 - 1994) at the Ruhr-University of Bochum (Germany) and received his Diploma in May 1995. Starting in summer 1995, he performed his PhD thesis work under the direction of Professor Karl Wieghardt at the Max-Planck-Institute in Mülheim / Ruhr (Germany) and received his Ph. D. (Dr. rer. nat, summa cum laude) in January 1998. He then was awarded a DFG postdoctoral fellowship and, from 1998 to 2000, proceeded to gain research experience in the laboratory of Professor Christopher C. Cummins at the Massachusetts Institute of Technology (MIT, Cambridge, MA, USA). In January 2001, he was appointed to the faculty of the University of California, San Diego (UCSD) as an Assistant Professor and was named an Alfred P. Sloan Fellow in 2004. In 2006 he accepted an offer (C4/W3) to be the Chair of the Institute of Inorganic & General Chemistry at the Friedrich-Alexander-University of Erlangen-Nürnberg, Germany.

#### **Professional Career**

Oct. 1989	Study of Chemistry at the Ruhr-University-Bochum in Germany
May 1995	Diploma (Ruhr-University-Bochum)
July 1995	PhD Studies at the Max-Planck-Institute in Mülheim/Ruhr, Germany under the supervision of Prof. Dr. Karl Wieghardt
Jan. 1998	Dissertation (Dr. rer. nat) "Molecular and Electronic Structure of High-Valent Transition- Metal Nitrido Complexes"
Feb. 1998	Postdoctoral Studies at the Max-Planck-Institute Mülheim/Ruhr (Germany)
Oct. 1998	Postdoctoral Studies at the Massachusetts Institute of Technology (MIT) under the direction of Prof. Christopher C. Cummins, USA
Jan. 2001	Assistant Professor at the University of California, San Diego (UCSD), USA
Jan. 2006	University Full Professor (W3/C4) Chair of Inorganic and General Chemistry
orial Activities	

# **Editorial Activities**

2005	Volume Editor, Elsevier "Comprehensive Organometallic Chemistry III, Vol. 2"
2009	International Advisory Board, Wiley-VCH "European Journal of Inorganic Chemistry"
2011	International Advisory Board, ACS "Inorganic Chemistry" (2-yr term)
2013	Guest Editor, Wiley-VCH "European Journal of Inorganic Chemistry" Special Issue on "Small Molecule Activation by Reactive Metal Complexes"
2014	International Advisory Board, Taylor & Francis "Journal of Coordination Chemistry"
2014	Associate Editor, ACS "Organometallics"

#### Awards & Honors

2002	Hellman Fellow, Christ & Warren Hellman Young Faculty Award, USA
2003	Faculty Career Development Award, UC Academic Senate, USA
2004	Alfred P. Sloan Award, USA
2009	Israel Chemical Society, Lifetime Honorary Membership, IL
2009	Visiting Professorship, University of Manchester, UK
2009	Japanese Society for the Promotion of Science Award (JSPS), JP
2010	Dalton Transactions European Lectureship Award, UK
2010	MBRAUN Lecturer, Pacifichem 2010, Honolulu Hawaii, USA
2011	Fellow of the Royal Society of Chemistry, FRSC, UK
2012	Visiting Professor, Université Paul Sabatier, Toulouse, F
2015	JSPS Professorship "Brain Circulation Project" Nagoya Institute of Technology, JP
	http://www.nitech.ac.jp/eng/research/partners.html

## **Publications and Invitations**

Karsten Meyer has published 130+ publications in peer-reviewed journals, an H-Index of 41 with a total of approx. 4700 citations, and an average citation per item of 34. The list of publications includes, among others, reports and articles in *Science, Nature, Nature Communications*, the *Journal of the American Chemical Society* (JACS), and *Angewandte Chemie*. He has given more than 150 invited talks, including opening and plenary lectures, at conferences as well as research and academic institutions worldwide.

## **Ten Selected Publications**

D.P. Halter, F.W. Heinemann, J. Bachmann and K. Meyer\* "Uranium-Mediated Electrocatalytic Production of H<sub>2</sub> form Water" *Nature* **2015**, accepted for publication. A.-C. Schmidt, F.W. Heinemann, W.W. Lukens Jr.\* and K. Meyer\* "Molecular and Electronic Structure of Dinuclear Uranium-di-Oxo Complexes with Diamond Core Structural Motifs" J. Am. Chem. Soc. 2014, 136, 11980 – 11993. H.S. La Pierre, A. Scheurer, F.W. Heinemann, W. Hieringer and K. Meyer\* "Synthesis and Characterization of a Uranium(II) Monoarene Complex Supported by δ Backbonding" Angew. Chem. Int. Ed. 2014, 53, 7158 - 7162. F. Scholz, D. Himmel, F.W. Heinemann, P.v.R. Schleyer, K. Meyer\* and I. Krossing\* "Crystal Structure Determination of the Nonclassical 2-Norbornyl Cation" Science 2013, 341, 62 – 64. F. Kropp, M.M. Khusniyarov, F.W. Heinemann, K.M. Lancaster, S. DeBeer, E. Bill and K. Meyer\* "Manganese Nitride Complexes in Oxidation States III, IV, and V: Synthesis and Electronic Structure" J. Am. Chem. Soc. 2012, 134, 15538 – 15544. J.J. Scepaniak, C.S. Vogel, M.M. Khusniyarov, F.W. Heinemann, K. Meyer\* and J.M. Smith\* "Synthesis, Structure, and Reactivity of an Iron(V) Nitride" Science 2011, 331, 1049 – 1052. S.C. Bart, C. Anthon, F.W. Heinemann, E. Bill, N.M. Edelstein and K. Meyer\* "Carbon Dioxide Activation with Sterically Pressured Mid- and High-Valent Uranium Complexes" J. Am. Chem. Soc. 2008, 130, 12536 – 12546. A.R. Fox, S.C. Bart, K. Meyer and C.C. Cummins "Towards Uranium Catalysts" *Nature* **2008**, *455*, 341 – 349. C. Vogel, F. W. Heinemann, J. Sutter, C. Anthon and K. Meyer\* "An Iron Nitride Complex" Angew. Chem. Int. Ed. 2008, 47, 2681 - 2684. I. Castro-Rodriguez, H. Nakai, L. N. Zakharov, A.L. Rheingold and K. Meyer\* "A Linear, O-Coordinated  $\eta^1$ -CO<sub>2</sub> Bound to Uranium" Science 2004, 305, 1757 – 1759.

For a complete and up-to-date list of publications, please see: http://www.inorganic-chemistry.net/kmpages/publications.html