

Hahn, F. Ekkehardt, Prof. Dr. rer. nat.
*** 1955**



Professor of Chemistry (Inorganic Chemistry)
Institut für Anorganische und Analytische Chemie
Westfälische Wilhelms-Universität Münster,
Germany

Scientific Career

1978 – 1983 Studies of Chemistry, TU Berlin (Dipl.-Chem.) and University of Oklahoma (M.S.)
1985 Dr. rer. nat., Technische Universität Berlin (Prof. H. Schumann)
1985 – 1988 Postdoctoral Fellow (NATO Postdoctoral Fellowship), University of California, Berkeley, USA (Prof. Kenneth N. Raymond)
1991 Habilitation, Technische Universität Berlin (Inorganic Chemistry)
1993 – 1998 Professor, Inorganic Chemistry, Freie Universität Berlin
since 1998 Professor and Chair of Inorganic Chemistry, Westfälische Wilhelms-Universität Münster

Scientific Awards, Appointments and Professional Recognition

1981 – 1982 Fulbright fellowship for studies at the University of Oklahoma, USA
1983 – 1985 FCI predoctoral fellowship for studies towards the Dr. rer. nat.
1985 – 1987 NATO postdoctoral fellowship
1991 Winnacker-Stipendium
1996 Convention Intercantonale Romande pour L'Enseignement du 3^e Cycle en Chemie lectureship, Switzerland
1996 J. C. Clarence Karcher Lecture, University of Oklahoma, USA
2001 – 2006 Spokesperson of the Germany/Holland International Research Training Group (IRTG 673) "Template Directed Chemical Synthesis"
2001 – 2007 Coordinator (together with Prof. C. Bolm, RWTH Aachen) of the DFG (German Research Foundation) priority program SPP 1118 "Use of Secondary Interactions for the Direct Functionalization of Less Reactive Substrates"
since 2001 Member Editorial Advisory Board *Zeitschrift für Naturforschung B*
since 2001 Coordinator ERASMUS student exchange programs with the Universidad de Zaragoza and Cardiff University
since 2002 Corresponding Member Academia de Ciencias Exactas, Fisicas, Quimicas y Naturales de Zaragoza, Spain.
since 2006 Permanent Secretary International Conferene on Organometallic Chemisty
2006 – 2008 Dean Faculty of Chemistry and Pharmacy, Westfälische Wilhelms-Universität, Münster
2007 – 2010 Julius von Haast Fellowship, New Zealand Ministry of Research, Science and Technology
since 2008 Member Editorial Board *Dalton Transactions*
2009 – 2013 Honorary Professor School of Chemistry, Cardiff University, UK
2009 Future in Chemistry Lecture, University of British Columbia, Vancouver, Canada
since 2010 Member Editorial Advisory Board *Organometallics*
2010 Fellow of the Royal Society of Chemistry, UK
since 2011 Member Editorial Board *Journal or Organometallic Chemistry*

Guest/Visiting Professorships

Shanghai Institute of Organic Chemistry, China; UC Berkeley, USA; National University of Singapore, Singapore; Universidad de Zaragoza, Spain; University of Auckland, New Zealand; National Taiwan University, Taipei, Taiwan; Institute for Material Research, A-star, Singapore.

Scientific Output

since 1981 > 320 scientific publications (peer reviewed), 10 book chapters and editor of one book (together with Prof. Martin Albrecht, RWTH-Aachen)
since 1983 > 110 conference contributions (invited and plenary lectures)
since 1985 > 170 lectures for scientific colloquia
since 1992 mentor for 75 doctoral students (54 completed dissertations), for 78 Diploma and M.S. theses and for 5 Habilitations (4 completed Habilitations)

The Five Most Important Recent Publications

A. Rit, T. Pape, F. E. Hahn, "Self-Assembly of Molecular Cylinders from Polycarbene Ligands and Ag^I or Au^{III}", *J. Am. Chem. Soc.* **2010**, 132, 4572-4573.

T. Kösterke, T. Pape, F. E. Hahn, "Synthesis of NHC Complexes by Oxidative Addition of 2-Chloro-*N*-methylbenzimidazole", *J. Am. Chem. Soc.* **2011**, 133, 2112-2115.

M. Schmidtendorf, T. Pape, F. E. Hahn, "Stepwise Preparation of a Molecular Square from NR,NR- and NH,O-Substituted Dicarbene Building Blocks", *Angew. Chem. Int. Ed.* **2012**, 51, 2195-2198.

R. Maity, H. Koppetz, A. Hepp, F. E. Hahn, "Heterobimetallic Carbene Complexes by a Single-Step Site-Selective Metallation of a Tricarbene Ligand", *J. Am. Chem. Soc.* **2013**, 135, 4966-4969.

Y.-F. Han, G.-X. Jin, F. E. Hahn, "Postsynthetic Modification of a Dicarbene-Derived Metallacycle via Photochemical [2 + 2] Cycloaddition", *J. Am. Chem. Soc.* **2013**, 135, 9263-9266.

Research Profile

The Hahn group works on a variety of project centered around the coordination chemistry of N-heterocyclic carbene (NHC), germylene, stannylene and isocyanide ligands and on the assembly of supramolecular structures from poly-(benzene-*o*-dithiolato) and poly-NHC ligands.

1. Preparation of complexes bearing reactive NH,NH-substituted NHC ligands

Complexes bearing NHC ligands are normally obtained by deprotonation and subsequent coordination of N,N'-dialkylated heterocyclic azolium precursors. We have introduced an alternative method for the generation of complexes bearing "protic" NH,NH-substituted NHC ligands. Such complexes are obtained from complexes with 2-amino functionalized alkyl or aryl isocyanide ligands by intramolecular nucleophilic attack of the amine nucleophile at the coordinated isocyanide group under formation of the NH,NH-diaminocarbene heterocycle. Since 2-aminoethyl or 2-aminophenyl isocyanides are not stable, various synthons for these ligands like 2-azidoethyl isocyanide, 2-azidophenyl isocyanide or 2-nitrophenyl isocyanide have been developed and converted into NH,NH-NHCs in metal template controlled reactions. The coordinated NH,NH-NHCs can be N,N'-dialkylated and this reaction also gives access to novel macrocycles like [11]ane-P₂C^{NHC} and [16]ane-P₂C^{NHC}₂ featuring NHC and phosphine donor groups. Recently, the oxidative addition of the C2-X (X = H, halogen) bond of neutral azoles followed by protonation of the free ring nitrogen atom has also been shown to lead to complexes bearing NH,NR-substituted NHC ligands. In complexes of catalytically active metals, the N-H group of such ligands can function as a molecular recognition unit by formation of hydrogen bonds to selected substrates thereby controlling the selectivity of a catalytic transformation. The oxidative addition of the C2-X bond of neutral azoles to transition metals has recently been extended to 8-chloro caffeine and 8-bromo adenine allowing the utilization of these biomolecules in organometallic chemistry.

2. Synthesis of metallosupramolecular structures from polycarbene ligands

Rigid, linear benzobis(imidazolin-2-ylidenes) have been prepared from the diazolium precursors. These ligands can act as bridging ligands in the synthesis of supramolecular molecular squares containing various metal centers as vertices. Tris- or tetrakis-imidazolium substituted benzenes have also been prepared. These polycarbene precursors react with silver oxide under formation of three-dimensional supramolecular structures containing three or four silver atoms sandwiched in between two tris- or tetracarbene ligands. Exchange of the silver(I) ions for gold(I) or copper(I) is possible. The metallosupramolecular assemblies constitute an interesting new type of container molecules which can act as hosts for selected substrates. Molecular squares with four bridging β,β' -functionalized benzene-1,4-diisocyanides have been prepared. Upon activation of the β,β' -substituents the diisocyanide bridges can be converted into bridging dicarbene ligands. The diisocyanide \rightarrow dicarbene transformation leads to a shrinkage of the molecular square. The reaction is reversible and is controlled by the oxidation state of the metal centers. It gives access to molecular squares which can change their size depending on the oxidation state of the metals placed at the vertices.

3. N-Heterocyclic germylenes and stannylenes

N-Heterocyclic germylenes and stannylenes (tetrylenes) are accessible from suitable secondary 1,2-diamines and $E[N(SiMe_3)_2]_2$ ($E = Ge, Sn$), or by deprotonation of the 1,2-diamines and subsequent reaction with ECl_2 ($E = Ge, Sn$). These methods have also been used for the generation of rigid, linear bisgermylenes and bisstannylenes. N-Heterocyclic germylenes and stannylenes exhibit amphiphilic behavior possessing a nucleophilic sp^2 -orbital and an empty, electrophilic p-orbital. The coordination chemistry of novel N-heterocyclic germylenes and stannylenes is studied to gain information about their mode of bonding in transition metal complexes. In a recent study we demonstrated that N-heterocyclic plumbylenes, in contrast to their lighter carbene, germylene and stannylene congeners, do not act as σ -donors towards low valent transition metals, but instead function as acceptors of electron density from the transition metal they interact with. Very recently, the first example of "protic" NH,NH- and NH,NR-functionalized NHGes and NHSns have been prepared. These compounds can be deprotonated at the ring-nitrogen atom so give compounds with a nucleophilic nitrogen atom and an electrophilic E^{II} atom. These studies are aimed towards the development of new Tetrylenes which can act as bifunctional catalysts.

4. Supramolecular chemistry of bis(benzene-o-dithiolato) and benzene-o-dithiolato/catecholato ligands

The Hahn group has prepared bis(benzene-o-dithiol) and mixed benzene-o-dithiol/catechol ligands with different spacer groups between the donor units and studied their coordination chemistry. Triple-stranded dinuclear helical complexes with these ligands were synthesized and characterized by X-ray diffraction and NMR spectroscopic studies. Depending on the metal and its oxidation state, the $\{MS_6\}^{n-}$ polyhedra in these helicates can adopt an octahedral or trigonal-prismatic coordination geometry which allows to switch on or off the helicity of the triple-stranded dinuclear complexes by a redox-reaction at the S_6 -coordinated metal center. 1,3,5-Tris(benzene-o-dithiol)benzenes with different spacers between the phenylene core and the benzene-o-dithiol donors have also been prepared. These ligands react to give either mononuclear metal complexes or tetrahedral clusters of type $[M_4L_4]^{n-}$ where four ligands cap the trigonal faces of the tetrahedron. The tetrahedral clusters can serve as molecular hosts for different small cations. Recently, subcomponent self-assembly reactions between o-thiolatobenzaldehyde complexes and diamines leading to helical dinuclear complexes and the metal exchange in such complexes have been studied.