Angewandte
Author Profile

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A. S. K. Hashmi

The author presented on this page has published more than ***25 articles*** *in Angewandte Chemie in the last 10 years, most recently:* "A Highly Efficient Gold-Catalyzed Photoredox α-C-(sp^3)—H Alkynylation of Tertiary Aliphatic Amines with Sunlight": J. Xie, S. Shi, T. Zhang, N. Mehrkens, M. Rudolph, A. S. K. Hashmi, *Angew. Chem. Int. Ed.* **2015**, *54*, 6046; *Angew. Chem.* **2015**, *127*, 6144.

A. Stephen K. Hashmi

Date of birth:	January 15, 1963
Position:	Full Professor of Organic Chemistry and Vice-Rector for Research and Structure, University of Heidelberg
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Education:	1983–1988 Undergraduate degree, Ludwig-Maximilians-Universität München (LMU) 1989–1991 PhD with Prof. Günter Szeimies, LMU 1991–1993 Postdoc with Prof. Barry M. Trost, Stanford University 1993–1998 Habilitation with Prof. Johann Mulzer, Freie Universität Berlin
Awards:	**1998** Dr. Otto Röhm Memorial Foundation Award; **2001** Karl Ziegler Fellowship; **2002** ORCHEM Prize, Organic Chemistry Division, Gesellschaft Deutscher Chemiker (GDCh; German Chemical Society); **2010** Hector Research Prize; **2014** Fred Pattison Senior Lectureship, Western University, Ontario
Current research interests:	Ligand development, methodology development, and detailed mechanistic studies in homogeneous transition-metal catalysis; mechanistic studies include isotope labeling, in situ spectroscopy from IR to EXAFS, and computational chemistry. In addition, the development of highly active catalysts by efficient modular methods is a focus of current activities.
Hobbies:	Watching good movies and chopping down trees in my garden (a renewable resource that always grows back).

In a spare hour, I finally get some sleep.

My favorite way to spend a holiday is to travel to Australia.

My biggest inspiration is to think about chemistry when cutting down trees in my garden. There are still many trees in my garden.

My favorite time of day is the peaceful moment when I can do science—as my career proceeds, administrative and representative tasks consume more and more of my time.

I admire full commitment, and people who are still scientifically "hungry" and not yet "saturated".

I advise my students to always ask "why"—causality is the key to understanding.

The secret of being a successful scientist is to conduct experiments on the basis of hypotheses and new ideas, but then continually watch out for and embrace unexpected new findings.

My favorite name reaction is the Lobry de Bruyn–Alberda van Eckenstein rearrangement, such a long name and what a wonderful sound for a simple but important modification of the keto–enol tautomerization.

My science "heroes" are Michael Faraday and Alexander von Humboldt.

If I had one year of paid leave I would still do research.

The principal aspect of my personality is calmness and openness (the transparency of my actions).

My favorite painter is Salvadore Dali.

My favorite musician is Alan Silvestri.

I am waiting for the day when someone will discover a more efficient way of travelling than flying.

Looking back over my career, I would, although there were tough moments and a high degree of uncertainty, choose this path again.

The most significant historic event of the past 100 years was the end of the Second World War.

My first experiment was to scratch off the heads of a full box of matches, drop candle wax on this very versatile (from the point of view of a small boy) material, and ignite this mixture—on my mother's kitchen table!

Has your approach to publishing your results changed since the start of your career?

Yes! Initially, I invested too much time in each manuscript, trying to round it off in a perfect way. Eventually, I learned that the outcome of a refereeing process, independent of the journal, is strongly influenced by the very, very personal "taste" of each of the referees—a taste that is impossible to prognosticate as you do not know who the referee will be. For one referee the manuscript is too long, for the other referee for some reason it is too short. One referee finds the science exciting, the other one for some reason would have expected all your results and does not see any new science. Now I write the manuscript according to the way I see the results, and then, like a tree bows in the wind, I submit to the demands of the referees—unless they ask for additional experiments which take another year or demand scientifically incorrect changes in the manuscript.

What do you think the future holds for your field of research?

It is amazing that after 15 years of intensive research in the field of homogeneous gold catalysis, new reactivity patterns are still being discovered. The explanation probably is that for the entire 20th century, the field was neglected and that the series of papers published on the asymmetric aldol reaction from 1986–1999 all focused on one single reaction type and a single class of substrates—and these asymmetric aldol reactions can equally well be conducted with silver. The exponential growth of the field was initiated by the first enyne-type reactions (Ref. [2] below) and the first hydroarylation reactions (Ref. [1] below). After many new discoveries in the subsequent years in the field of homogeneous gold catalysis, two years ago the principles of dual activation opened entirely new options for the field. The recent developments in photoredox catalysis with gold are also highly exciting.

My 5 top papers:

1. "A New Gold-Catalyzed C−C Bond Formation": A. S. K. Hashmi, L. Schwarz, J.-H. Choi, T. M. Frost, *Angew. Chem. Int. Ed.* **2000**, *39*, 2285; *Angew. Chem.* **2000**, *112*, 2382.
   This publication really opened up the field of homogeneous gold catalysis. The preceding milestone publication of Y. Ito, M. Sawamura, and T. Hayashi, and a series of subsequent papers by these authors and A. Togni, which all focused only on exactly this one type of aldol reaction, was very important for asymmetric catalysis in general—but at the same time it was not a good example for any advantages of gold catalysis, as this reaction can very efficiently be initiated by silver catalysts too. Furthermore, covering the classical reactivity pattern of an aldol-type conversion, the preceding work did not show the full potential of gold catalysis, which is probably the reason why our publication still is the research paper with the highest number of citations in the field of homogeneous gold catalysis.
2. "Highly Selective Gold-Catalyzed Arene Synthesis": A. S. K. Hashmi, T. M. Frost, J. W. Bats, *J. Am. Chem. Soc.* **2000**, *122*, 11553.
   This paper followed the one listed above and described a previously unknown reactivity pattern, the furan-yne reaction as the first reported gold-catalyzed enyne-type reaction. The reactivity pattern is broadly applicable, and the mechanism is very complex, involving gold-catalyzed steps, pericyclic steps, and general acid catalysis, this is why the reaction kept us busy for almost one decade. It has even been named the "Hashmi phenol synthesis".
3. "Gold Catalysis: Mild Conditions for the Synthesis of Oxazoles from *N*-Propargylcarboxamides and Mechanistic Aspects": A. S. K. Hashmi, J. P. Weyrauch, W. Frey, J. W. Bats, *Org. Lett.* **2004**, *6*, 4391.
   This paper clearly demonstrated the full potential of homogeneous gold catalysis for the synthesis of heterocycles. Subsequent work could show that with gold(I) catalysts the alkylidene oxazolines, previously considered to be inaccessible intermediates of the formation of the oxazolines, can be isolated and then be utilized as versatile synthetic intermediates in a number of conversions ranging from highly selective radical-chain oxidation reactions with molecular oxygen to Alder ene reactions with a variety of enophiles.
4. "The Role of Gold Acetylides as Selectivity Trigger and the Importance of *gem*-Diaurated Species in the Gold-Catalyzed Hydroarylating-Aromatization of Arene-Diynes": A. S. K. Hashmi, I. Braun, M. Rudolph, F. Rominger, *Organometallics* **2012**, *31*, 644.
   This manuscript is the first one in a whole series on dual activation by gold as the basis for the formation of benzofulvenes and benzocyclobutenes, and even for selective C_{sp^3}−H and X−H insertion reactions. It gave, for the first time, clear experimental proof for the mechanism of dual activation in homogeneous gold catalysis. That said, I should also mention a closely related paper on parallel and independent investigations from L. Zhang's group.
5. "Highly Active Mononuclear NAC−Gold(I) Catalysts": M. C. Blanco Jaimes, C. R. N. Böhling, J. M. Serrano-Becerra, A. S. K. Hashmi, *Angew. Chem. Int. Ed.* **2013**, *52*, 7963; *Angew. Chem.* **2013**, *125*, 8121.
   Many investigations still use 1–5 mol% of gold, but is this really necessary in all cases? This publication represents the optimum outcome after seven man-years of catalyst development with this ligand type: 32000000 turnovers could be reached, which was verified by ICP studies and spiking experiments.

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