

Synthesis and Properties of Cyclic Sandwich Compounds

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The ground-breaking discovery of the first sandwich complex, ferrocene, marked the birth of modern organometallic chemistry. The structure of sandwich compounds, consisting of a central metal ion complexed by two planar aromatic ligands, is reminiscent of a classical sandwich, with the flat ligands representing two slices of bread covering the filling, the central metal. The appreciation for this unprecedented structural motif culminated in the award of the 1973 Nobel Prize in Chemistry to Fischer and Wilkinson for their work on elucidating the molecular structure of ferrocene.

Ever since, the sandwich motif has inspired organometallic chemists on their journey towards exciting novel compounds for a plethora of applications and sparked the hunt for larger and larger sandwiches. Going beyond the prototypical sandwich structure, $[M(C_nH_n)_2]$, multidecker sandwich complexes with alternating aromatic ligands and metals have been assembled (*Synth. React. Inorg. Met.-Org. Chem.* **1972**, *2*, 239–248; *J. Phys. Chem. A* **2005**, *109*, 9–12; *New J. Chem.* **2011**, *35*, 517–528; *J. Phys. Chem. C* **2014**, *118*, 5896–5907; *J. Am. Chem. Soc.* **2017**, *139*, 9895–9900). However, no structural motif apart from longer and longer one-dimensional chains has been reported until the publication of the title article, and the existing rare examples of circular oligomeric metallopolymers were held together by bridging units between individual sandwich subunits, instead of direct metal–ligand interactions alone (*Chem. Lett.* **1994**, *23*, 67–68; *Angew. Chem. Int. Ed.* **1997**, *36*, 387–389; *Angew. Chem. Int. Ed.* **2007**, *46*, 9069–9072; *Nat. Chem.* **2016**, *8*, 825–830).

Professor Peter Roesky at the Karlsruhe Institute of Technology (Germany) told SYNFORM: “In recent work by our group, we realized a bending in the sandwich structure of lanthanide quadruple-decker complexes featuring a triisopropylsilyl-substituted cyclooctatetraenediide ligand as the slice of bread (*Angew. Chem. Int. Ed.* **2021**, *60*, 24493–24499). Now, what happens when growing a bent sandwich chain further and further? Right – at one point the chain ends will meet, resulting in a circular sandwich complex.”

Intrigued by this realization, the group dived into the synthesis of half-sandwich complexes. Professor Roesky explained: “These consisted of only one metal ion and one aromatic ligand, based on the cyclooctatetraene derivative described above, which would formally constitute an ideal monomeric starting point for constructing longer and longer bent chains. And indeed, starting from solvent-stabilized half-

sandwich complexes of the type $[M(\text{Cot}^{\text{TIPS}})(\text{thf})_3]$ ($M = \text{Sm, Eu, Yb, Sr}$; $\text{Cot}^{\text{TIPS}} = 1,4\text{-}(\text{iPr}_3\text{Si})_2\text{C}_8\text{H}_6^{2-}$; thf = tetrahydrofuran) enabled us to let bent chains grow until the ends met (see Figure 1), giving birth to an entirely new compound class, cyclic metallocenes, or *cyclocenes*, for short.”

Their initial synthetic attempts focused on Eu(II). Professor Roesky said: “Already, by shining UV-light on the reaction mixture, a visual change in the luminescence from blue (starting material) to orange was observed (see Figure 2), evidencing the formation of a new species even without elaborate analytics.”

However, succeeding in the synthesis of these compounds only marked the first of many, many milestones. “The fact that the center of the cyclocenes is empty generates a substantial amount of unfilled space within the solid-state structure, rendering the crystallographic characterization inherently difficult,” remarked Professor Roesky. He continued: “Thus, a careful optimization of the crystallization conditions needed to be carried out to obtain single crystals sufficiently large to result in X-ray diffraction data of publishable quality. Apart from the synthetic challenge, refinement of the obtained structures proved to be a formidable and time-consuming task.”

To explore the reasons for the formation of the cyclic structures, the authors expanded the general synthetic strategy from Eu(II) to metal ions of similar ionic radii, Sm(II) and Sr(II). Professor Roesky recalled: “Isostructural 18-membered cyclocenes were obtained in all these experiments, giving an indication that the size of the metal ion plays a crucial role, and that the lanthanide f-orbitals are not structure-determining. In line with this, subsequent experiments carried out with the smaller ion Yb(II) resulted in a differently sized cyclocene, a four-membered ring.”

“Elaborate quantum chemical calculations with TURBOMOLE (<https://turbomole.org>) corroborated and rationalized these experimental findings,” said Professor Roesky. He continued: “The bending of the individual sandwich subunits within the cyclocenes proved to be determined by the steric demand of the ligand’s substituents. While unsubstituted cyclooctatetraene yielded the well-known linear sandwich structure, the introduction of bulky groups induced a deviation from linearity, the extent of which was shown to be dependent on the size of the ring substituents.”

Professor Roesky explained that the energy gained upon closure of the ring is decisive, making cycloenes the preferred structure over any other conceivable arrangement.

“The fact that employing Yb led to a smaller ring than Sm, Eu and Sr was traced back to the higher Lewis acidity of Yb, rendering the removal of all THF molecules from the half-sandwich starting material unfeasible,” said Professor Roesky. He went on: “Instead, one solvent molecule remained attached to the Yb ion, resulting in a more pronounced bending and consequently a smaller cycloene.”

Professor Roesky explained that carrying out quantum chemical calculations on molecular systems of this size (up to 1386 atoms and about 25000 cartesian basis functions for the 18-membered-ring structure) with moderate computational resources and energy consumption was solely enabled by the high efficiency of modern quantum chemical software packages.

“In summary, we pioneered the synthesis of cyclic multi-decker sandwich complexes, overcoming the previous limitation of metallocene chemistry to linear structural motifs,” said Professor Roesky. He added: “Our approach is based on the structurally induced self-assembly of monomeric half-sandwich complexes to discrete molecular nanorings.”

Professor Roesky acknowledged that while it is still too early to estimate the future impact of this work to the full extent, the synthesis and structural characterization of the archetypical cycloenes undoubtedly add to the synthetic chemistry toolbox, opening a new chapter in the intriguing world of organometallic chemistry.

The work has laid the foundation for future explorations of cycloenes all over the periodic table. “Constructing rings of different sizes and making use of the large empty space in the ring center for host–guest chemistry are the initial focus of our research,” said Professor Roesky, continuing: “Stabilizing the structures in solution would allow for exciting further experiments to be carried out. Apart from that, establishing ways of communication between the metal ions in the ring may lead to unprecedented electronic properties. Future applications may, for instance, lie in the use of cycloenes as switchable molecular gateways or channels.”

Professor Roesky concluded: “We have made the first step in a new direction, now being excited and looking forward to the surprises the future holds in store for us.”

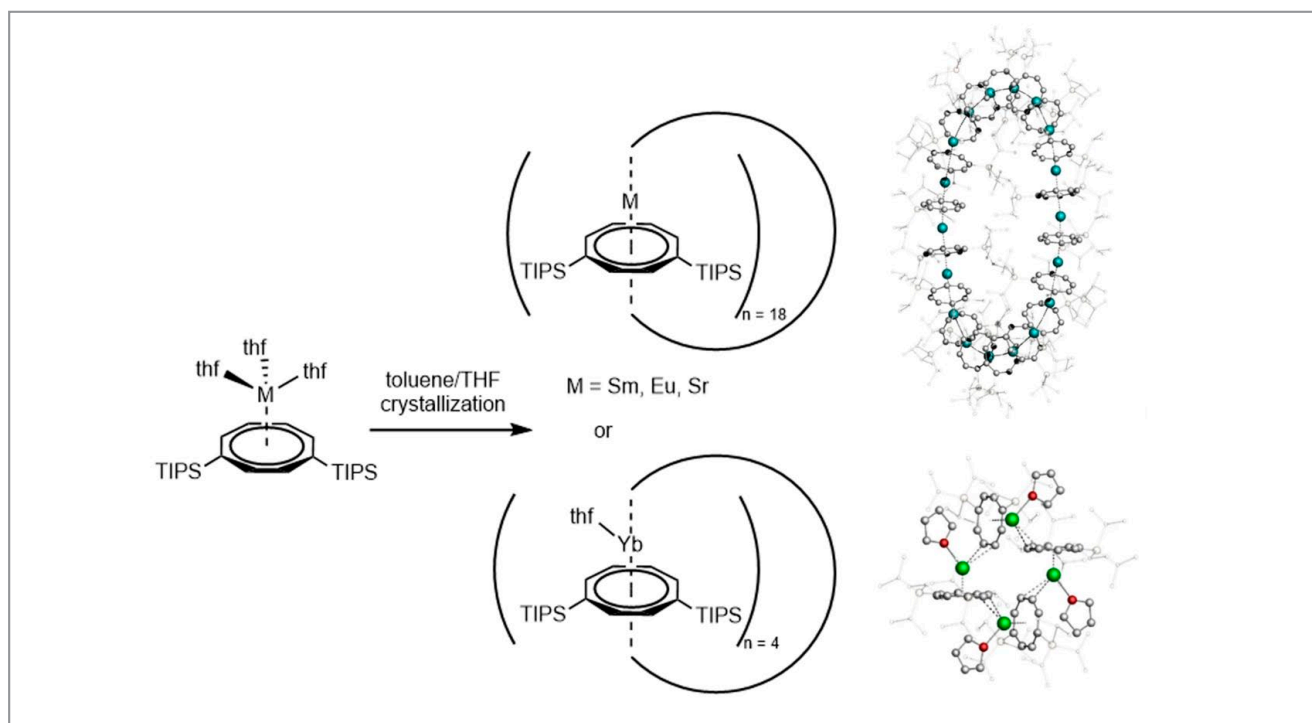


Figure 1 Synthesis and representative solid-state molecular structures of the 18-membered (Sm, Eu, Sr) and 4-membered (Yb) cycloenes (reproduced with permission from *Nature* **2023**, *620*, 92–96).

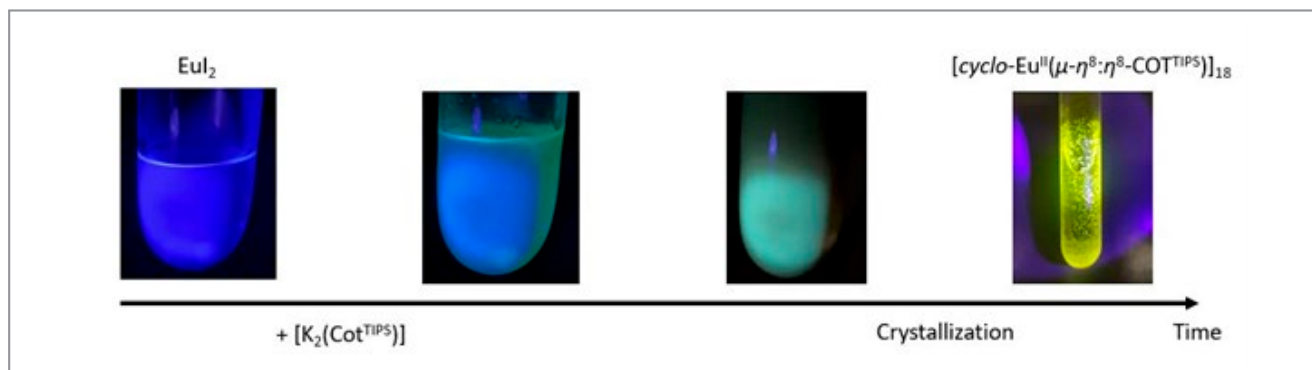


Figure 2 Formation and luminescence of the 18-membered Eu cyclocene under UV light.

Matthias Fenske

About the authors



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Luca Münzfeld obtained his master's degree in chemistry at Karlsruhe Institute of Technology (KIT, Germany) in 2018. Subsequently, he pursued a PhD at the same university in the group of Professor Peter W. Roesky. Becoming bored with academia, he switched to the dark side in 2021 and started making vitamins in industry. He received his PhD in 2022 with distinction for his work on lanthanide sandwich compounds featuring unique structural motifs and properties.



Dr. A. Hauser

Adrian Hauser studied chemistry at the Karlsruhe Institute of Technology (KIT, Germany) and received his master's degree in 2019 under the supervision of Prof. Dr. Peter W. Roesky. He subsequently completed his PhD in the same research group, working on the synthesis of carbon-based lanthanoid sandwich compounds and the activation of group 15 elements. In September 2023, he decided to turn his back on academic research and earn the big bucks in vitamin synthesis.



S. Gillhuber

Sebastian Gillhuber finished his master's degree in chemistry under supervision of Prof. Florian Weigend at the Karlsruhe Institute of Technology (KIT, Germany) in 2021. He subsequently joined the groups of Prof. Peter W. Roesky (KIT) and Prof. Christopher Barner-Kowollik (Queensland University of Technology, QUT, Australia) for joint PhD studies, working on metal-functionalized polymers.



Dr. S. Lebedkin

Sergei Lebedkin received a PhD in chemical physics at the Institute of Chemical Physics of the Russian Academy of Sciences (Russian Federation) in 1993. After postdoctoral research at the Max Planck Institute for Nuclear Physics in Heidelberg (Germany), he worked at the Research Centre Karlsruhe (Germany) as a research fellow. He joined the group of Prof. Manfred Kappes at the Institute of Nanotechnology (now part of KIT, Germany) in 1999. His research interests include Raman and luminescence spectroscopy and microscopy applied to metal-organic complexes and nanosized metal-cluster compounds.

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Pauline Hädinger studied chemistry at the Karlsruhe Institute of Technology (KIT, Germany) and obtained her M.Sc. in inorganic chemistry in 2021. Currently, she is a PhD student, working on functionalized silylenes under the supervision of Dr. Alexander Hinz.



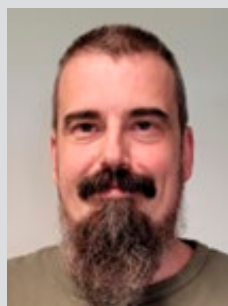
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Dr. C. Zovko

Christina Zovko undertook her chemistry studies at the Karlsruhe Institute of Technology (KIT, Germany). She began her doctorate in the group of Professor Peter W. Roesky in the field of inorganic chemistry. Following her PhD, she successfully completed her Master of Business Administration at the Collège des Ingénieurs. Since 2023 she has been working as a Division Controller in the chemical industry.



Dr. M. Gamer

Michael Gamer graduated in chemistry from the University of Karlsruhe (TH, Germany) in 1999. He started his PhD thesis under the supervision of Prof. P. W. Roesky in Karlsruhe and finished it at the Free University of Berlin (Germany) in 2003. Since 1996 he has been associated with the Roesky group in various positions, since 2008 in a permanent position as 'Akademischer Rat' at the Karlsruhe Institute of Technology (Germany).



Prof. F. Weigend

Florian Weigend obtained his doctoral degree in chemistry from the University of Karlsruhe (TH, Germany) in 1999 and completed his habilitation in theoretical chemistry in 2007. After positions as researcher and group leader at the Institute of Nanotechnology at the Karlsruhe Institute of Technology (KIT, Germany), he joined the University of Marburg (Germany) in 2020 as the head of the applied quantum chemistry unit.

Since 2007, he has been a member and CEO of TURBOMOLE GmbH. His research interests include the development and implementation of basis sets and relativistic methods for the calculation of molecular properties as well as the application of the developed methods to gather an in-depth understanding of the properties of molecular systems of chemical interest.



Prof. M. M. Kappes

Manfred Kappes received a PhD in physical chemistry at MIT (USA) in 1981. After postdoctoral research at the University of Bern (Switzerland), he joined Northwestern University (USA) as an assistant professor in 1987 and became an associate professor in 1991. In 1992 he moved to Karlsruhe (Germany) where he is a professor in the institute of physical chemistry of KIT with a joint appointment at the institute of nanotechnology. His research interests include optical spectroscopy of nanosystems at low temperatures (ranging from CNTs to trapped molecular ions), hybrid mass spectrometry including method development as well as structure and reactivity of transition-metal clusters (both bare and ligand-stabilized).

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Prof. P. W. Roesky

Peter Roesky obtained his diploma in chemistry in 1992 from the University of Würzburg (Germany) and his doctoral degree from the Technical University of Munich (Germany) in 1994. After postdoctoral work at Northwestern University, USA (1995–1996), he completed his habilitation at the University of Karlsruhe (Germany) in 1999. He was appointed a full professor at the Freie Universität Berlin (Germany) in 2001, during which he

joined the faculty of chemistry and biochemistry. In 2008, he became a full professor of inorganic functional materials at the Karlsruhe Institute of Technology (KIT, Germany). From 2013 to 2015, he served as Dean of the Faculty of Chemistry and Biosciences at KIT. His current research interest revolves around the synthetic inorganic and organometallic chemistry of s-block metals, silicon, phosphorus, gold, and lanthanides.