Supramolecular coordination chemistry with poly-NHC ligands

F. Ekkehardt Hahn Universität Münster

26 de Septiembre de 2017 12:00 Sala de Grados de la Facultad de Ciencias

CICLO CONFERENCIAS ISQCH 2017



Facultad de Ciencias, Universidad de Zaragoza - CSIC C/ Pedro Cerbuna, 12. Zaragoza 50009. Spain





Supramolecular coordination chemistry and self-assembly with poly-NHC ligands

F. Ekkehardt Hahn

Institut für Anorganische und Analytische Chemie, Universität Münster, Münster, Germany fehahn@uni-muenster.de, https://www.uni-muenster.de/Chemie.ac/hahn/hahn.html

Three-dimensional, cylinder-like metalosupramolecular assemblies like $[\mathbf{1}]^{4+}$ have been obtained from 1,2,4,5-tetraimidazolium substituted benzene and silver oxide.¹ Cation $[\mathbf{1}]^{4+}$ reacts with [AuCl(SMe₂)] under transmetalation giving the tetranuclear gold(I) complexes. Similar behavior was observed with the trinuclear cylinder-like assembly obtained from 1,3,5-tris(imidazolium) substituted benzene and Ag₂O.² Even hexanuclear assemblies from two hexa-NHC ligands and six metal atoms have been obtained.³

Molecular squares with bridging dicarbene ligands like in $[\mathbf{2}]Cl_4$ were synthesized from the tetranuclear assembly featuring four bridging β , β' -OSiR₃-substituted 1,4-phenyldiisocyanide ligands by hydrolysis of the O-SiR₃ bonds followed by intramolecular cyclization of the 1,4-phenyldiisocyanides to di(NH,O-NHC) ligands.⁴ Two different types of bridging dicarbene ligands were used to prepare $[\mathbf{3}](BF_4)_8$ starting from the assembly with two ditopic dicarbene and two β , β' -OSiR₃-substituted 1,4-phenyldiisocyanide ligands.⁵ Finally, the direct preparation of molecular squares from suitable metal precursors and four equivalents of benzobisimidazolium salts has recently been demonstrated.⁶

Finally, self-sorting phenomena with trigonal tris-NHC ligands were studied. An equimolar mixture of three trigonal tris-NHC ligands, but different size backbone groups, reacts with Ag_2O in a one- pot reaction to give selectively three cylinder-like trinuclear complexes, each featuring three silver atoms sandwiched in between two identical tris-NHC ligands.⁷ No mixed-ligand products were observed. The tris-NHC ligands can be transmetalated to gold without destruction of the metalosupramolecular structure. Related self-sorting phenomena using tetra-NHC ligands will also be discussed.⁸



References

- 1. A. Rit, T. Pape, F. E. Hahn, J. Am. Chem. Soc. 2010, 132, 4572.
- 2. A. Rit, T. Pape, A. Hepp, F. E. Hahn, Organometallics **2011**, *30*, 334.
- 3. C. Segarra, G. Guisado-Barrios, F. E. Hahn, E. Peris, Organometallics 2014, 33, 5077.
- 4. F. Conrady, R. Föhlich, C. Schulte to Brinke, T. Pape, F. E. Hahn, J. Am. Chem. Soc. 2011, 133, 11496.
- 5. M. Schmidtendorf, T. Pape, F. E. Hahn, Angew. Chem. Int. Ed. 2012, 51, 2195.
- 6. N. Sinha, F. Roelfes, A. Hepp, F. E. Hahn, Chem. Eur. J. 2017, 23, 5939.
- 7. N. Sinha, T. T. Y. Tan, E. Peris, F. E. Hahn, Angew. Chem. Int. Ed. 2017, 56, 7393.
- 8. N. Sinha, F. E. Hahn, Acc. Chem. Res. 2017, in press, DOI:10.1021/acs.accounts.7b00158.



F. Ekkehardt HAHN studied chemistry at the Technische Universität Berlin (Dipl.-Chem. 1983) and the University of Oklahoma (M.S. 1982). Subsequently, he carried out research on organolanthanides in the research group of Prof. H. Schumann at the Technische Universität Berlin where he graduated with a Dr. rer. nat. in 1985. From 1985-1988 he worked as postdoctoral associate on microbial iron transport with Prof. K. N. Raymond at the University of California Berkeley. After returning to Berlin he received the habilitation in 1990 from the Technische Universität Berlin. He was appointed Professor of Inorganic Chemistry at the Freie Universität Berlin (1992-1998). Since 1998 is Full Professor of Inorganic Chemistry at the Institut für Anorganische und Analytische Chemie in Münster. His research interests comprise the organometallic coordination chemistry of isocyanides and N-heterocyclic carbenes, the use of carbene complexes in catalytic transformations and the construction supramolecular assemblies from poly(benzene-o-dithiolato) ligands which are used as host molecules for selected substrates. Prof. Hahn is currently member of the Editorial Boards of Zeitschrift für Naturforschung and Dalton

Transactions. Since 2006 he serves as Permanent Secretary of the Advisory Board of the International Conference on Organometallic Chemistry (ICOMC).