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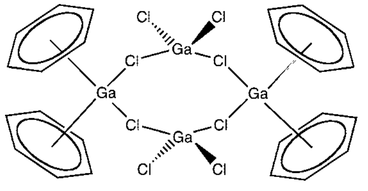
Editor's Page

Introduction to the Review by Schmidbaur and Schier in This Issue of *Organometallics*

The preparation and handling of our cover molecule, $[(C_6H_6)_2Ga \cdot GaCl_4]_2$ (**1**) required considerable care and experimental skill on the part of the synthetic chemists (Hubert Schmidbaur and Theodore Zafiropoulos) and the crystallographer (Ulf Thewalt), as described in *Organometallics* (**1983**, *2*, 1550). First, the starting material, $Ga^{I}[Ga^{III}Cl_4]$, had to be prepared by the reaction of Hg_2Cl_2 with liquid gallium metal in benzene. This mixed-valence gallium chloride dissolved in warm benzene to give a colorless solution. Large, transparent, air-sensitive crystals of **1** were obtained by slow crystallization from a saturated solution at room temperature. As the authors report, "this product loses benzene very rapidly, even at room temperature, if the partial pressure of benzene is reduced in the atmosphere above the material by purging with nitrogen or argon or under vacuum. At only slightly elevated temperatures all of the benzene is evaporated and pure $Ga[GaCl_4]$ remains." Thus, as the authors note, manipulation of this compound "requires great care and thoroughly controlled conditions." Despite this obviously rather limited stability of our cover molecule, its structure could be determined by X-ray diffraction when a crystal was mounted in a glass capillary under argon at dry ice temperature. The authors described the structure as "consisting of centrosymmetrical $[(C_6H_6)_2Ga \cdot GaCl_4]_2$ units and additional benzene molecules filling the space between such entities." The $GaCl_4$ units were classified "as tetrachlorogallate(III) anions having a multifunctional bridging role for the remaining gallium(I) components," each of which is additionally weakly bonded to two neutral benzene ligands as shown.



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Obviously, there is a very big difference between the rather unstable $[(C_6H_6)_2Ga]^+$ unit in **1** and the analogous transition-metal−dibenzene sandwich cations, as typified by the $[(C_6H_6)_2Cr]^+$ cation, in which the benzene ligands are strongly bonded to the Cr^+ ion. It is the weakly bound arene and other aromatic complexes of the main-group elements of groups 13 (Ga, In, Tl), 14 (Ge, Sn, Pb), and 15 (As, Sb, Bi) that are the subject of the review in this issue by Professor Hubert Schmidbaur and Dr. Annette Schier of the Institute of Inorganic Chemistry of the Technical University of Munich. This very interesting area of main-group-element chemistry had its beginnings in the late 19th century, but for a long time it was only a collection of unconnected, not well understood observations. This changed, first in the late 1950s, when the groups of Rundle, Corbett, and Amma determined a few selected structures, and subsequently, in the early 1980s, when the group of Professor Schmidbaur entered this area. He and his co-workers have made many important contributions which served to develop, extend, and clarify this area with outstanding synthetic and structural work that, along with the work of others, is summarized in the present review.

Professor Schmidbaur studied chemistry at the University of Munich, carrying out his Diplom and doctoral research under the guidance of Professor Max Schmidt. He was awarded the Dr. rer. natur. degree in 1960. In 1962, with the Max Schmidt group, he moved to the University of Marburg. There he completed the research for his Habilitation in inorganic chemistry in 1964. A move to the University of Würzburg followed, where he was associate professor (1965−1969) and Professor of Inorganic Chemistry (1969−1973). In 1973 he accepted a call to the Technical Unviersity of Munich (Garching Campus) as Professor of Inorganic and Analytical Chemistry. He has been at TU Munich since 1973 and became Emeritus Professor in 2003.

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Professor Schmidbaur, during the course of his long and very distinguished research career, has made a great many important and very interesting original contributions to various areas of chemistry, for the most part to the chemistry of the groups 14 (Si, Ge, Sn, Pb) and 15 (P, As, Sb, Bi) and gold. His research in organosilicon and -germanium chemistry began in the 1950s in Munich, but after his formal retirement he was still publishing papers in this area. The early silicon chemistry was concerned with the preparation and reactivity of compounds that contained Si−O−Si and Si−O−M linkages, in which M could be a nonmetal such as S and P and a main-group metal of groups 13−15, as well as a transition metal. A very interesting area was opened up in the mid 1960s involving the chemistry of silyl-substituted phosphorus and sulfur ylides. Along the way, the isolation as pure, distillable liquids of $(CH_3)_3P{=}CH_2$ and $(CH_3)_2S^+(O)CH_2^-$ was of notable importance. This led to a substantial and very successful effort in organophosphorus chemistry, e.g., of carbodiphosphoranes and phosphinoboranes, to mention just two areas of interest. A later interest in Si−H-rich silanes led to the synthesis of novel species such as $C(SiH_3)_4$, $C_6(SiH_3)_6$, and $[(H_3Si)_3CSiH_2]_2O$. Work with compounds of this general type as CVD precursors for solid-state silicon materials was of special interest.

It was Professor Schmidbaur's extensive and innovative research in the chemistry of gold which gained him many new admirers. Especially noteworthy and spectacular were his synthesis and structural characterization of unprecedented hypercoordinated carbon, nitrogen, and phosphorus compounds such as $[(LAu)_6C]^{2+}[BF_4]_2^-$, $[(LAu)_5C]^+[BF_4]^-$, $[(LAu)_5N]^{2+}[BF_4]_2^-$, and $[(LAu)_6P]^{3+}[BF_4]_3^-$, where $L = R_3P$, as well as the "golden wheel", $[CSAu(PPh_3)]_6$. Perusal of Professor Schmidbaur's lengthy publication list reveals other research areas, such as his studies of other aspects of the organic chemistry of the heavier group 13 (Al, Ga, In) and 15 (As, Sb, Bi) elements and some organotransition-metal chemistry, as well as bioinorganic chemistry involving principally compounds of magnesium and beryllium with appropriate ligands.

This lifetime of original and innovative research has been well rewarded—with the ACS's Frederic Stanley Kipping Award in Organosilicon Chemistry, the Wacker Silicon Prize, the Alfred Stock Medal of the German Chemical Society, the Gottfried Wilhelm Leibniz Prize of the German Science Foundation, and the Centenary and Ludwig Mond Medals of the Royal Society of Chemistry, to name just a few.

The coauthor of the present review, Dr. Annette Schier, studied chemistry at the TU Munich, carrying out her research for the Diplom and Dr. rer. nat. (1983) under the guidance of Professor Schmidbaur. Except for absences as a postdoctoral fellow at the Australian National University (1984−1985) and as a Visiting Professor at Chalmers University of Technology in Sweden (2004), she has remained at the TU Munich as a collaborator in research with Professor Schmidbaur (experimental chemistry and X-ray crystallography). She also lectures in inorganic chemistry and supervises laboratory courses. At present she holds the rank of Academic Director.

My special thanks go to Professor Kraig A. Wheeler of Eastern Illinois University and Professor Arnold L. Rheingold for the cover figure.

Dietmar Seyferth
Editor

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