



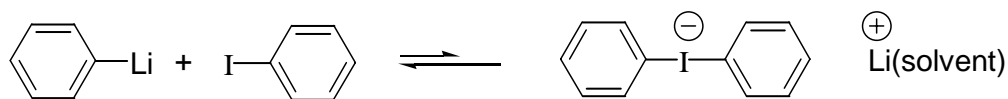
...the  Lithium company

The Arfvedson-Schlenk award of the German Chemical Society is given to honour outstanding achievements in the chemistry of the element lithium. The inorganic chemistry of this element has been developed in the past centuries to the point that it constitutes a well established body of knowledge. Likewise, the chemistry of organolithium compounds has come a long way since the pioneering studies of Schlenk, Ziegler, Gilman and Wittig. Organolithium compounds have grown to become essential reagents in organic synthesis in general and, hence, developed into a flourishing branch of chemical industry. In line with this, our knowledge of organolithium chemistry appears to be comprehensive and complete. Yet on closer scrutiny we realize that we know a lot about organolithium chemistry in a descriptive sense, be it reactions and structures, yet we lag behind in our mechanistic understanding of organolithium chemistry. While the eye-catching progress in computational chemistry, when applied to organolithium chemistry provides suggestive rich details in mechanistic organolithium chemistry, one still requires the hard-core facts about the mechanisms of organolithium reactions, in order to allow any rational progress in this field.

This brings us to this years winner of the Arfvedson-Schlenk award, Prof. Hans J. Reich of the University of Wisconsin. He is a pioneer in elucidating the relationship between structure and reactivity of organolithium reagents. The findings of his group have been real eye-openers for those that use organolithium reagents and, hence, are now on good grounds honoured with the award. Let me just highlight a few of Hans Reich's outstanding findings:

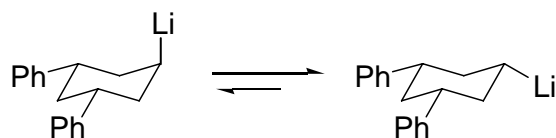


The lithium/halogen exchange reaction and its congeners the lithium/metalloid exchange reaction are standard methods to generate constitutionally complex organolithium reagents. The nature of this process was for long a playing ground for mechanistic speculations (SET-reactions, four-centre transition states, S_N2 -reactions and ate-complex formation). It was Hans Reich who found kinetic evidence that an intermediate is involved in the degenerate lithium/iodine exchange between phenyl-lithium and iodobenzene. By subsequent low-temperature NMR-studies he was able to demonstrate that the intermediate is the symmetrical diphenyliodine-ate complex.



Today the formation of ate-complexes is the generally accepted mechanism for these lithium/halogen exchange reactions.

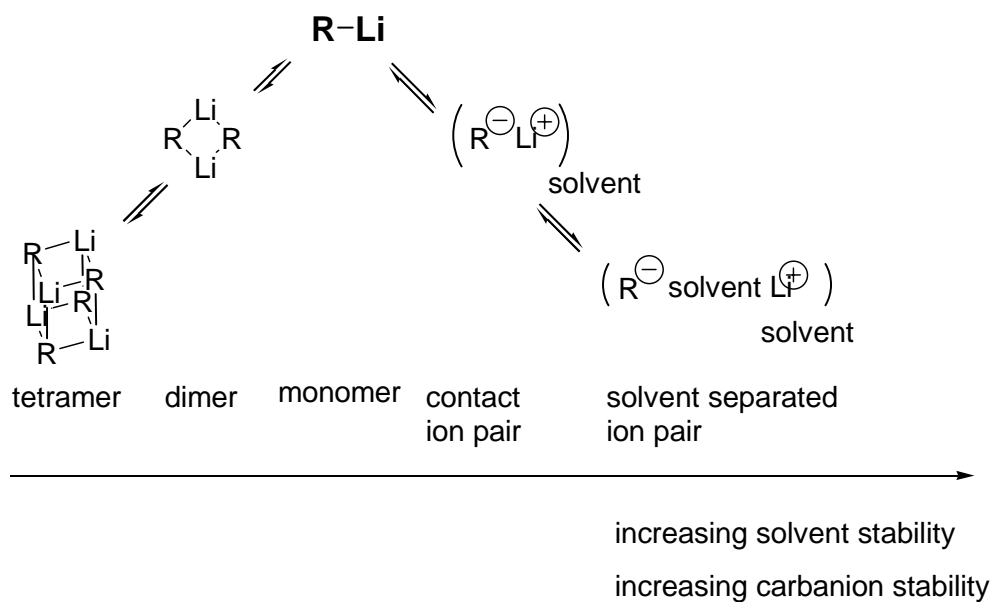
In most reactions of organolithium compounds the carbon-lithium bond has to be broken. Notwithstanding any debate about the nature of this bond, fundamental information about this “bond” can be obtained from its dynamics. Hans Reich set out to study the dynamics of an organolithium entity in which the lithium bearing carbon atom constitutes a key element of stereochemical information. He thus generated separately both epimers of 3,5-diphenylcyclohexyl-lithium and studied their interconversion, a reaction which corresponds to the racemisation of an organolithium compound.



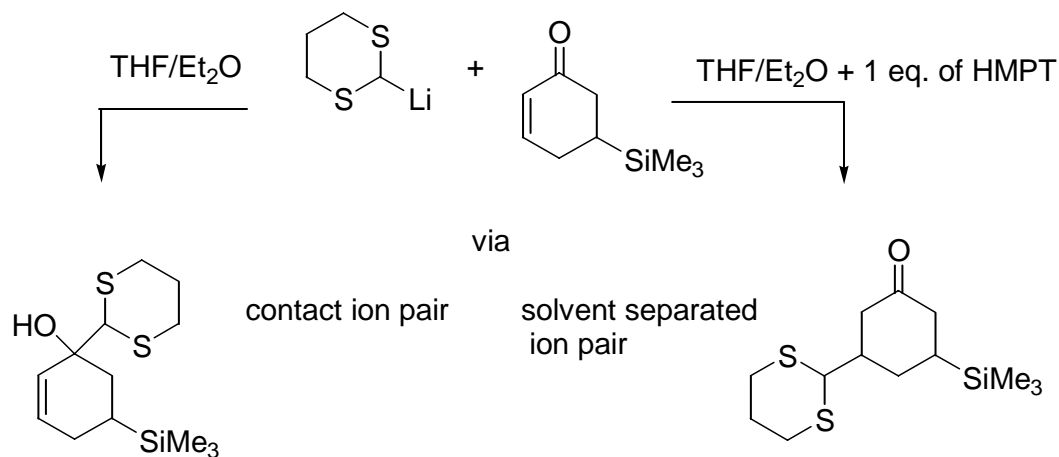
The interconversion of the two epimers was slow at -78° in THF. It was slowed down by addition of a tridentate ligand for the lithium cation, i.e. conditions that stabilize the

monomeric organolithium species. It was accelerated by higher concentrations, i.e. conditions that favour formation of higher aggregates. This provided the experimental basis to derive a convincing mechanism for the racemisation of organolithium compounds.

Anyone who wants to discuss mechanisms of organolithium reactions is confronted with the fact, that they are not the simple species, as we write them. Depending on the nature of the organic residue R and the solvent, organolithium compounds form aggregates, i.e. equilibrium mixtures from dimers to tetramers and hexamers. Some exist as monomers indeed.

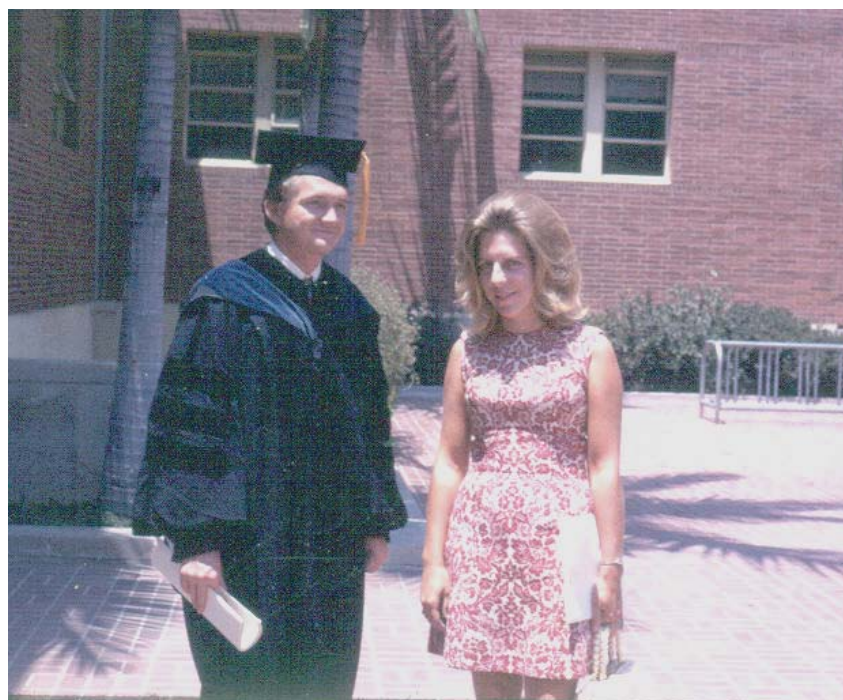


But to understand the reactions of organolithium compounds one has to recognize their structures as ion pairs. Hardcore experimental information on the ion pair nature of organolithium compounds became available after Hans Reich developed a NMR method based on 2J coupling of ^7Li to ^{31}P of HMPA as solvent, and on 1J coupling to ^{13}C of the organic part of organolithium compounds. This way it became possible to distinguish contact ion pairs from solvent separated ion pairs and ultimately to unravel their different reactivity e.g. towards α,β -unsaturated ketones or in nucleophilic substitution reactions.

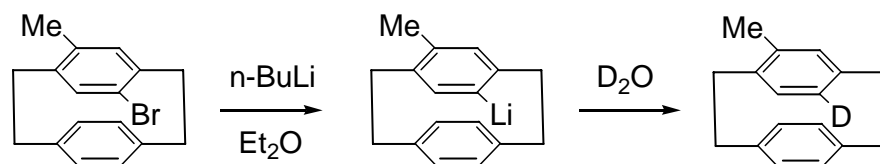


Once being able to control the extent of ion pair separation of organolithium compounds Hans Reich could learn, which reactions prefer to go via the solvent separated and which via the contact ion pair. Teaching us to view organolithium chemistry as a chemistry of ion pairs is probably the greatest merit of Hans Reich's contributions.

These lessons could have been learned decades earlier, but these discoveries were made only after Hans Reich came along. Was there a special constellation in his training to lead him onto this track? Hans Reich was born in Danzig and moved with his parents after the end of world war II to Canada. His schooling and his subsequent undergraduate studies in Alberta went uneventfully. Hans Reich turned to the UCLA for graduate studies and did prolific doctoral studies on para-cyclophanes in the group of Prof. D. J. Cram. In this period he met his wife, Ieva, also an outstanding chemist,



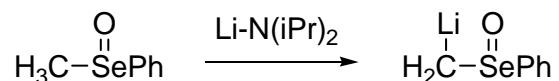
and made first contacts with organolithium chemistry:



After receiving his PhD Dr. Reich moved – geographically a tiny bit, but scientifically substantially – to do postdoctoral work at CalTech with J.D. Roberts. There he learned all the intricacies of NMR-spectroscopy, which became a major asset to his later studies on organolithium compounds. To crown his scientific pedigree Dr. Reich moved to Harvard for a second postdoc with R. B. Woodward to work on the vitamin B12 synthesis project. In 1970,

finally, he translocated to the University of Wisconsin, where he moved up the ranks to full professor. I will not mention the awards and numerous visiting professorships that Prof. Reich attained. Rather let's trace organolithium chemistry in his career:

It was in the early 70ies that he discovered the α -lithiation of alkyl-phenyl-selenoxides and developed its chemistry.



From then onwards Hans Reich got more and more involved in organolithium chemistry until it became his major research topic in the 1980es. But there was no obvious line in his scientific development that led Prof. Reich to dive into organolithium chemistry. Was it some feature of his personality that led Prof. Reich to find his challenge in organolithium chemistry?

Certainly Hans is inquisitive. He looks at the total system, but focuses as well on any detail.



This is best illustrated by the types of photographs Hans likes to take. Here are given a few examples:



These are like a fingerprint of the man behind the camera. This fingerprint mirrors his approach to organolithium chemistry, the desire to gain understanding in a holistic approach incorporating all the details.



Beyond that, Hans is a sociable person with a certain connection to Germany. Asking former members of his group, what feature they would consider as “typical Hans”, the answers quickly converge on his perfect memory of the published literature and his marvellous card-file for backup. In a way Hans rivals and surpasses “Scifinder”.

This review revealed many ingredients that made Hans a successful scientist and, given his fortunate pick of organolithium chemistry as his workpiece, rendered him the most prominent candidate for the 2007 Arfvedson-Schlenk award.

Congratulations Hans!



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**ARFVEDSON-SCHLENK-AWARD
2007**