

200 Years of Lithium and 100 Years of Organolithium Chemistry

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Abstract. The element lithium has been discovered 200 years ago. Due to its unique properties it has emerged to play a vital role in industry, esp. for energy storage, and lithium-based products and processes support sustainable technological developments. In addition to the many uses of lithium in its inorganic forms, lithium has a rich organometallic chemistry. The development of organometallic chemis-

try has been hindered by synthetic problems from the start. When *Wilhelm Schlenk* developed the basic principles to handle and synthesize air- and moisture-sensitive compounds, the road was open to further developments. After more information was available about the stability and solubility of such compounds, they started to play an essential role in other fields of chemistry as alkyl or aryl transfer reagents.

1 Lithium – from the Beginning to Its Current Role

1.1 Lithium's History

The year 2017 is very remarkable with respect to the biography of lithium. First, the “Li world” is celebrating its bicentenary “birthday” in this year; second, organolithium compounds were first prepared 100 years ago, in 1917.

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According to current cosmologist's theories, the first lithium has been generated at the very beginning of the universe, only some minutes after the Big Bang, about 14 billion years ago. Lithium was created by fusion reactions from deuterium, tritium, and helium nuclei. However, most of the lithium was created later and even arises today by different mechanisms, the most important being associated with novae outbursts.^[1]

In 1800, the Brazilian scientist *José Bonifácio de Andrada e Silva* (1763–1838) discovered two new minerals on the Swedish island of Utö, which were called petalite and spodumene. But it wasn't until 1817 that the Swedish scientist *Johan August Arfvedson* (1792–1841), who worked in the laboratories of the renowned chemist and professor of medicine and pharmacy, Baron *Jöns Jacob Berzelius*^[2] (1779–1848), was able to isolate a sulfate compound, which did not contain any of the known alkali or alkaline earth metals. The new element, originally called “lithion” was finally named “lithium”, derived from the Greek word “lithos” for stone. With the discovery of this new element, another gap in the periodic Table was filled. Only one year later, *Sir Humphry Davy* (1778–1829) and *William Thomas Brande* (1788–1866) prepared lithium metal by electrolysis of lithium oxide, although only in trace amounts. The lithium metal combusted within seconds once exposed to air. In 1854, *Robert Wilhelm Bunsen* (1812–1899)



Ulrich Wietelmann studied chemistry at the TU Dortmund and LMU Munich, where he received his PhD with Prof. Heinrich Nöth on reactions of reactive boron nitrogen species. In 1986, he started his professional career with Chemetall/Metallgesellschaft in the Marketing & Sales of the Lithium division. In 1993 he took a position as head of R&D Lithium. Since 2004 he changed responsibilities within the R&D department and focused on research and battery materials. He is now manager for Business Development & Innovation at Albemarle Germany GmbH in Frankfurt a.M., Germany.



Jan Klett studied chemistry at the University of Stuttgart. He worked with Karl Klinkhammer on his doctorate about copper silanides. He followed Karl Klinkhammer to the University of Mainz, where he completed his thesis in 2006. In 2006 he moved to Scotland and worked as a postdoctoral researcher with Robert E. Mulvey at the University of Strathclyde. He started his independent research career with a research fellowship of the Royal Society of Edinburgh/BP Trust (2009–2012). After his return to Germany in 2013 he worked in the group of Dietmar Stalke at the University of Göttingen on a research project funded by the DAAD. Currently he is a junior research group leader at the University of Mainz. His research interests are the organometallic chemistry of the heavier alkali metals and alkali metal mixed alkyl/alkoxy aggregates. In 2017 he was awarded the Arfvedson-Schlenk prize for his contributions to the organometallic chemistry of lithium.

and Augustus Matthiessen (1831–1870) were the first to produce lithium metal in larger quantities from molten lithium chloride also by an electrolytical process. This process was followed by Metallgesellschaft AG in Germany for the first commercial production of lithium metal in 1923.^[3]

Wilhelm Schlenk (1879–1943) is well-known to all chemists for his technology developed to safely handle air-sensitive, reactive compounds and especially for the “Schlenk flask”, which is a ball-shaped glass device with a nitrogen valve.

Schlenk started his scientific career at the Ludwig Maximilian University in Munich, where he studied the structure of stable radicals. In 1913 he took a position at the University of Jena and focused first on addition compounds of sodium and olefins as well as polycyclic aromatic hydrocarbons (“Schlenk addition compounds”). In 1917 he published the first synthesis of organolithium compounds (MeLi, EtLi, PhLi) from highly toxic organomercury compounds and Li metal (Scheme 1).^[4]



Scheme 1. Formation of ethyllithium by the transmetalation of diethylmercury with lithium metal.

Schlenk recognized the high reactivity of those Li compounds, when he wrote that “methyllithium ignites in air and burns with a luminous red flame and a golden-colored shower of sparks”.^[5] This highly dangerous synthetic route is – of course – unsuitable for the industrial synthesis of organolithium compounds; instead the *K. Ziegler* method, first published in 1930, is applied (see below).^[6]

Since the year 1999 Albemarle (formerly Chemetall/Rockwood Lithium) donates the “Arfvedson Schlenk-Award” together with the *Gesellschaft Deutscher Chemiker* (GDCh) for outstanding scientific and technical achievements in the field of lithium chemistry (Figure 1, Table 1). In this year, *Jan Klett*, University of Mainz, has been awarded for his remarkable contributions in the development and characterization of novel hydrocarbon-soluble superbase systems.

1.2 Unique Properties of Lithium

The unique properties and hence the versatility of lithium and its compounds are linked to the exposed position of lithium in the upper left corner of the periodic Table of elements.



Figure 1. Official Medal donated for the Arfvedson Schlenk Award.

Lithium (chemical symbol Li), the 3rd element (atomic number 3), is a member of the group 1, beside other highly reactive alkali metals. With a density of only $0.53 \text{ g}\cdot\text{cm}^{-3}$, lithium is the lightest solid element and is lighter than most liquids. But when exposed to water, it reacts violently, yielding lithium hydroxide and hydrogen gas, which may spontaneously ignite. Despite of its low density, lithium is harder than the other alkali metals and exhibits higher melting and boiling points, ionization potential and ionization energy. In the metallic and ionic forms, lithium has the smallest atomic radius of all metals.

The low lattice energy of lithium salts LiX comprising large anions X like bromide or iodide effects low lattice energies and low melting points hence. Many lithium salts are important ingredients especially for eutectic mixtures with other metal salts. Amongst all alkali metals, lithium has the highest electronegativity and heat capacity. Lithium's standard electrode potential is -3.045 V , which is the lowest of all elements. This extreme electrode potential combined with its low weight makes it an ideal choice for utilization in high-voltage batteries. In addition to its powerful reduction potential, lithium metal is highly soluble in liquid ammonia and such solutions are useful for selective reductions of aromatic compounds (*Birch* reduction).

While the properties of lithium differ significantly from those of the other alkali metals, they closely resemble the prop-

Table 1. Degree of aggregation of selected organolithium compounds and their complexes with Lewis basic ligands: 1, monomer; 2, dimer; 4, tetramer; 4a, tetramer with 4 ligands; 4b, tetramer with 2 ligands; 4c, open tetramer with 2 ligands; 6, hexamer; ∞ , polymeric. For graphical representation see Scheme 11.

Alkyl lithium	–	Et_2O	THF	TMEDA	TMCDA	PMDTA
LiMe	4	4a	4a	$4b\infty^b$	2	–
Li <i>i</i> Pr	6	–	–	2	2	–
Li <i>n</i> Bu	6	–	4a	2, $4b\infty^b$	2, 4c	4c
Li <i>t</i> Bu	4	2	–	–	1	–
$\text{LiCH}_2\text{SiMe}_3$	6	4b	–	2	–	1
$\text{LiCH}(\text{SiMe}_3)_2$	$1\infty^a$	–	2	1	–	1
LicPent	6	–	4a	–	–	–
LiPh	$2\infty^a$	–	–	–	2	1

a) Linear polymer. b) Polymeric networks.

erties of magnesium. This phenomenon known as “diagonal relationship” is based on similar charge density attributed to the comparable ratio between ionic radius and positive ion charge. These “anomalies” are mainly the result of the small radius of the lithium cation, which exhibits the highest polarization power among all the alkali metal ions. This produces a strong trend to solvation and the formation of carbon–metal bonds. Although the latter exhibit covalent properties, they are nowadays considered to be more than 80% ionic. Various lithium compounds, such as alkyllithium compounds and inorganic salts are easily soluble and stable in organic solvents and are thus easy-to-handle, a prerequisite for their success in industrial applications.

1.3 Lithium's Role for Society

Today's globalizing world is facing an ever increasing rate of changes causing pressure on society and daily life. In order to cope with these challenges, several major fields of change, so-called megatrends, can easily be identified. The alkali metal lithium is playing an important role in solving such challenges presented by at least three of these megatrends.

Nowadays more than 7 billion humans require access to sustainable energy sources. The energy production has to be decarbonized, which means to use more efficient and above all renewable resources like wind and solar. However, those energies are fluctuating and they thus need to be buffered by stationary energy storage systems. Lithium batteries are excellent candidates for that purpose because of their long calendar life time and high rate capabilities. The second megatrend to mention herein is the extended mobility, the challenge is: lower carbon footprint and the major answer is: electro-mobility. The energy storage system for today's electric vehicles comprises high-performance lithium batteries. Besides that, novel light-weight materials like lithium-containing metal alloys are used as construction materials in the aviation and other high-tech industries. Thanks to a key and unique property of lithium – it is the lightest solid element existing – less energy is consumed just by weight savings. The third megatrend is the growing health sector, which is dominated by the needs to improve the quality of life, especially for the over-aging population and its specific illnesses like dementia and cardiovascular diseases. Lithium itself is a remedy to cure manic depression and lithium-containing compounds are used by the pharma industry as tools for organic synthesis to efficiently produce novel drugs.

Besides these major applications, lithium-containing products and materials are indispensable in a variety of further industrial products and processes: specialty glasses and glass ceramics, high-end lithium greases, air conditioning, production of synthetic rubber, rubber vulcanization, aluminum electrolysis, brazing fluxes etc.

1.4 Resources and Demand Situation

The increasing demand of lithium for lithium ion batteries, especially for the electrification of cars, raised the question of long term lithium supply. Projected growth has promoted a

large number of lithium exploration and exploitation projects over the past years, providing a more robust picture of global lithium availability.

The 2015 United States Geological Survey (USGS) estimated the total reserves to be 13.5 million tons of lithium in reserves and in approximately 40 million tons of lithium resources, which are a significant increase when compared to the USGS estimates from 2008 (reserves: about 4 million tons lithium; resources: about 14 million tons lithium).

The overall consumption of lithium metal and chemicals in 2015 was estimated at 180,000 tons of LCE (lithium carbonate equivalents). An additional 20,000 tons of LCE's were consumed in the form of various minerals. Therefore, the total world demand is estimated at approximately 200,000 tons of LCE (i.e. approximately 38,000 tons of Li). The largest demand for lithium is found in China, Japan and Korea, followed by Europe and America. About 50% of the consumption is directly in the form of carbonate. Lithium hydroxide accounts for nearly 10% of the demand. Various lithium salts as well as the metal and metal-based products account for a total of about 30%.

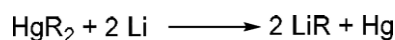
In relation to the 2015 annual consumption of approximately 0.04 million tons of lithium, the estimates of resources and reserves suggest long term availability of lithium to support the rapidly growing energy storage and other markets.

2 Organolithium Compounds

Lithium stood in the shadow of its heavier siblings sodium and potassium since its discovery. But on the ground of organometallic chemistry it overtook them soon by lengths. This class of lithium compounds had to wait for its discovery for a century after lithium and its inorganic compounds became available. Soon lithium could follow magnesium in its footsteps,^[7] with which it is associated by the “Schrägbeziehung”^[8] (diagonal relationship in the periodic system of elements). Lithium rapidly developed a rich organometallic chemistry. It started with the first synthesis of organometallic lithium compounds by *Wilhelm Schlenk* in 1917.^[4] Besides several congeneric sodium compounds he presented the successful isolation of methyllithium (LiCH₃), ethyllithium (LiC₂H₅), and phenyllithium (LiC₆H₅).

2.1 Preparation of Organolithium Compounds

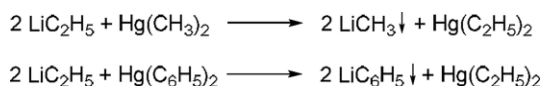
In his preparation of these organolithium compounds, *Schlenk*^[5] used lithium metal and divalent organic mercury compounds as starting materials undergoing a transmetalation^[4] (Scheme 2). Since *Frankland's*^[9] initial discovery, the organometallic chemistry of mercury was already well developed. This can be attributed to the stability of organomer-



Scheme 2. Formation of organolithium compounds by the transmetalation of dialkylmercury or diarylmercury with lithium metal in inert organic solvents (*R* = organic group).

cury against air and moisture on one hand, and the use in pharmacological applications on the other hand.

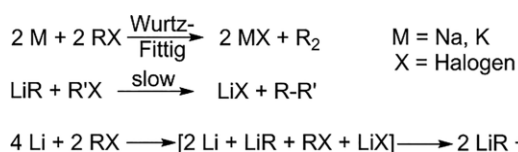
The reasons for this comparable late advent of organic lithium compounds might be seen in the low availability of lithium metal at that time and the high reactivity of the organic lithium compounds against air and moisture. This instability in ambient atmosphere made it necessary to develop new techniques for the handling of such compounds. *Schlenk* therefore developed procedures, which are still in use in many laboratories today. The metal displacement reaction using organomercury (Scheme 2) benefits from the low tendency of mercury compounds to form metalates, which bind the formed organoalkali compound, as it was observed by *Wanklyn*^[10] for corresponding reactions using dialkylzinc. Already these very first examples prepared by *Schlenk* (LiCH_3 , LiC_2H_5 , and LiC_6H_5) demonstrate the importance of the chosen organic solvent used in synthesis. Only ethyllithium is soluble in alkanes such as petroleum ether and can be easily separated from metallic mercury and excess lithium metal by filtration and subsequently isolated by crystallization. The separation from metallic by-products was not successful for methyllithium and phenyllithium, which are both insoluble in alkanes. But *Schlenk* did not give up because of this problem and presented an alternative reaction: the metal-metal exchange. In this case ethyllithium, the only accessible and pure organolithium compound, was used in a reaction with dimethylmercury or diphenylmercury (Scheme 3).



Scheme 3. Metal-metal-exchange reaction of ethyllithium with dimethylmercury or diphenylmercury.

This reaction exploits the precipitation of the desired product, while both the starting materials and the by-product stay in solution and can be easily separated by filtration. The use of organomercury in such metal-metal exchange reactions has the advantage that no halogenides are involved, which could be incorporated in the products. However, the high toxicity of mercury compounds makes this synthetic approach unfavorable, especially for large scale reactions.

In 1929 *Karl Ziegler* observed that some alkyllithium compounds showed little reactivity towards organic halides.^[6] That is in contrast to their heavier alkali metal congeners which undergo a C–C coupling of the organic groups equivalent to the Wurtz-Fittig synthesis^[11] (Scheme 4). The different behavior of lithium in such reactions makes organolithium accessible by use of metallic lithium and organic halides. The formation

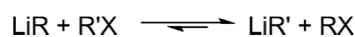


Scheme 4. Outcomes of reactions of alkali metal or organoalkali compounds with organic halides.

of the lithium halide in crystalline form makes this direct synthesis thermodynamically favorable.

Analogous to the preparation of Grignard compounds it was now possible by direct synthesis to produce alkyllithium compounds of a wide range of alkyl and aryl groups in good yields and under convenient inert-gas conditions. Best results were achieved when alkyl chlorides were used in alkanes or benzene, but also alkyl bromides and solutions in ether provided satisfactory results. *Wittig*^[12] and *Gilman*^[13] modified and improved the syntheses very successfully.

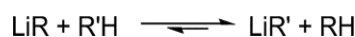
Only a few years later, in 1938, *Wittig*^[14] and *Gilman*^[15] simultaneously observed that it is possible to replace bromine in organic halides by lithium when alkyllithium or phenyllithium is used. The halogen metal exchange reaction produces the desired lithium compound in combination with a new organic halide; the equilibrium of the four components lies on the side of the organolithium compound with the best stabilization of negative charge of the highly polar Li–C bond (Scheme 5).



Scheme 5. Halogen metal exchange reaction.

This turned out to be a very useful synthesis for the preparation of aryllithium compounds. The reaction proceeds fast at low temperatures which favors it over undesired deprotonations. Such reaction conditions enable the introduction of lithium atoms on aromatic rings next to reactive functional groups such as NO_2 , COOR , or CONH_2 .

Alkyl compounds of the heavier alkali metals showed their potential to remove hydrogen atoms from organic molecules in early stages of their exploration.^[16] In a smaller range but in a more controllable and efficient fashion alkyllithium compounds are also able to perform metalations (Scheme 6).

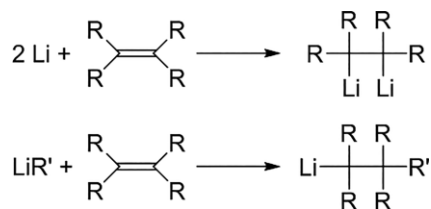


Scheme 6. Metalation of acidic hydrocarbons by alkyllithium.

However, only hydrocarbons with a comparable high acidity and the potential to stabilize the resulting negative charge by delocalization can be transferred into lithium compounds by this reaction. The usefulness of this reaction lies in the direct substitution of a hydrogen atom by a lithium atom, which then can be replaced by a wide range of organic electrophiles.

The first observation of a direct hydrogen lithium exchange was observed by *Schlenk* in a reaction of fluorene with ethyllithium.^[17] During the exploration of the halogen metal exchange reaction, *Gilman*^[15] and *Wittig*^[14,18] observed that replacement of hydrogen atoms of aromatic rings can be directly replaced by lithium. *Gilman* treated *p*-bromoanisole with *n*-butyllithium and *Wittig* studied reactions of anisole with phenyllithium. In both cases they found that the respective hydrogen atom in the *ortho* position to the methoxy group was replaced by lithium.

The addition of metallic lithium or lithium compounds to alkenes opens additional pathways to obtain organolithium compounds (Scheme 7). This so-called carbometalation can also be regarded as the insertion of a C_2 unit into the Li–C bond.



Scheme 7. Reductive addition of elemental lithium (Schlenk-Addition) or alkyllithium (Ziegler-Addition, carbometalation) to C–C double bonds of alkenes.

Schlenk observed that alkenes formed dark colored products in reactions with sodium.^[19] He assumed an addition of two sodium atoms to the double bond of the alkene. Later, he was able to reproduce this reductive addition with lithium metal^[17] and obtained the corresponding dilithium species. Almost simultaneously Ziegler observed the addition of *n*-butyllithium and 1,1-diphenylethene in benzene.^[20] Years later he described the insertion of ethene into the Li–C bond of *n*-butyllithium.^[21] With excess ethene the reaction didn't stop there and finally lead to the polymerization^[22] of ethene. For the further development of this theme Karl Ziegler was awarded the Nobel prize in Chemistry together with Giulio Natta in 1963.

2.2 The Benefits of Alkyllithium

The initial head-start of the heavier alkali metals sodium and potassium in organometallic chemistry was made up by lithium shortly after the initial discoveries. Although the availability for sodium and potassium was considerably better than lithium, there are two reasons why these two metals fell behind. The first reason lies in the tendency to undergo Wurtz-Fittig C–C coupling reactions when organic halides are treated with elemental sodium or potassium. Although a few examples are reported for the successful direct synthesis of alkylsodium^[23] the broad application was limited by demanding synthetic requirements. Secondly, the solubility of alkyllithium is in almost every case better in comparison to its corresponding sodium or potassium counterpart. Already in the very early stages of the exploration of organometallic alkali metal compounds, the solubility often decided if a new compound could be isolated in adequate purity and subsequently characterized or not. The reason for this can be found in the polarity of the metal–carbon bond, which has a higher polarity in the case of sodium and potassium than for lithium.

On one hand this high bond polarity and the larger size of sodium and potassium atoms leads to stronger interactions between molecular units. This leads to the formation of oligomeric aggregates with often strong intermolecular interactions, or even polymeric arrangements.

On the other hand the high bond polarity leads to an increased reactivity. This often results in aggressiveness towards exactly the more polar solvents which are needed to dissolve and recrystallize the corresponding compounds.

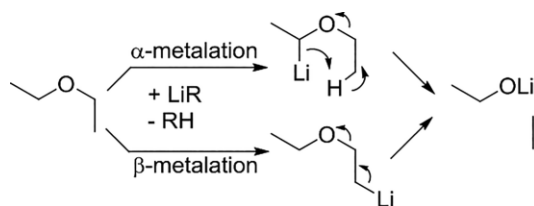
When after 1960 the availability of lithium improved substantially,^[24] the chemical and practical advantages lead to an

even faster development of the organometallic lithium chemistry.

2.3 Alkyllithium and Solvents

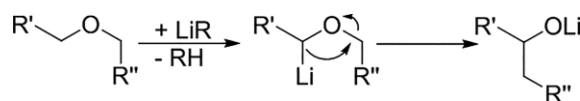
For most alkyllithium compounds both aspects described above, poor solubility and uncontrollable reactivity, don't play a dominant role. In many cases the solubility in inert solvents (alkanes, such as *n*-hexane, *n*-heptane, and cyclohexane) is very good; the most important examples are ethyllithium, *n*-butyllithium, and *tert*-butyllithium. For alkane-insoluble alkyllithiums, such as methyllithium or phenyllithium, it is possible to use solutions in ethers.

However, ether as a solvent of alkyllithium compounds is not invulnerable to unwanted side-reactions. The oxygen atom with its Lewis-donor function in ethers not only enables the coordination to alkyllithium. In the same time it is weakening C–H bonds of the organic side-chains (especially in the α -position), which makes the corresponding proton accessible for deprotonations. Already Schorigin^[25] and Schlenk^[18] observed the undesired reaction of alkylsodium with diethyl ether. Besides sodium ethanolate (NaOC₂H₅) Schorigin could also identify ethane and ethene as products of the reaction of ethylsodium with diethyl ether. The preparation of many alkyllithium compounds is possible in ethers, and some reaction of alkyllithium in ethers take place faster and with better yields. However, with the exception of methyllithium, alkyllithium cannot be stored as solution in ether for long times. Ziegler described the decomposition by ether cleavage of diethyl ether by *n*-butyllithium.^[26] He identified lithium ethanolate (LiOCH₂CH₃), butane, and ethene as reaction products. A range of possible reaction mechanisms were discussed, one possibility is the metalation of the ether at the β -position, directly followed by an β -elimination of ethene^[27] (Scheme 8). A detailed discussion of mechanisms observed in ether cleavage reactions caused by alkali metals and their alkyl compounds can be found in an excellent review by Maercker.^[28]



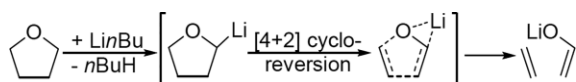
Scheme 8. Ether cleavage of diethyl ether following a metalation in α - or β -position by alkyllithium.

To some degree also the Wittig rearrangement^[29] takes place, in the case of the reaction of alkyllithium and dialkyl ether a metalation at the α -position takes place and the formation of a branched alkoxide^[27,30] is observed (Scheme 9).



Scheme 9. Alternative ether cleavage: a Wittig-rearrangement following an α -metalation.

After some results suggested that tetrahydrofuran (THF) undergoes ether cleavage when in touch with alkylsodium^[31] or alkyllithium,^[32] a systematic study of ethyllithium in THF followed to gain more information about this increasingly important solvent in alkyllithium chemistry.^[33] The identified products were ethane, ethene, and the lithium enolate of acetaldehyde (LiOCH=CH₂). A later study using NMR spectroscopy of a mixture of THF and *n*-butyllithium by Bates^[34] found also butane, ethene, and lithium acetenolate as decomposition products. Beyond that it was also possible to trap a α -metalated THF by deuteration. On the basis of these findings a mechanism based on an α -metalation followed by a [4+2] cyclo-reversion was presented (Scheme 10).



Scheme 10. Ether cleavage of THF by α -metalation with *n*-butyllithium followed by a [4+2] cycloreversion.

A beautiful example of an ether cleavage of THF by *tert*-butyllithium described by Lagow^[35] shows the subsequent carbometalation of the formed ethene by excess alkyllithium, resulting in the formation of neoheptyllithium (LiC₂H₄tBu). The presence of HMPA in solutions of *n*-butyllithium in *n*-hexane/THF leads a very unusual ether cleavage producing lithium but-3-en-1-oxide (LiOC₂H₄CH=CH₂).^[36]

In addition to the knowledge about mechanisms and decomposition products of the reaction of ethers with alkyllithium, it is also important to know more about the stability of these systems. In this context the thermal or kinetic stability is of practical interest; it gives a guideline which alkyllithium can be reasonably handled at certain temperatures without substantial decomposition. An early comparative study^[37] by Gilman combined a range of alkyl- and aryllithium compounds with diethyl ether, and *n*-butyllithium with several dialkyl ethers, respectively. The results gave the following order, with the most reactive first and the least reactive last: alkyllithium in diethyl ether: iso-butyllithium > dodecylithium > *n*-propyllithium > ethyllithium > *n*-amyllithium (*n*-pentyllithium) > *n*-butyllithium > phenylethynyllithium; aryllithium in diethyl ether: α -naphthyllithium > phenyllithium > triphenylmethylithium > β -naphthyllithium > *p*-xenyllithium (*p*-biphenyllithium); *n*-butyllithium in dialkyl ethers: di-*n*-hexyl ether > di-*n*-butyl ether > diisopropyl ether > diethyl ether > di-*n*-dodecyl ether. Additional work on ether cleavage by Gilman^[32] examined the formation of methylithium, phenyllithium, and *n*-butyllithium in THF, the thermal stability decreased in that order. In similar study, Gilman examined solutions of *n*-butyllithium and *n*-decyllithium in 1:1 mixtures of diethyl ether and cyclic ethers.^[38] He found that ether cleavage took place faster with THF than with tetrahydropyran (THP), but the slowest reaction was observed in pure diethyl ether and in diethyl ether/2,2,4,4-tetramethyltetrahydropyran. Honeycutt presented a detailed rate study of *n*-butyllithium in *n*-hexane^[39] at different temperatures. A more recent, comprehensive study by Stanetty^[40] covered combinations of *n*-butyllithium, *sec*-butyllithium, and *tert*-butyllithium in diethyl ether,

THF, THP, and 1,2-dimethoxyethane^[41] (DME). Systematic measures of half-life times were performed in a temperature range from -70 °C to $+35$ °C. In all solvents *n*-butyllithium was the most stable, *tert*-butyllithium showed the fastest progress of ether cleavage. As shown above, solutions in diethyl ether and THP showed the slowest decomposition, while DME lead to much faster decay than compared to THF. This row of experiments was also repeated with *N,N,N',N'*-tetramethylethylenediamine (TMEDA) as chelating ligand. In each case the presence of this ligand led to higher reactivity of the corresponding alkyllithium towards the used ethereal solvent.

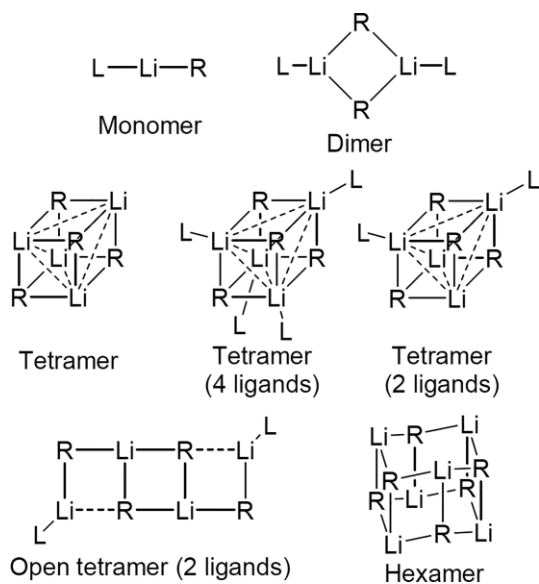
The addition of chelating donor reagents such as TMEDA also enables the reaction of alkyllithium with the methyl position of toluene,^[42] which is in general inert under these conditions. Alkanes such as *n*-pentane, *n*-hexane, and cyclohexane are in general not metalated by alkyllithium; the same is true for benzene in the absence of donating solvents such as TMEDA.

2.4 Aggregation of Alkyllithium in Solid State, Solution and Gas-phase

The solubility of many alkyllithium compounds in solvents plays an important role both in their synthesis and in subsequent synthetic applications. Good solubility also enables a reliable characterization and identification. The products then can be checked for impurities such as starting compounds, by-products, or decomposition products. Accordingly, there was a large interest in the structure of alkyllithium compounds, which in turn provides valuable information about the nature of the lithium carbon interaction.^[43] In the same time the singular reactivity of this class of compounds can be unlocked. In many cases it was possible to obtain crystalline material which allowed the structure determination by X-ray crystallography. Due to the high reactivity the use of crystal preparation at low temperatures and under inert gas atmosphere is of great use.^[44] As it turned out, alkyllithiums form aggregated species, in most cases hexameric aggregates are found (Table 1).

The structure of the insoluble methylithium had to be determined by X-ray^[45] and neutron^[46] powder diffraction by E. Weiss, who summarized these and many other results in an excellent review.^[47] Both methylithium and ethyllithium^[48] turned out to be tetrameric with considerable interactions between the tetrameric units. In the case of *tert*-butyllithium^[49] and bis(trimethylsilyl)methylithium,^[50] where the alkyl groups are extremely bulky, tetramers and linear polymers are found, respectively. In phenyllithium the electron density in the aromatic π system allows additional interactions, which in the end lead to a polymeric chain of dimers.^[51] Hexameric aggregates are found for *isopropyllithium*,^[52] *n*-butyllithium,^[49] trimethylsilylmethylithium,^[53] cyclohexyllithium,^[54] and cyclopentyllithium.^[55] In tetrameric and hexameric arrangements the basic structural element is a tetrahedron or octahedron formed by lithium atoms, respectively (Scheme 11). In the tetrahedron all four, and in the octahedron six of eight Li₃ triangles are μ_3 -capped by the metalated α -carbon atom of the

alkyl group. The bonding situation is best described as an electron-deficient four center (3Li+1C) 2 electron bond (4c2e).^[43]



Scheme 11. Aggregation of alkyllithium compounds and interaction with Lewis-basic ligands (L = Ligand, R = Alkyl).

The electron-deficiency of lithium–carbon interactions combined with coordinative unsaturation in alkyllithium compounds makes them accessible for interactions with Lewis basic molecules such as ethers or amines. The addition of solvent molecules often breaks down the oligomers into smaller units.^[56] This effect can be observed in the solid-state structures. The ligand coordinates to the lithium atom and, in many cases, only allows the interaction of lithium with one or two alkyl ligands. Donors with more than one donor atom, such as 1,2-dimethoxyethane (DME), *N,N,N',N'*-tetramethylethylenediamine (TMEDA), *N,N,N',N'*-tetramethylcyclohexane-1,2-diamine (TMCDA), or *N,N,N',N',N''*-pentamethyldiethylenetriamine (PMDTA), can act as bi- or tridentate ligand. But they also regularly act as monodentate ligand and can then act as bridging ligand between two alkyllithium aggregates. Methyl lithium combined with diethyl ether^[57] or THF^[58] in a 1:1 ratio forms tetrameric units ($[\text{LiMe-Et}_2\text{O}]_4$ and $[\text{LiMe-THF}]_4$). The same motif is found for *n*-butyllithium^[59] and cyclopentyllithium^[55] with THF ($[\text{LinBu-THF}]_4$, and $[\text{LicPent-THF}]_4$).

For the combinations trimethylsilyllithium/ Et_2O ,^[60] methyl lithium/TMEDA,^[61] and *n*-butyllithium/TMEDA^[59,62] also tetramers are found, but only two of the four lithium atoms are coordinated by the ligand ($[\text{LiCH}_2\text{SiMe}_3]_4\text{-2Et}_2\text{O}$, $[\text{LiMe}]_4\text{-2TMEDA}$, $[\text{LinBu}]_4\text{-2TMEDA}$). The TMEDA ligands of the latter two compounds are found in bridging position between tetrameric units. If *n*-butyllithium is coordinated by TMCDA^[63] or PMDTA^[64] in a ratio 2:1 an open tetramer is formed, where the four *LinBu* units form a ladder instead of a cube (TMCDA-*LinBu*- $[\text{LinBu}]_2$ -*LinBu*-TMCDA, or PMDTA-*LinBu*- $[\text{LinBu}]_2$ -*LinBu*-PMDTA). When the concentration of the ligand TMEDA^[59] or TMCDA^[63] is high enough, *n*-butyllithium can also form dimers instead

of tetramers ($[\text{LinBu-TMEDA}]_2$, or $[\text{LinBu-TMCDA}]_2$). Dimers are also found for *tert*-butyllithium/ Et_2O ^[49] ($[\text{Li}t\text{Bu-Et}_2\text{O}]_2$), bis(trimethylsilyl)methyl lithium/THF^[65] ($[\text{LiCH}(\text{SiMe}_3)_2\text{-THF}]_2$), isopropyllithium/TMEDA^[66] ($[\text{Li}i\text{Pr-TMEDA}]_2$), trimethylsilylmethyl lithium/TMEDA^[67] ($[\text{LiCH}_2\text{SiMe}_3\text{-TMEDA}]_2$), methyl lithium/TMCDA^[68] ($[\text{LiMe-TMCDA}]_2$), isopropyllithium/TMCDA^[68] ($[\text{Li}i\text{Pr-TMCDA}]_2$), and phenyllithium/TMCDA ($[\text{LiPh-TMCDA}]_2$).^[69] If the corresponding alkyl group and the coordinating bi- or tridentate ligand is bulky enough, the formation of monomers is observed: *tert*-butyllithium/TMCDA,^[70] trimethylsilylmethyl lithium/PMDTA,^[67] bis(trimethylsilyl)methyl lithium/TMEDA,^[65] bis(trimethylsilyl)methyl lithium/PMDTA,^[71] and phenyllithium/PMDTA.^[72]

The addition of Lewis-basic donors and the breaking down of alkyllithium oligomers into smaller aggregates leads to higher reactivity towards solvents or organic substrates.^[64,73] However, the dependency between aggregation and reactivity is far from being simple.^[74] In addition, the solid-state structures not necessarily represent the aggregates, which are present in solution. To improve the understanding of the reactivity of alkyllithium compounds in solution and the effects of donor molecules, many efforts were undertaken to identify aggregates present in solution. Early results were obtained by cryoscopy^[75] and ebullioscopy.^[76] A detailed study by Lewis and Brown^[77] examined the aggregate sizes by cryoscopy of *n*-butyllithium, trimethylsilylmethyl lithium, isopropyllithium, and *tert*-butyllithium in cyclohexane. All studied compounds in cyclohexane showed the presence of hexamers. Interestingly, benzene solutions of trimethylsilylmethyl lithium showed a shift from tetramers to mixtures of tetramers and hexamers when the concentration was increased. ¹H, ¹³C, and especially ⁷Li NMR spectroscopy developed into a useful tool to examine the aggregation degree of lithium compounds in solution.^[78] More recently, ¹H diffusion ordered spectroscopy (DOSY) NMR enables an estimation of molecular sizes in solution from consideration of diffusion coefficients and can operate in a large temperature range.^[79]

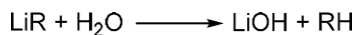
Further alkyllithium compounds and the combination of alkyllithium compounds with other lithium compounds, such as lithium amides,^[80a] lithium alkoxides and enolates,^[80b] represent a large field of lithium compounds. More valuable information can be found in a number of detailed and excellent reviews.^[81]

2.5 Reactivity of Alkyllithium Towards Air and Water

Already in the very first experiments designed to form organometallic compounds of the alkali metals, it was clear that precautions are necessary to avoid the contact of the reaction mixtures with air and water. This is not surprising, considering that most experiments involved elemental alkali metals, which tempestuous behavior towards oxygen and water was already well known. Accordingly, many alkyl compounds of lithium are pyrophoric in isolated form.^[82]

The controlled reaction of alkyllithium with water (or alcohols) can be used to measure the content of alkyllithium

solution (Scheme 12). It is also possible by calorimetric measurements to gain information of the heat of formation of the corresponding alkyllithium by this reaction.^[83]



Scheme 12. Reaction of alkyllithium with water.

In order to avoid such reactions, the removal of traces of water from any reagent and solvent is a basic requirement for most organometallic syntheses.

The reaction of organometallic compounds with oxygen was an unwanted side-reaction from the beginning and a lot of effort was undertaken to keep it away from the reagents by using Schlenk techniques. An insight what happens to alkyllithium when it gets in contact with molecular oxygen was presented by Müller and Töpel.^[84] The addition of oxygen (diluted with nitrogen) to freshly prepared *n*-butyllithium in benzene lead to an exothermic reaction, after aqueous work-up the product was identified as *n*-butanol. However, other experiments suggested the formation of alkyl peroxide, which reacts with excess alkyllithium to the corresponding lithium *n*-butanolate in an auto-oxidation (Scheme 13).



Scheme 13. Reaction of *n*-butyllithium with molecular oxygen. The initially formed lithium *n*-butyl peroxide reacts with excess alkyllithium to lithium *n*-butanolate.

Several years later, Hock was able to isolate the *n*-butyl peroxide by conducting the reaction at -75°C with 30% yield.^[85] Similar reactions using aryllithium compounds produce more complicated results.^[86] Besides the peroxides also phenols and biaryls are found in the product mixtures.

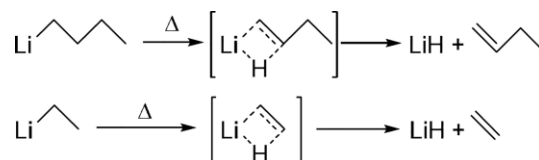
2.6 Decomposition of Alkyllithium by β -Elimination

Not only external factors, such as solvents, oxygen, and water, can lead to the decomposition of organolithium compounds. There are also inherent properties in alkyllithium, which can lead to decomposition and reduce the storage life of these compounds. These processes in solution are normally slow at ambient temperature, but over longer periods regularly signs of decomposition such as precipitations can be observed.

The first indications how alkyllithium decomposes at higher temperatures were presented by Thomson and Stevens in 1933.^[87] During experiments to form alkali metal tetraalkyl borates they found that ethyllithium in ligroin (high boiling petroleum ether) decomposes at 120°C ; the precipitated solid was identified as lithium hydride. This was in accordance to an experiment which was carried out with ethylsodium^[88] by Carothers and Coffman. In this case, ethane, ethene, and sodium hydride were identified as products of the thermal decomposition.

Ziegler observed the decomposition of pure, liquid *n*-butyllithium by β -elimination during distillation experiments.^[89] Closer examinations revealed the formation of 1-butene and lithium hydride as products of the thermal decomposition

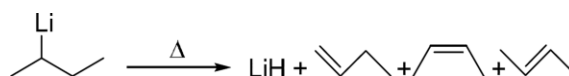
(Scheme 14). This reaction could be seen as reversion of the carbometalation (see above, chapter 2.1) with $R = \text{H}$. An addition of metal hydrides to alkenes^[90] is known as hydrometalation for other metals such as aluminum but not for lithium. The β -elimination demands for the presence of a C–H bond in β -position relative to the Li–C (or M–C) bond in α -position. The corresponding β -H atom leaves the alkyl group together with the lithium atom as lithium hydride, while a double bond is formed between the two involved carbon atoms.



Scheme 14. Thermally induced β -elimination of *n*-butyllithium and ethyllithium. In addition to lithium hydride, the formation of 1-butene or ethene takes place, respectively.

A detailed kinetic study by Finnegan^[91] of the decomposition of a decane solution of *n*-butyllithium revealed a reaction rate of first order. On the basis of these results and the observed kinetic isotope effect a four-center transition state was postulated (Scheme 13). A study working on *n*-octyllithium reached the same conclusion.^[92] In accordance with the proposed mechanism, the involvement of radicals was denied by Bryce-Smith, who examined thermal decomposition of solutions of *n*-butyllithium in *isopropylbenzene*.^[93]

The products of the thermal decomposition reaction of pure *sec*-butyllithium or its solution in octane^[94] were 1-butene, *cis*-2-butene, and *trans*-2-butene (Scheme 15).



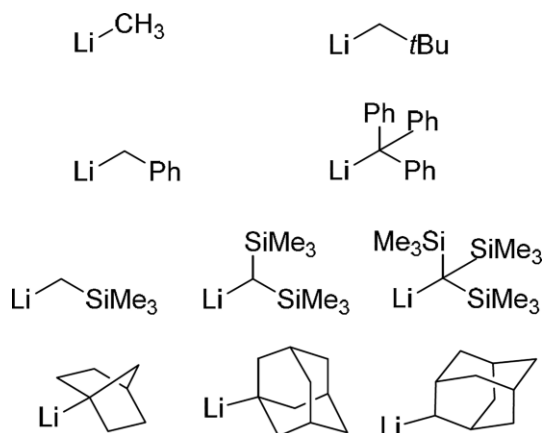
Scheme 15. Thermally induced β -elimination of *n*-butyllithium with the formation of lithium hydride, 1-butene, *cis*-2-butene, and *trans*-2-butene.

Several studies by Finnegan^[95] show, that the alkyl compounds of potassium suffer substantial β -elimination already at ambient temperature. The comparable kinetic stability of alkyllithium in this respect stands out compared to its heavier alkali metal congeners.

After the β -elimination was identified as a route leading to the decomposition of alkyllithium it became clear that this reaction can be prevented by design of the alkyl groups. By avoiding the presence of C–H bonds in β -position the possibility of decay by β -elimination can be ruled out.

Since its first synthesis by Schlenk,^[4] methyllithium stood out because of its comparatively high stability. This robustness might result from the unique structure in the solid state as well in solution; however the absence of β -hydrogen atoms may also contribute to that. By substituting one or more of the “ α ”-hydrogen atoms by suitable organic groups this structural feature could be kept and exploited. This concept proved to be very successful and still is applied until today. Beginning with benzylolithium,^[96] which owes its stability also to delocalization of its negative charge in the adjacent π system, a number

of corresponding α -substituted methyl groups has been developed (Scheme 16). Another important example of phenyl-substituted methyllithium is triphenylmethyllithium^[97] (LiCPh_3). Silyl-substituted methyllithium, such as trimethylsilylmethyllithium ($\text{LiCH}_2\text{SiMe}_3$), bis(trimethylsilyl)methyllithium^[98] [$\text{LiCH}(\text{SiMe}_3)_2$], and tris(trimethylsilyl)methyllithium^[99] [$\text{LiC}(\text{SiMe}_3)_3$], enabled important contributions to organometallic chemistry. *Lappert* used the high stability of bis(trimethylsilyl)methyllithium to isolate and characterize the corresponding sodium, potassium, rubidium, and cesium compounds.^[100] Though β -hydrogen atoms are present in 1-norbornyllithium,^[101] 1-adamantyllithium,^[102,103] and 2-adamantyllithium^[102], these compounds are resistant towards β -elimination. This is because the elimination of lithium hydride and the formation of a double bond between the two involved carbon atoms would violate Bredt's rule.^[104]

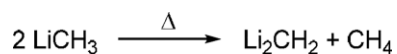


Scheme 16. Alkyllithium compounds inaccessible to β -hydride elimination. The absence of β -hydrogen atoms or the unfavorable steric situation to form C–C double bonds rule out this reaction path.

2.7 Selfmetalation of Alkyllithium

Alkyllithium compounds which have no β -hydrogen atoms accessible to β -hydride elimination can still decompose in an alternative reaction. This process could be described as self-metalation, where one alkyllithium acts as a base towards another one. The result is the formation of the corresponding alkane and a dilithio alkane. This process was first postulated for the thermal decomposition of ethylsodium.^[88,105] Besides the formation of ethene by β -hydride elimination, considerable amounts of ethane were observed. However, no dimetalated species could be observed.

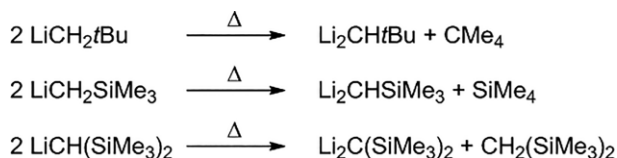
Ziegler could show that during the thermal decomposition of methyllithium at 200 °C the evolution of methane took place.^[106] The solid residue was examined by powder diffractometry, hydrolysis confirmed the formation of Li_2CH_2 (Scheme 17).



Scheme 17. Thermal decomposition (pyrolysis) of methyllithium by selfmetalation.

An optimized procedure for the pyrolysis of methyllithium was developed by *Lagow*.^[107] This study involved the use of isotopic variations of methyllithium $^7\text{LiCH}_3$, $^6\text{LiCH}_3$, and $^7\text{LiCD}_3$. The pyrolysis resulted in the formation of corresponding $^7\text{Li}_2\text{CH}_2$, $^6\text{Li}_2\text{CH}_2$, and $^7\text{Li}_2\text{CD}_2$ in good yields. The insoluble solids were examined by solid state ^{13}C NMR and X-ray powder diffraction.

Lagow also succeeded with the pyrolysis^[108] of neopentyllithium, trimethylsilylmethyllithium, and bis(trimethylsilyl)methyllithium (Scheme 18).



Scheme 18. Thermal decomposition (pyrolysis) of neopentyllithium, trimethylsilylmethyllithium, and bis(trimethylsilyl)methyllithium by selfmetalation.

In all three cases the gaseous products of pyrolysis were trapped and identified, the solid residues were identified by destructive hydrolysis with heavy water (D_2O). Bis(trimethylsilyl)dilithiomethane [$\text{Li}_2\text{C}(\text{SiMe}_3)_2$] was slightly soluble in deuterated benzene; a ^1H NMR could be recorded, which showed a singlet at $\delta = 0.09$ ppm. The number of structurally characterized organometallic dilithium compounds is still comparably small. Two recent examples mentioned here are a dilithium butanediide/lithium chloride complex,^[109] and a dilithium cyclopentylidide/lithium amide/*n*-butyllithium cage.^[110]

2.8 Outlook

A century of intensive research of the organometallic chemistry of lithium still leaves a lot of room for recent and exciting developments. The use of new solvent systems, such as deep eutectic solvents allows to perform reactions in the presence of water and without protective atmosphere.^[111] The introduction of new ligands for alkyllithium compounds allows the fine-tuning of reactivities,^[112] and new insight into the interactions of lithium and heavier alkali metals in organometallic bases such as Lochmann-Schlosser superbases,^[113] open new perspectives for interesting new developments.

2.9 Conclusions

Organolithium chemistry has seen a rapid development since the discoveries by *Wilhelm Schlenk*. The difficulties connected with the handling of these highly air- and moisture sensitive compounds have been mastered; remaining routes of decomposition are well understood and can be avoided by appropriate measures. In addition, the commercial availability and the combined basic, nucleophilic, and reducing properties of alkyllithium compounds make them one of the most important classes of organometallic compounds. Alkyllithium compounds account for important developments in organic synthesis, in many cases they were the starting point for important

contributions to the organometallic chemistry of the transition metals. In future, the introduction of new solvent systems or specialized ligands will add new facets to the “Li world”.

Supporting Information (see footnote on the first page of this article): Chronological lists of Arfvedson Schlenk Prize awardees from 1999 to 2017.

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Keywords: Alkali metals; Lithium; Synthesis; Organometallic chemistry

References

- [1] L. Izzo, M. Della Valle, E. Mason, F. Matteucci, D. Romano, L. Pasquini, L. Vanzi, A. Jordan, J. M. Fernandez, P. Bluhm, R. Brahm, *Astrophys. J. Lett.* **2015**, *808*, L14.
- [2] J. J. Berzelius, *J. Chem. Physik* **1817**, 44–48.
- [3] a) E. Haller, M. Boese, R. Sahmen, G. Wilcke, *Gmelins Handbuch der Anorganischen Chemie*, 8th ed., System-No. 20, “Lithium“, Verlag Chemie GmbH, Berlin 1927; b) U. Wietelmann, M. Steinbild, *Lithium and Lithium Compounds*, in *Ullmann's Encyclopedia of Industrial Chemistry*, Published Online: 26.03.2014, DOI: 10.1002/14356007.a15_393.pub2.
- [4] W. Schlenk, J. Holtz, *Ber. Dtsch. Chem. Ges.* **1917**, *50*, 262–274.
- [5] a) T. T. Tidwell, *Angew. Chem. Int. Ed.* **2001**, *40*, 331–337; b) R. Anwander, *Nachr. Chem.* **2011**, *59*, 951–953.
- [6] K. Ziegler, H. Colonius, *Justus Liebigs Ann. Chem.* **1930**, *479*, 135–149.
- [7] a) D. Seyferth, *Organometallics* **2009**, *28*, 1598–1605; b) D. Seyferth, *Organometallics* **2009**, *28*, 2–33; c) D. Seyferth, *Organometallics* **2006**, *25*, 2–24.
- [8] A. F. Holleman, E. Wiberg, N. Wiberg, *Lehrbuch der anorganischen Chemie*, 101st ed., de Gruyter, Berlin **1995**.
- [9] E. Frankland, *Justus Liebigs Ann. Chem.* **1853**, *85*, 329–373.
- [10] J. A. Wanklyn, *Justus Liebigs Ann. Chem.* **1858**, *108*, 67–79.
- [11] H. H. Schlubach, E. C. Goes, *Ber. Dtsch. Chem. Ges.* **1922**, *55*, 2889–2902.
- [12] G. Wittig, M. Leo, *Ber. Dtsch. Chem. Ges.* **1931**, *64*, 2395–2405.
- [13] H. Gilman, E. A. Zoellner, W. M. Selby, *J. Am. Chem. Soc.* **1932**, *54*, 1957–1962.
- [14] G. Wittig, U. Pockels, H. Dröge, *Ber. Dtsch. Chem. Ges.* **1938**, *71*, 1903–1912.
- [15] H. Gilman, W. Langham, A. L. Jacoby, *J. Am. Chem. Soc.* **1939**, *61*, 106–109.
- [16] P. Schorigin, *Ber. Dtsch. Chem. Ges.* **1908**, *41*, 2723–2728.
- [17] a) W. Schlenk, E. Bergmann, *Justus Liebigs Ann. Chem.* **1928**, *463*, 1–97; b) W. Schlenk, E. Bergmann, *Justus Liebigs Ann. Chem.* **1928**, *463*, 98–227; c) H. Gilman, J. W. Morton, *Org. React.* **1954**, *8*, 258–293.
- [18] G. Wittig, G. Fuhrmann, *Ber. Dtsch. Chem. Ges.* **1940**, *73*, 1197–1218.
- [19] W. Schlenk, J. Appenrodt, A. Michael, A. Thal, *Ber. Dtsch. Chem. Ges.* **1914**, *47*, 473–490.
- [20] K. Ziegler, F. Crössmann, H. Kleiner, O. Schäfer, *Justus Liebigs Ann. Chem.* **1929**, *473*, 1–35.
- [21] K. Ziegler, H.-G. Gellert, *Justus Liebigs Ann. Chem.* **1950**, *567*, 195–203.
- [22] K. Ziegler, K. Bähr, *Ber. Dtsch. Chem. Ges.* **1928**, *61*, 253–263.
- [23] a) A. A. Morton, F. D. Marsh, R. D. Coombs, A. L. Lyons, S. E. Penner, H. E. Ramsden, V. B. Baker, E. L. Little, R. L. Letsinger, *J. Am. Chem. Soc.* **1950**, *72*, 3785–3792; b) N. I. Pakuro, A. A. Arest-Yakubovich, L. V. Shcheglova, P. V. Petrovsky, L. A. Chekulaeva, *Russ. Chem. Bull.* **1996**, *105*, 838–840.
- [24] J. Deberitz, G. Boche, *Chem. Unserer Zeit* **2003**, *37*, 258–266.
- [25] P. Schorigin, *Ber. Dtsch. Chem. Ges.* **1910**, *43*, 1931–1938.
- [26] K. Ziegler, H.-G. Gellert, *Justus Liebigs Ann. Chem.* **1950**, *567*, 185–195.
- [27] A. Maercker, W. Demuth, *Justus Liebigs Ann. Chem.* **1977**, *1977*, 1909–1937.
- [28] A. Maercker, *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 972–989.
- [29] G. Wittig, L. Löhmann, *Justus Liebigs Ann. Chem.* **1942**, *550*, 260–268.
- [30] U. Schöllkopf, *Angew. Chem. Int. Ed. Engl.* **1970**, *9*, 763–773.
- [31] a) R. L. Letsinger, D. F. Pollart, *J. Am. Chem. Soc.* **1956**, *78*, 6079–6085; b) G. Wittig, A. Rückert, *Justus Liebigs Ann. Chem.* **1950**, *566*, 101–113.
- [32] H. Gilman, B. J. Gaj, *J. Org. Chem.* **1957**, *22*, 1165–1168.
- [33] A. Rembaum, S.-P. Siao, N. Indictor, *J. Polym. Sci.* **1962**, *56*, 17–19.
- [34] R. B. Bates, L. M. Kroposki, D. E. Potter, *J. Org. Chem.* **1972**, *37*, 560–562.
- [35] T. Kottke, R. J. Lagow, D. Hoffmann, R. D. Thomas, *Organometallics* **1997**, *16*, 789–792.
- [36] J. Clayden, S. A. Yasin, *New J. Chem.* **2002**, *26*, 191–192.
- [37] H. Gilman, A. H. Haubein, H. Hartzfeld, *J. Org. Chem.* **1954**, *19*, 1034–1040.
- [38] H. Gilman, G. L. Schwebke, *J. Organomet. Chem.* **1965**, *4*, 483–487.
- [39] S. C. Honeycutt, *J. Organomet. Chem.* **1971**, *29*, 1–5.
- [40] P. Stanetty, M. D. Mihovilovic, *J. Org. Chem.* **1997**, *62*, 1514–1515.
- [41] J. J. Fitt, H. W. Gschwend, *J. Org. Chem.* **1984**, *49*, 209–210.
- [42] L. Assadourian, R. Faure, G. Gau, *J. Organomet. Chem.* **1985**, *280*, 153–158.
- [43] M. Schlosser, *Struktur und Reaktivität polarer Organometalle. Eine Einführung in die Chemie organischer Alkali- und Erdalkalimetall-Verbindungen*, vols. 14, Springer, Berlin, Heidelberg **1973**.
- [44] T. Kottke, D. Stalke, *J. Appl. Crystallogr.* **1993**, *26*, 615–619.
- [45] E. Weiss, E. A. C. Lucken, *J. Organomet. Chem.* **1964**, *2*, 197–205.
- [46] E. Weiss, T. Lambertsen, B. Schubert, J. K. Cockcroft, A. Wiedenmann, *Chem. Ber.* **1990**, *123*, 79–81.
- [47] E. Weiss, *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1501–1523.
- [48] H. Dietrich, *Acta Crystallogr.* **1963**, *16*, 681–689.
- [49] T. Kottke, D. Stalke, *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 580–582.
- [50] J. L. Atwood, T. Fjeldberg, M. F. Lappert, N. T. Luong-Thi, R. Shakir, A. J. Thorne, *J. Chem. Soc.* **1984**, 1163–1165.
- [51] R. E. Dinnebier, U. Behrens, F. Olbrich, *J. Am. Chem. Soc.* **1998**, *120*, 1430–1433.
- [52] U. Siemeling, T. Redecker, B. Neumann, H.-G. Stammer, *J. Am. Chem. Soc.* **1994**, *116*, 5507–5508.
- [53] B. Teclé, A. F. M. Maqsoodur Rahman, J. P. Oliver, *J. Organomet. Chem.* **1986**, *317*, 267–275.
- [54] R. Zerger, W. Rhine, G. Stucky, *J. Am. Chem. Soc.* **1974**, *96*, 6048–6055.
- [55] C. Su, R. Hopson, P. G. Williard, *J. Am. Chem. Soc.* **2013**, *135*, 12400–12406.
- [56] V. H. Gessner, C. Däschlein, C. Strohmam, *Chem. Eur. J.* **2009**, *15*, 3320–3334.
- [57] K. Götz, V. H. Gessner, C. Unkelbach, M. Kaupp, C. Strohmam, *Z. Anorg. Allg. Chem.* **2013**, *639*, 2077–2085.
- [58] C. A. Ogle, B. K. Huckabee, H. C. Johnson, P. F. Sims, S. D. Winslow, A. A. Pinkerton, *Organometallics* **1993**, *12*, 1960–1963.
- [59] M. A. Nichols, P. G. Williard, *J. Am. Chem. Soc.* **1993**, *115*, 1568–1572.

- [60] T. Tatic, K. Meindl, J. Henn, S. K. Pandey, D. Stalke, *Chem. Commun.* **2010**, 46, 4562–4564.
- [61] H. Köster, D. Thoennes, E. Weiss, *J. Organomet. Chem.* **1978**, 160, 1–5.
- [62] N. D. R. Barnett, R. E. Mulvey, W. Clegg, P. A. O’Neil, *J. Am. Chem. Soc.* **1993**, 115, 1573–1574.
- [63] C. Strohmman, V. H. Gessner, *J. Am. Chem. Soc.* **2008**, 130, 11719–11725.
- [64] C. Strohmman, V. H. Gessner, *Angew. Chem. Int. Ed.* **2007**, 46, 4566–4569.
- [65] M. v. Pilgrim, M. Mondeshki, J. Klett, *Inorganics* **2017**, 5, 39.
- [66] C. Strohmman, V. H. Gessner, A. Damme, *Chem. Commun.* **2008**, 3381–3383.
- [67] T. Tatic, H. Ott, D. Stalke, *Eur. J. Inorg. Chem.* **2008**, 2008, 3765–3768.
- [68] C. Strohmman, V. H. Gessner, *J. Am. Chem. Soc.* **2007**, 129, 8952–8953.
- [69] P. K. Eckert, B. Schnura, C. Strohmman, *Chem. Commun.* **2014**, 50, 2532–2534.
- [70] C. Strohmman, T. Seibel, K. Strohfeltdt, *Angew. Chem. Int. Ed.* **2003**, 42, 4531–4533.
- [71] M. F. Lappert, L. M. Engelhardt, C. L. Raston, A. H. White, *J. Chem. Soc.* **1982**, 1323–1324.
- [72] U. Schümann, J. Kopf, E. Weiss, *Angew. Chem. Int. Ed. Engl.* **1985**, 24, 215–216.
- [73] a) H. J. Reich, D. P. Green, *J. Am. Chem. Soc.* **1989**, 111, 8729–8731; b) A. J. Chalk, T. J. Hoogboom, *J. Organomet. Chem.* **1968**, 11, 615–618.
- [74] D. B. Collum, *Acc. Chem. Res.* **2002**, 35, 448–454.
- [75] F. Hein, H. Schramm, *Z. Phys. Chem. A* **1930**, 151.
- [76] a) G. Wittig, F. J. Meyer, G. Lange, *Justus Liebigs Ann. Chem.* **1951**, 571, 167–201; b) W. Bauer, D. Seebach, *Helv. Chim. Acta* **1984**, 67, 1972–1988.
- [77] H. L. Lewis, T. L. Brown, *J. Am. Chem. Soc.* **1970**, 92, 4664–4670.
- [78] G. Fraenkel, A. Chow, W. R. Winchester, *J. Am. Chem. Soc.* **1990**, 112, 6190–6198.
- [79] R. Neufeld, M. John, D. Stalke, *Angew. Chem. Int. Ed.* **2015**, 54, 6994–6998.
- [80] a) R. E. Mulvey, S. D. Robertson, *Angew. Chem. Int. Ed.* **2013**, 52, 11470–11487; b) D. Seebach, *Angew. Chem. Int. Ed. Engl.* **1988**, 27, 1624–1654.
- [81] a) F. Mongin, A. Harrison-Marchand, *Chem. Rev.* **2013**, 113, 7563–7727; b) A. Harrison-Marchand, F. Mongin, *Chem. Rev.* **2013**, 113, 7470–7562; c) H. J. Reich, *Chem. Rev.* **2013**, 113, 7130–7178.
- [82] a) B. J. Wakefield, *The Chemistry of Organolithium Compounds*, Pergamon Press, Oxford **1974**; b) T. ‘L.’ Rathman, J. A. Schwindeman, *Org. Process Res. Dev.* **2014**, 18, 1192–1210; c) J. A. Schwindeman, C. J. Woltermann, R. J. Letchford, *J. Chem. Health Saf.* **2002**, 9, 6–11.
- [83] P. A. Fowell, C. T. Mortimer, *J. Chem. Soc.* **1961**, 3793–3796.
- [84] E. Müller, T. Töpel, *Ber. Dtsch. Chem. Ges.* **1939**, 72, 273–290.
- [85] a) H. Hock, F. Ernst, *Chem. Ber.* **1959**, 92, 2716–2723; b) H. Hock, F. Ernst, *Chem. Ber.* **1959**, 92, 2723–2732.
- [86] H. Hock, H. Kropf, F. Ernst, *Angew. Chem.* **1959**, 71, 541–545.
- [87] T. Thomson, T. S. Stevens, *J. Chem. Soc.* **1933**, 555–557.
- [88] W. H. Carothers, D. D. Coffman, *J. Am. Chem. Soc.* **1929**, 51, 588–593.
- [89] K. Ziegler, H.-G. Gellert, *Justus Liebigs Ann. Chem.* **1950**, 567, 179–184.
- [90] K. Ziegler, *Angew. Chem.* **1956**, 68, 721–729.
- [91] a) R. A. Finnegan, H. W. Kutta, *J. Org. Chem.* **1965**, 30, 4138–4144; b) R. A. Finnegan, H. W. Kutta, *J. Org. Chem.* **1965**, 30, 4138–4144.
- [92] M. Y. Li, J. San Filippo, *Organometallics* **1983**, 2, 554–555.
- [93] D. Bryce-Smith, *J. Chem. Soc.* **1955**, 1712–1714.
- [94] W. H. Glaze, J. Lin, E. G. Felton, *J. Org. Chem.* **1965**, 30, 1258–1259.
- [95] a) R. A. Finnegan, *Tetrahedron Lett.* **1962**, 3, 1303–1308; b) R. A. Finnegan, *Tetrahedron Lett.* **1963**, 4, 851–857; c) R. A. Finnegan, *Trans. N. Y. Acad. Sci.* **1965**, 27, 730–740.
- [96] F. Hein, E. Petzchner, K. Wagler, F. A. Segitz, *Z. Anorg. Allg. Chem.* **1924**, 141, 161–227.
- [97] A. v. Grosse, *Ber. Dtsch. Chem. Ges.* **1926**, 59, 2646–2654.
- [98] P. J. Davidson, M. F. Lappert, *J. Chem. Soc.* **1973**, 317.
- [99] M. A. Cook, C. Eaborn, A. E. Jukes, D. R. M. Walton, *J. Organomet. Chem.* **1970**, 24, 529–535.
- [100] P. B. Hitchcock, M. F. Lappert, W.-P. Leung, L. Diansheng, T. Shun, *J. Chem. Soc.* **1993**, 1386–1387.
- [101] P. T. Lansbury, J. D. Sidler, *Tetrahedron Lett.* **1965**, 6, 691–695.
- [102] G. Molle, J.-E. Dubois, P. Bauer, *Tetrahedron Lett.* **1978**, 19, 3177–3180.
- [103] P. T. Lansbury, J. D. Sidler, *Chem. Commun. (London)* **1965**, 373.
- [104] J. Bredt, *Justus Liebigs Ann. Chem.* **1924**, 437, 1–13.
- [105] W. H. Carothers, D. D. Coffman, *J. Am. Chem. Soc.* **1930**, 52, 1254–1259.
- [106] K. Ziegler, K. Nagel, M. Patheiger, *Z. Anorg. Allg. Chem.* **1955**, 282, 345–351.
- [107] J. A. Gurak, J. W. Chinn, R. J. Lagow, H. Steinfink, C. S. Yannoni, *Inorg. Chem.* **1984**, 23, 3717–3720.
- [108] H. Kawa, B. C. Manley, R. J. Lagow, *Polyhedron* **1988**, 7, 2023–2025.
- [109] R. Fischer, H. Görls, M. Westerhausen, *Angew. Chem. Int. Ed.* **2009**, 48, 9958–9961.
- [110] A. A. Fyfe, A. R. Kennedy, J. Klett, R. E. Mulvey, *Angew. Chem. Int. Ed.* **2011**, 50, 7776–7780.
- [111] a) C. Vidal, J. García-Álvarez, A. Hernán-Gómez, A. R. Kennedy, E. Hevia, *Angew. Chem. Int. Ed.* **2014**, 53, 5969–5973; b) G. Dilauro, M. Dell’Aera, P. Vitale, V. Capriati, F. M. Perna, *Angew. Chem. Int. Ed.* **2017**, 56, 10200–10203.
- [112] U. Kroesen, C. Unkelbach, D. Schilbach, C. Strohmman, *Angew. Chem. Int. Ed.* **2017**, 56, 14164–14168.
- [113] P. Benrath, M. Kaiser, T. Limbach, M. Mondeshki, J. Klett, *Angew. Chem. Int. Ed.* **2016**, 55, 10886–10889.

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