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Abstract

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TERNARY COMPLEXES OF METHYLLITHIUM

The high stability of methyllithium in diethyl ether distinguishes it from aliphatic organolithium compounds, which readily cleave ether ([1]), and places it, as it were, in the same category as the more stable, with respect to ether, aromatic compounds—phenyllithium and tolyllithium. These compounds, as we described earlier ([2]), form complexes of the composition $2RLi \cdot LiX \cdot 2(C_2H_5)_2O$ in ethereal solutions.

It could be assumed that the cause of the low reactivity of methyllithium with respect to ether is likewise the formation of ternary complexes. From ethereal solutions of methyllithium obtained by the action of lithium on methyl bromide or on methyl iodide, we isolated ternary crystalline complexes of the composition $CH_3Li \cdot LiJ \cdot 2(C_2H_5)_2O$ and $CH_3Li \cdot LiBr \cdot 2(C_2H_5)_2O$, stable on storage under nitrogen or argon ([3]). When lithium iodide is present in excess in solution relative to methyllithium, the less soluble diethyl etherate of lithium iodide precipitates first. When lithium bromide is present in excess in solution, crystalline precipitates separate with an increasing content of lithium bromide and ether, for example:

$$CH_3Li \cdot 2LiBr \cdot 3(C_2H_5)_2O \quad \text{or} \quad CH_3Li \cdot 5LiBr \cdot 7(C_2H_5)_2O.$$

Consequently, in these complexes the ratio of CH_3Li and LiBr varies, similarly to what has been described for double complexes of aliphatic organolithium compounds with lithium halide salts ([4]).

Double complexes of the composition $RLi \cdot nLiX$ (n from 1.4 to 6) are obtained in hydrocarbons by the action of alkyl halides on aliphatic RLi ([4]). These complexes are distinguished by low reactivity toward oxygen; in air they do not burn and only slowly decompose. Addition of ether converts RLi again into a reactive form. Gilman' s test without addition of ether is negative ([4]). Apparently, n-butyllithium, marketed by American firms as a polymerization catalyst, is such a double complex, since it is described as a relatively stable "white powder" ([5]).

From an ethereal solution of methyllithium, obtained by the action of lithium on methyl chloride, a monoetherate of methyllithium, $CH_3Li \cdot (C_2H_5)_2O$, can be

isolated. The presence of a small impurity of lithium chloride can probably be explained by complex formation ([6]). On evacuating a heated cuvette with the etherate of methyllithium until the ether lines disappeared in the IR spectrum, we obtained the IR spectrum of methyllithium in the vapor phase ([7]).

When an ethereal solution of methyllithium (from CH_3Cl) is precipitated with an excess of *n*-pentane and the precipitate is dried in vacuum at 100°, a fine powder of methyllithium is isolated. This precipitate has the IR spectrum usual for crystalline methyllithium ([7]), but dissolves poorly in simple ethers, even on heating (solutions from 0.2 to 0.5 N). Probably, upon destruction of the ether complex of methyllithium by *n*-pentane, it precipitates in a strongly associated form.

When crystalline methyllithium is dissolved in ether, there apparently occurs a breakdown of the primary associate with formation of the etherate, through the use of the unshared pair of electrons on the ether oxygen and the free orbitals of the lithium atom; this does not sharply affect the electronic C–Li bond, and bands of "free" or weakly bound CH_3Li molecules are observed (1010 cm^{-1}). With time the band shifts (to 900 cm^{-1}), which indicates the formation of a more complex type of complex ([8]).

The formation of a triple complex of CH_3Li with halide salts and ether has no noticeable effect on the investigated region of the IR spectrum (2000–650 cm^{-1}, NaCl prism, 100 μ cuvette).

On pyrolysis of the methyllithium precipitate under the conditions described by Ziegler ([6]), methylenedilithium, CH_2Li_2, was obtained as a mobile fine precipitate, extremely readily ignited on exposure to air. Methyllithium and methylenedilithium were tested as catalysts for the polymerization of ethylene with titanium tetrachloride (1 : 1), and samples of highly crystalline polyethylene were obtained ([9]).

According to the data available to us, the ability to form triple complexes with ether and lithium bromide is not limited to aliphatic and aromatic RLi and extends to lithium acetylides. When pure acetylene is passed into an ethereal solution of RLi (R–CH_3, C_6H_5, $CH_3C_6H_4$) containing an equal amount of lithium bromide, a precipitate of lithium acetylide is formed, incorporating lithium bromide and ether in multiple ratios:

$$2HC \equiv CLi \cdot LiBr \cdot 4(C_2H_5)_2O \quad \text{and} \quad 3HC \equiv CLi \cdot LiBr \cdot 5(C_2H_5)_2O.$$

With a deficiency of lithium bromide, relative to RLi in the initial solution, precipitates of composition 4HC CLi per 1LiBr were obtained. In a control experiment, on prolonged passage of acetylene into a solution of lithium bromide etherate, no precipitate formed.

We also observed that crystalline cyclopentadienyllithium, obtained by the action of cyclopentadiene on an ethereal solution of *n*-tolyllithium (containing

LiBr), when precipitated from solution contains no admixture of lithium bromide.

Experimental Part

All work was carried out in apparatus under a slight pressure of nitrogen or argon. The procedure was the usual one for organolithium compounds ([10]).

Preparation of methyllithium etherate. An ethereal solution of methyllithium was obtained in the usual way ([6]) from methyl chloride and lithium and filtered under argon. The clear solution was concentrated twofold (1.95 *N*). Into an apparatus under argon were placed 50 ml of the solution, which was cooled to −70°. Snow-white, lustrous crystals of methyllithium etherate separated. The solution was warmed to room temperature—the crystals went into solution, leaving a slight turbidity of lithium chloride. The solution was filtered under argon through a dry folded filter, in a special apparatus ([10]). The completely clear and colorless solution was again cooled to −70°. The crystals of methyllithium etherate were suction-filtered on a glass porous filter at −50° and dried in vacuum at 20 mm for 1 hour at −20°. For the analysis see Table 1, Nos. 1 and 2. The precipitate contains, as an impurity, 2% lithium chloride; cf. ([6]). IR spectrum of the ethereal solution of methyllithium (see ([8])).

Preparation of methyllithium (without ether). Under argon, 400 ml of a 1.95 *N* ethereal solution of methyllithium (from CH_3Cl) was taken and concentrated to a volume of ~150 ml, diluted with 250 ml of dry *n*-pentane, and cooled to −60°. The fine, heavy precipitate that separated is difficult to filter. The precipitate was washed 5 times by decantation with *n*-pentane and dried in vacuum (5 h at 10^3, 4 mm). 17 g were obtained. According to analysis, the lithium chloride impurity was 8%. The IR spectrum repeats the previously known spectrum of methyllithium ([7]). On boiling a portion of this precipitate in diethyl ether for 1 hour, 0.24

N solution; upon repeated treatment with ether, a 0.1 *N* solution was obtained. By pyrolysis at 240° [6], methyllithium was obtained—a very mobile, slightly yellowish powder, which ignites extremely readily on exposure to air. According to analysis, it contains ~ 50% lithium. Methyllithium and methylsodium were used for the polymerization of ethylene with $TiCl_4$ (1 : 1) [9].

Preparation of the triple complex of methyllithium with lithium bromide and ether. An ethereal solution of methyllithium was prepared in the usual manner from 3.5 g of lithium (0.5 g-atom) and 19 g of methyl bromide (0.2 mole) in 200 ml of ether. The solution was filtered from turbidity under nitrogen. Yield 85%. The IR spectrum of this solution repeats the spectrum of an ethereal solution of methyllithium [8]. This solution was concentrated twofold and left for 2 days at −10°. The precipitated snow-white crystals were filtered off and dried in a stream of nitrogen until free-flowing. According to analysis, the crystals correspond to the composition $CH_3Li \cdot LiBr \cdot 2(C_2H_5)_2O$, see Table 1, Nos. 3 and 4. On dilution of a 1 *N* solution of methyllithium (obtained from CH_3Cl)

with an excess of a 1 N ethereal solution of lithium bromide etherate [2] and subsequent concentration, crystals of composition $CH_3Li \cdot 5LiBr \cdot 7(C_2H_5)_2O$ were isolated; the filtrate contained CH_3Li and LiBr in the ratio 1 : 3. From the filtrate, after evaporation, crystals of composition $CH_3Li \cdot 4LiBr \cdot 6(C_2H_5)_2O$ were isolated, and in another case $CH_3Li \cdot 2LiBr \cdot 3(C_2H_5)_2O$.

The crystalline triple complexes obtained are readily soluble in ether and keep well in ampoules under argon. If the complex of composition $CH_3Li \cdot 5LiBr \cdot 7(C_2H_5)_2O$ is dissolved in ether, filtered from turbidity, an ethereal solution of methyllithium (from CH_3Cl) is added to the clear solution to the ratio $2CH_3Li$: 1LiBr, and this solution is concentrated, a complex of composition $CH_3Li \cdot LiBr \cdot 3(C_2H_5)_2O$ precipitates; the excess methyllithium and part of the lithium bromide remain in solution.

Table 1

No.	Sample weight, g	H_2SO_4 0.1 N	$AgNO_3$ 0.1 N	CH_3Li, %	LiX, %	Ether content by difference, %	Reduced molar fractions CH_3Li	Reduced molar fractions LiX	Reduced molar fractions $(C_2H_5)_2O$
1	0.3048	29.6	1.70	21.33	2.36	76.31	1	–	1.06
2	0.1455	15.15	0.85	22.87	2.47	74.66	1	–	0.97
3	0.9580	35.10	40.00	8.06	36.32	55.62	1	1.14	2.06
4	0.6271	23.50	25.95	8.24	36.01	55.75	1	1.13	2.04
5	1.0115	33.60	34.00	7.29	45.00	47.71	1	1.01	1.94
6	1.2668	41.80	42.30	7.24	44.67	48.09	1	1.01	1.97
7	0.5318	–	18.50	–	46.54	53.46	–	1	2.07
8	0.4636	–	16.20	–	46.54	53.24	–	1	2.05

Preparation of the triple complex of methyllithium with lithium iodide and ether. An ethereal solution of methyllithium was prepared in the usual manner from 31.2 g (0.22 M) of methyl iodide and 3.5 g (0.5 g-atom) of lithium in 230 ml of absolute ether, and filtered under nitrogen [10]. A perfectly clear and colorless 0.93 N solution was obtained, calculated as methyllithium, and 1.01 N calculated as lithium iodide. Yield 95%. The IR spectrum of the solution is close to the spectrum of an ethereal solution of methyllithium [8]. This solution was concentrated to a volume of 100 ml and filtered from turbidity. On standing for 2 days at 0°, large transparent, colorless crystals were obtained. They were filtered off and dried until free-flowing in a stream of nitrogen. According to analysis, they correspond to the composition $CH_3Li \cdot LiJ \cdot 2(C_2H_5)_2O$, see Table 1, Nos. 5 and 6. On storage in ampoules

under argon for a long time, no yellowing is observed, and the methyllithium does not lose its reactivity.

When an excess of an ethereal solution of lithium iodide [11] is added to a solution of methyllithium (obtained from CH_3Cl), after concentration and cooling, needle-shaped crystals of lithium iodide dietherate separate (see below); upon repeated evaporation, a further small portion of diethi-

of lithium iodide. The filtrate contained CH_3Li and LiJ in a ratio of 1 : 2 and did not yield crystals even upon prolonged cooling. Apparently, the complex of composition $CH_3Li \cdot 2LiJ$ is more soluble than lithium iodide etherate or the complex $CH_3Li \cdot LiJ \cdot 2(C_2H_5)_2O$.

Preparation of lithium iodide etherate. An ethereal solution of lithium iodide was prepared from lithium hydride and iodine in an ether medium (11), filtered from excess lithium hydride under nitrogen. A completely colorless and transparent solution was obtained, which turned yellow on storage in the light. The yield was 94%, calculated on the amount of iodine taken. Into the apparatus under nitrogen were placed 200 ml of a 0.63 N solution of lithium iodide, concentrated approximately twofold, and cooled to −20°. Long, thin, transparent needles of lithium iodide etherate separated. They were rapidly suction-filtered on a porous filter at 0° and dried in a stream of nitrogen at 0° until free-flowing. According to analysis, the precipitate corresponds to the composition $LiJ \cdot 2(C_2H_5)_2O$; see Table 1, Nos. 7 and 8. The crystals rapidly turn yellow in the light, even under argon.

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Note: Figure translations are in progress. See original paper for figures.