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COMPLEX METAL ALKYLS

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The coordination of negative ions to acceptor atoms to form complex anions is an old and well-established phenomenon. More common examples of compounds formed in this fashion include the fluoborates, fluosilicates, and chloroaluminates.

The first example of complex anion formation involving exclusively alkyl groups bonded to the central atom was realized by Schlesinger and Brown (1) in the synthesis of $LiB(C_2H_5)(CH_3)_3$ although the possibility of forming compounds of the type MBR_4 (where R represents an alkyl or aryl group) was recognized earlier (2). Several examples of complex formation between the alkyls of electropositive metals and zinc alkyls are mentioned in the literature but these were not considered by the investigators as involving complex anions.

This paper describes the preparation and some properties of three additional complex alkyl compounds of this type: $LiAl(CH_3)_4$, $Li_2Zn(CH_3)_4$, and $LiB(CH_3)_4$.

EXPERIMENTAL

All preparations were carried out in nitrogen atmospheres and all material transfer was performed in a nitrogen-filled dry box.

$LiAl(CH_3)_4$. Aluminum trimethyl was prepared by adding 22 g. of anhydrous aluminum chloride dissolved in 250 ml. of dry ether to the methylmagnesium bromide prepared from 20 g. of magnesium. After 2 hours' reflux, the excess ether was distilled off, then at 60° the aluminum trimethyl etherate was distilled from the magnesium halide on a vacuum chain. This material was transferred to a flask containing a filtered ether solution of the lithium methyl prepared from 1 g. of lithium with methyl chloride. (This represented an 85% excess of aluminum trimethyl assuming a 100% yield in both preparations.) It was observed that some heat was liberated in the process of mixing. The resulting ether solution was evaporated to remove the ether, then was heated in a vacuum system at 80° until the pressure was below 50 microns. There remained a quantity of white solid $LiAl(CH_3)_4$.

This compound may be stable in very dry air although in the usual laboratory atmosphere it became warm and ignited spontaneously after a few minutes exposure. The dry salt is very soluble in ether and will adsorb ether vapor rapidly. If the dry salt is added to water or alcohol, a violent reaction occurs with inflammation and the reacting solid is heated to incandescence. If the ether solution of the compound is poured into water, a large evolution of methane ensues together with a white precipitate of aluminum hydroxide. The ether solution reacts rapidly with silicon tetrachloride to effect methylation.

The compound was analyzed by dissolving a weighed sample in ether, then adding this solution to dilute HCl to decompose the complex and form the chlorides of aluminum and lithium. Aluminum was precipitated as $Al(OH)_3$, ignited, and weighed as Al_2O_3. Lithium was separated and weighed as Li_2SO_4.

Anal. Calc'd for $LiAl(CH_3)_4$: Li, 7.4; Al, 28.69.
Found: Li, 7.3, Al, 28.85.

$Li_2Zn(CH_3)_4$. Zinc dimethyl was prepared by adding 27 g. of anhydrous zinc chloride in ether to the methylmagnesium bromide prepared from 5.5 g. of magnesium. This was

followed by reflux for an hour and finally by distillation of the ether and the volatile product in a vacuum system into a storage bulb. To this solution of zinc dimethyl was added the filtered ether solution of lithium methyl prepared from 1.5 g. of lithium with methyl chloride. A portion of the resulting mixture was evaporated on the vacuum chain and pumped at room temperature to remove ether and excess zinc methyl. The solid that remained was analyzed for lithium and zinc by dissolving in dilute acid, separation of the zinc as ZnS, and determination as $Zn(NH_4)PO_4$. Lithium was determined as Li_2SO_4.

Anal. Calc'd for $Li_2Zn(CH_3)_4 \cdot C_2H_5O$: Li, 6.51; Zn, 30.7.
Found: Li, 6.43; Zn, 31.4.

Since the ratio of Li to Zn was almost two to one, and tests for chloride in the water solution of the compound were negative, it was considered that a very stable etherate was present. (Many alkyls, particularly those of acceptor atoms, are noted for the formation of very stable etherates. In some cases a physical separation of the alkyl from the ether is extremely difficult or may even be impossible.) Heating under vacuum to 60° did not materially alter the analyses.

$Li_2Zn(CH_3)_4 \cdot C_2H_5O$ did not catch fire upon exposure to air although it did pick up moisture rapidly, obviously with decomposition and the evolution of gas. If a small amount was ignited on a spatula, it burned readily. The solid reacted with water with considerable violence and the evolution of gas, but no inflammation, to produce a strongly alkaline solution and a flocculent white precipitate. This solution showed no reducing properties.

$LiB(CH_3)_4$. Boron trimethyl was prepared by adding 25 g. of boron fluoride etherate to the methylmagnesium bromide solution formed from 12.5 g. of magnesium. The reaction mixture was distilled and the boron methyl, together with some ether, was collected in a trap cooled with Dry Ice. This solution was added cold to the clear filtered ether solution of lithium methyl prepared from 1 g. of lithium with methyl chloride. The resulting mixture was evaporated under vacuum and the ether, together with excess boron trimethyl, was removed to leave a crystalline white solid. This solid was heated *in vacuo* at 60° for several hours, then was analyzed.

Anal. Calc'd for $LiB(CH_3)_4$: Li, 8.95; Found: Li, 9.68.

Lithium was determined as Li_2SO_4. Analysis for boron on complex organoboron compounds was attempted by fusion with Na_2O_2 followed by potentiometric titration but this was found to be a very unsatisfactory procedure. The main difficulty appeared to be getting complete removal of the organic groups from the boron by the oxidation procedure. Tests for halogen in this compound were negative.

$LiB(CH_3)_4$ appears to be stable in very dry air, although in moist air it was observed occasionally to ignite spontaneously. The solid is quite soluble in ether, and, if a relatively large amount of water is added rapidly to the dry salt, it dissolves quickly with no apparent reaction to form a highly alkaline solution with strong reducing properties, *i.e.* decolorizes $KMnO_4$ solution rapidly. Placing a drop of water on a small pile of the solid usually caused ignition. Acidification of the water solution of $LiB(CH_3)_4$ released large volumes of spontaneously inflammable gas having the characteristic odor of boron trimethyl. Addition of hydrogen peroxide to the solution produced a slow evolution of gas bubbles as did methanol. Ethanol and acetone produced no gas evolution. The amount of gas released upon acidification of the water solution decreased if the solution was allowed to stand exposed to air, and after a few hours, the gas evolved was no longer spontaneously inflammable.

The water solution was found to be conducting, and a fresh sample was electrolyzed in a small electrolysis apparatus. About half again as much gas was evolved at the anode as at the cathode. This gas was not spontaneously inflammable. It was analyzed on the mass spectrometer, and its principal components were identified tentatively as methane, ethane, and cyclopropane.

DISCUSSION

The formation of a complex ion by coordination of a methyl group to an acceptor atom presumably involves a transfer of a *negative* methyl ion, *i.e.*, a methyl group carrying an unshared electron pair. This behavior is not unexpected since the physical characteristics of alkali metal methyls suggests a certain degree of ionic character for the alkyl group in these compounds. Indeed, methyl groups (in addition to hydrogen atoms) are rather unique in that they can take part in various reactions as positive ions, free radicals, or negative ions, to form stable compounds. This behavior is shown to a lesser degree by ethyl groups, and the degree of electronegative character decreases as the size of the straight chain aliphatic group increases.

Many other groups, such as alkoxyl, hydroxyl, hydride ion, halide ion, etc., coordinate to acceptor atoms to form complex ions, and a large number of mixed compounds must be possible. For example, Finholt, Bond, and Schlesinger have indicated the formation of $LiAlH_2(CH_3)_2$ (3).

Complex alkyls, such as those described here, may be of considerable interest in studying relative reactivities of various organic groups. It is possible that some, such as $LiAl(CH_3)_4$, may be useful as alkylating agents in special syntheses.

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REFERENCES

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