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ALKYNYLALUMINUM COMPOUNDS

II *. SYNTHESIS AND STRUCTURE OF THE BIMETALLIC COMPLEXES WITH ALKYNYL BRIDGES

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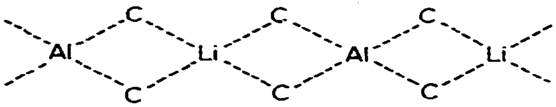
Summary

$Me_2(MeC{\equiv}C)_2AlM$ (M = Li, Na) and $Me_2(Me_3CC{\equiv}C)_2AlLi$ were synthesized, and found to form stable 1 : 1 complexes with 1,4-dioxane. The low conductance and other properties indicate more covalent bonding to the alkali metal by the alkynyl groups than by the alkyl groups in Me_4AlM.

Introduction

The complexes of trialkylaluminum with alkali metal alkyls have been investigated by many authors. The structure of R_4AlM (R = alkyl group) depends on the alkali metal present. The potassium compounds are practically insoluble in saturated hydrocarbons and may reasonably be regarded as ionic salts $[R_4Al]^-K^+$ [1]. The lithium compounds are more covalent, Et_4AlLi and Me_4AlLi are polymeric in the crystalline state [2].



The ionic agregates (of $[R_4Al]Li$ and $[R_4Al]Na$ in hydrocarbon solution as well of $[Et_4Al]Li$ in the vapour state) which must be formed presumably contain Al—C bonds polarized by the alkali metal ion to the point at which the bonding may more appropriately be regarded as being of three centre electron-deficient type, as in crystalline $(Et_4Al)Li$ [2].

Analogous complexes containing four alkynyl group are also known. They

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* For part I see ref. 9.

were obtained from alkali-aluminumhydrides and alkyne [3]. The structures of the products were not investigated.

The alkynyl group is one of the strongest bridging ligands. It has the ability to use the π electrons in bridging bonds. In the structure of dimers of alkynylaluminum compounds the two aluminum—alkynyl—aluminum bridging bond lengths are different. In the diphenylphenylethynylaluminum they are 1.992 and 2.184 Å (4) (X-ray structure in solid state), in dimethylpropynylaluminum (gas phase electron diffraction) they are 2.050 and 2.15 Å (5). It is suggested that these differences are caused by involvement of π-electrons in the coordinative bonds.

The aim of this work was to synthesize Me_2ZYAlM and to investigate the influence of alkynyl groups (Z, Y) on their properties. Especially interesting is the way in which the aluminum, —C≡C— system, and alkali metals interact.

Results and discussion

a) $Me_2(MeC{\equiv}C)_2AlLi$

Di-μ-1-propynyl(tetramethyl)dialuminum reacts with propynyl-sodium or, -lithium in 1,4-dioxane to form dimethyl(dipropynyl)aluminolithium (I) or -sodium (II), which for somplicity will be referred to below as complexes.

$$Me_2Al{-}C{\equiv}CMe + MeC{\equiv}CM \xrightarrow{\text{1,4-dioxane}} Me_2(MeC{\equiv}C)_2AlM \cdot n(1,4)\text{dioxane}$$

where M = Li or Na.

The products of these reactions are practically insoluble in saturated and aromatic hydrocarbons (n-hexane, cyclopentane, benzene and toluene). Solubility is good in 1,4-dioxane (up to 18% at 20°C) but poor in 1,3-dioxane or tetrahydrofuran. The solubility depends strongly on temperature. The complexes are involatile at room temperature, even under a vacuum of 10^{-5} Torr. At higher temperatures they decompose slowly, yielding brown residues. Pure and dry crystals of the two complexes melt sharply (Table 1). Spectral data, aluminum and lithium (or sodium) analysis, and cryoscopic, and conductivity data are shown in Tables 1—3.

The molecular weights obtained cryoscopicaly in dioxane for both complexes are about 80—90 MU higher than those calculated for I or II. The analysis for aluminum and lithium or sodium show that the molar ratio Al/M is 1/1 in both cases, but the metals contents are lower than calculated for pure complexes. The hydrolyzed samples always contained dioxane in the organic layer. The IR spectra of the complexes in Nujol show the characteristic band for complexed 1,4-dioxane (at 1001 cm^{-1}), indicating the presence of dioxane. Prolonged exposure of the complexes to vacuum causes no mass (40 h, 10^{-5} Torr) decrease or change in the analysis.

On the basis of the experiments we formulated complexes as $Me_2(MeC{\equiv}C)_2AlM \cdot O_2C_4H_8$. These and other compounds discussed below can exist as monomeric complexes, but the low solubility in hydrocarbons suggests that dioxane bridged polymers are present in the solid. In dioxane the species is most likely to be $Me_2(MeC{\equiv}C)_2AlM \cdot (O_2C_4H_8)_n$ where $n > 1$ [6,7]. The following spectral results are consistent with the proposed formula. In the IR spectrum the C≡C

TABLE 1

PMR DATA, IR FREQUENCIES FOR THE C≡C BOND IN DIOXANE AND MELTING POINTS OF SUBSTRATES AND COMPLEXES OBTAINED

Compound	PMR(τ)			IR (cm^{-1})	Melting point (°C)
	CH_3C	$(CH_3)_3C{\equiv}C$	CH_3Al		
$CH_3C{\equiv}CAl(CH_3)_2 \cdot$ dioxane	8.30	—	10.98	2157	54–56 [a]
$CH_3C{\equiv}CNa$	insoluble	—	—	—	dec.
$((CH_3)_2[CH_3C{\equiv}C]_2Al)Na \cdot$ dioxane	8.23	—	11.14	2134	202–204
$CH_3C{\equiv}CLi$	insoluble			2058	dec.
$((CH_3)_2[CH_3C{\equiv}C]_2Al)Li \cdot$ dioxane	8.30	—	11.22	2133–2134	198–200
$(CH_3)_3CC{\equiv}CLi$	—	8.93	—	2054–2055	dec.
$((CH_3)_2(CH_3C{\equiv}C)[(CH_3)_3CC{\equiv}C]Al)Li \cdot$ dioxane	8.26	8.82	11.14	2111 2134	160–180
$(CH_3)_3CC{\equiv}CAl(CH_3)_2 \cdot$ dioxane	—	8.70	10.89	2143–2146	73– 74.5 [b]
$((CH_3)_2[(CH_3)_3CC{\equiv}C]_2Al)Li \cdot$ dioxane	—	8.88	11.16	2110–2112	190–194

[a] Pure dimer, not complexed with dioxane. [b] Pure dimer, not complexed with dioxane; melting was with decomposition.

TABLE 2

ANALYSES OF COMPOUNDS INVESTIGATED

Compound	Aluminium (%)			Alkali metal (%)		
	Found	calc. on pure comp.	calc. on comp. with 1 mol of dioxane	Found	calc. on pure comp.	calc. on comp. with 1 mol of dioxane
$Me_2(MeC{\equiv}C)_2AlLi \cdot$ dioxane	11.72	19.01	11.78	2,94	4.93	3.04
$Me_2(MeC{\equiv}C)_2AlNa \cdot$ dioxane	11.46	17.03	10.97	9.75	14.95	9.35
$Me_2(MeC{\equiv}C)(Me_3CC{\equiv}C)AlLi \cdot$ dioxane	9.96	15.69	10.38	2.47	4.07	2.69
$Me_2(Me_3CC{\equiv}C)_2AlLi \cdot$ dioxane	9.15	13.36	9.31	2.38	3.46	2.41
Me_4AlLi	27.9	28.72	14.83	7.25	7.45	3.85

bands which appear at 2157 cm^{-1} for $Me_2(MeC{\equiv}C)Al$ and 2057 cm^{-1} for $MeC{\equiv}CLi$ ($MeC{\equiv}CNa$ gives no $C{\equiv}C$ band in this region) disappear. There is only one new band, at 2134 cm^{-1}, in the complexes formed. Comparison of the PMR spectra of $Me_2(MeC{\equiv}C)Al$ with that of $Me_2(MeC{\equiv}C)_2AlM \cdot O_2C_4H_8$ (Me—Al $\tau = 10.98$; $MeC{\equiv}$ $\tau = 8.30$) indicates a shift of the Me—Al signal to $\tau = 11.14$ and 11.22 for the lithium and sodium derivatives, respectively, in the complexes. The Me—C≡ shifts to 8.22 in the case of the lithium derivative. The integrations agree exactly with the assumed composition for both compounds. The ^{13}C NMR spectra [8] show that the propynyl radicals are equivalent in the complex. Quadrupole coupling was observed for the carbon atoms thought to be bonded with aluminum (H_3C—Al, ≡C—Al). Very low specific conductances were observed. Fairly concentrated (for electrochemical measurements) solutions were used. The data for lower concentrations are not reliable, because they fall outside the range of the apparatus. The conductivity measurements indicate a very low degree of ionisation. To compare the results with those for a compound without alkynyl groups the conductivity of $(Me_4Al)Li$ (III) was measured under the conditions used for I (Table 3), and a significantly higher conductivity was observed. This shows that the lithium— or sodium—propynyl group interaction has more covalent character than the alkalimetal—alkyl group interaction.

b) $Me_2(Me_3CC{\equiv}C)_2AlLi$

Di-μ-t-butylethynyl(tetramethyl)dialuminum reacts in the 1,4-dioxane with t-butylethynyllithium to give dimethyl(di-t-butylethynyl)aluminolithium. It is very soluble in dioxane, scarcely soluble in toluene (less than 1%), and insoluble in saturated hydrocarbons. The dry complex melts sharply. It is more stable at room temperature than complexes I and II, and can be stored below 0° C.

The IR spectra show only one band in the region of $C{\equiv}C$ stretching vibrations, at 2110—2112 cm^{-1}. The PMR spectra show two bands with intensity ratio 3/1. The first signal at 8.88 ppm corresponds to the protons of tert-butyl radical. The signal at 11.18 ppm comes from the protons of the methyl groups bonded to the aluminum. As in ^{13}C NMR spectrum of I, both alkynyl groups in

TABLE 3

MOLECULAR WEIGHTS AND CONDUCTANCES OF COMPLEXES IN DIOXANE

	Molecular weight			Specific and Molecular Conductances		
	Found	Calc. on pure comp.	Calc. on comp. with 1 mol of dioxane	c (mol dcm^{-3})	κ (μS cm^{-1})	λ (Ω^{-1} cm^2 mol^{-1})
$Me_2(MeC{\equiv}C)_2AlLi \cdot$ dioxane	236	142	230	0.3339	4.91	1.32×10^{-2}
$Me_2(MeC{\equiv}C)_2AlNa \cdot$ dioxane	239	158	246	0.2026	4.43	2.42×10^{-2}
$Me_2(MeC{\equiv}C)(Me_3CC{\equiv}C)AlLi \cdot$ dioxane	258	184	272	0.3095	3.18	1.03×10^{-2}
$Me_2(Me_3CC{\equiv}C)_2AlLi \cdot$ dioxane	298	226	314	0.3108	3.04	0.98×10^{-2}
Me_4AlLi	103	94	182	0.2861	1.04×10^{-3}	3.65

complex VI are equivalent. The broadening of the signals is due to the quadrupole coupling of carbons bonded to the aluminum atom.

The aluminum and lithium analysis indicated a 1 : 1 molar ratio. The Al and Li contents agree well with a composition involving one molecule of dioxane. Cryoscopic measurements show a molecular weight about 70 MU higher than that calculated for pure $Me_2(Me_3CC{\equiv}C)_2AlLi$. The conductivity is slightly lower than that of I or II. The IR spectra of the dry solid complex in Nujol shows the characteristic bands of dioxane.

From these results we conclude that the structure of dimethyl(di-t-butylpropynyl)aluminolithium is analogous to that of dimethyl(di-t-propynyl)-aluminolithium.

c) Attempts to obtain $Me_2(Me_3CC{\equiv}C)(MeC{\equiv}C)AlLi$ (V)

Di-μ-t-1-propynyl(tetramethyl)dialuminum reacts with t-butylethynyllithium to give products identical with those from the reaction of di-μ-t-butylethynyl-(tetramethyl)dialuminum with propynyllithium. In both cases a "glassy" product melting over the same broad temperature range (about 20°C) was obtained after evaporation of the excess of dioxane used as a solvent.

The IR spectra show two bands in the region of C≡C stretching vibrations. The first band is at 2110—2112 cm^{-1} and the second at 2134 cm^{-1}, which closely correspond to the C≡C bond vibrations of I and IV.

In the ^1H NMR spectrum there are two resonances from protons of the propynyl radical, at 8.21 and 8.26 ppm, and two signals from protons of the t-butyl group, at 8.82 and 8.88 ppm. Only one signal was observed for the protons of $CH_3{-}Al$, at 11.14 ppm.

These observations suggest that the reaction gives a mixture of products. We considered the possibility of an equilibration reaction of V.

$$\underset{(V)}{Me_2PiBiAlLi} \xrightleftharpoons{\text{dioxane}} \underset{(I)}{Me_2Pi_2AlLi} + \underset{(IV)}{Me_2Bi_2AlLi} \qquad (2)$$

$$Pi = MeC{\equiv}C{-},\ Bi = Me_3CC{\equiv}C{-}$$

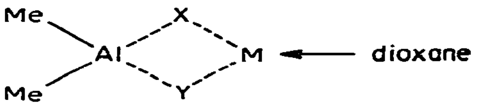
The IR and PMR spectra for a 1/1 mixture of pure I and IV are identical with those of the reaction products. Addition of complex I or IV to the reaction products caused an increase of the signals of $Me{-}C{\equiv}$ or $Me_3C{-}C{\equiv}$ protons, respectively. On the basis of these facts we propose the following assignment of the PMR spectrum: the signals at 8.21 and 8.26 ppm belong to the propynyl groups of complexes V and I respectively, and those at 8.88 and 8.82 ppm to the t-butyl groups of complexes V and IV respectively. The conductivity is intermediate between those of I and IV, as expected (Table 3), but this is not strong evidence in favor of the equilibration reaction 2.

Conclusion

1) Complexes of dimethylalkynylaluminum and alkynyls of sodium or lithium are formed containing one molecule of firmly-bound dioxane.

2) The results indicate the existence of a strongly covalent interaction

between the alkali metal and alkynyl groups even in polar solvents. The following monomeric structure is proposed



where X, Y are the same or different —C≡C—R groups. However, polymeric structures cannot be excluded for the solid, nor higher solvates in dioxane solutions.

3) The bridging bonds are very different from the ionic interaction between sodium cation and $[Me_4Al]^-$ anion in Me_4AlNa.

4) The complex with two different alkynyl groups (V) exists only in equilibrium with the symetrical complexes I and IV.

Experimental part

All operations were carried out under dry oxygen-free nitrogen. Solvents were dried over 4A molecular sieves and distilled from Na/K alloy-benzophenone.

Reactions

Sodium and lithium alkynyls were made in liquid ammonia. All other compounds were prepared in 1,4-dioxane. Attempts to make $Me_2(RC{\equiv}C)AlM$ in aromatic and aliphatic hydrocarbons were unsuccessful.

1) MeC≡CLi and MeC≡CNa. One mole of metal was added to 1.5 l of liquid ammonia and propyne was introduced in 10% molar excess. The mixture was stirred for about 2 h with the blue colour disappeared and 250 ml of petrol ether was then added. The ammonia was evaporated off and the petrol ether removed under vacuum. Residual solvent, ammonia and propyne were removed under vacuum (10^{-3} Torr) at room temperature. The white powder obtained contained 99% of MeC≡CM.

2) $Me_3CC{\equiv}CLi$. This compound was prepared analogously.

3) $Me_2(MeC{\equiv}C)Al$. 145.9 mmol (13.5 g) of dimethylaluminum chloride in 25 ml of cyclopentane was added to 161.2 mmol (10 g) of propynylsodium suspended in 50 ml of cyclopentane. The mixture was stirred magnetically for 15 h then the solvent was removed. The product was purified by vacuum distillation (10^{-4} Torr). Yield 80% calculated in terms of Me_2AlCl used.

4) $Me_2(Me_3CC{\equiv}C)Al$. $Me_2(Me_3CC{\equiv}C)Al$ was synthesized analogously from 48 mmol of sodium t-butylacetylene and 43 mmol of dimethylaluminum bromide. The product was purified by vacuum sublimation (10^{-4} Torr at room temperature)on to a finger cooled with liquid nitrogen. Yield 56% calculated in terms of the Me_2AlBr used.

5) $Me_2(MeC{\equiv}C)_2AlLi$. 24 mmol of dimethylpropynylaluminum in 15 ml of dioxane was added dropwise to a vigorously stirred dispersion of 24 mmol of propynyllithium in 20 ml of dioxane. A distinct exothermic effect was observed. After two hours the solutions was filtered and the filtrate was concentrated by solvent evaporation at 100°C until a few crystals appeared. The mixture was cooled slowly to room temperature and filtered. The solid obtained was recrystallized from dioxane as white crystals. Yield 55—60% (calcd. from $\mathrm{Me_2(MeC{\equiv}C)Al}$ taken).

6) $\mathit{Me_2(MeC{\equiv}C)_2AlNa}$. The complex was synthesized and purified analogously from 25 mmol of propynylsodium and 25 mmol dimethylpropynylaluminum. Yield 53—58% (calcd. from $\mathrm{Me_2(MeC{\equiv}C)Al}$ taken).

7) $\mathit{Me_2(MeC{\equiv}C)\,(Me_3CC{\equiv}C)AlLi}$. 15 mmol of dimethylpropynylaluminum in 25 ml of dioxane was added to 15 mmol t-butylethynyllithium well dispersed in 20 ml of dioxane. A minor exothermic effect was observed. After 2 h of stirring the solution was filtered. The filtrate was concentrated to 20 ml, and the product was precipitated by addition of 25 ml of n-pentane. It was filtered off, and dried under vacuum (10^{-3} Torr). Yield 76—79% (calcd. from $\mathrm{Me_2(MeC{\equiv}C)Al}$ taken).

The reverse method for the synthesis was also used; 20 mmol of dimethyl(t-butylethynyl)aluminum being mixed with 20 mmol of propynyllithium. Yield 78—82% calcd. from $\mathrm{Me_2(Me_3CC{\equiv}C)Al}$ taken. The PMR spectra and analyses of the two products were identical.

8) $\mathit{Me_2(Me_3CC{\equiv}C)_2AlLi}$. 15 mmol of dimethyl(t-butylethynyl)aluminum in 20 ml of dioxane was added to 15 mmol of t-butylethynyllithium in 20 ml of dioxane. The procedure was then as in 7. Yield 79—84% (calcd. from $\mathrm{Me_2(Me_3CC{\equiv}C)Al}$ taken).

Analytical methods

The PMR spectra were recorded in sealed tubes on a JEOL JNM C 100 MHz spectrometer.

The IR spectra, were recorded on Zeiss UR-10 spectrophotometer. 10% dioxane solutions in a cell of 0.10 mm thickness adapted for filling under nitrogen were used, or Nujol mulls sealed in polyethylene bags.

The molecular weights were measured cryoscopically in dioxane, using a standard apparatus modified for work under nitrogen.

The conductance was measured with a Raderkin apparatus. Analysis were made on a Perkin-Elmer atomic absorption apparatus.

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