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ALKYNYLALUMINUM COMPOUNDS

III*. SYNTHESIS AND STRUCTURE OF THE COMPLEXES OF DIMETHYLPROPYNYLALUMINUM WITH DIPROPYNYLBERYLLIUM AND DIPROPYNYLMAGNESIUM

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Summary

Complexes of formula $Me_4(MeC{\equiv}C)_4Al_2M$ (M = Be; Mg) have been synthesized. The low conductance and features indicate that the bonding is mainly covalent; σ-bonding of four alkynyl groups to Be or Mg atoms is suggested with the aluminum atoms coordinated through a combination of σ and π orbitals of the alkynyl groups.

Introduction

The synthesis and structures of complexes formed by dimethylalkynylaluminum compounds and alkynyl-lithium and -sodium were reported previously [1]. The present report concerns the investigation of complexes of dimethylpropynylaluminum with dipropynylberyllium and dipropynylmagnesium. Previously, only alkylalkynylaluminum complexes containing calcium, strontium and barium had been obtained [2]. Alkyl complexes of the general formula R_8Al_2M are also known for these three metals [3,4]. Dialkylmagnesium compounds associate similarly, to form R_8Al_2Mg [5,6], but in solution they exist in equilibrium with a complex of the formula $[R_5AlMg]_2$ [6]. The magnesium complexes break down into substrates R_3Al and R_2Mg at elevated temperature. An even weaker complex is formed from dimethylberyllium [6], it cannot be isolated from the solution in which it exists in equilibrium with the reactants.

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* For part II see ref. [1].

TABLE 1

MOLECULAR WEIGHT, ^{1}HMR DATA, IR FREQUENCES OF THE C≡C BOND IN DIOXANE-1,4, MELTING POINTS AND CONDUCTANCES OF SUBSTRATES AND COMPLEXES IN DIOXANE-1,4 AND TRIETHYLAMINE (TEA)

Compound	Molecular weight		^{1}HMR (ppm)		IR (cm^{-1})	M.p. (°C)
	Found	Calcd.	CH_3—C	CH_3—Al		
$MeC{\equiv}CAlMe_2 \cdot$ diox	179	184	8.30	10.98	2157	
$(MeC{\equiv}C)_2Be_2 \cdot$ 2 diox	339	350	8.63	—	2130	130
$(MeC{\equiv}C)_4Me_4Al_2Be$	254	279	8.40	11.28	2146	162—165 [b]
$[(MeC{\equiv}C)_2Mg]_n \cdot diox_m$	319	—	8.40	—	2096	142—144 [b]
$(MeC{\equiv}C)_4Me_4Al_2Mg$	272	294.3	8.25	11.14	2136—2137	189—196 [b]
$[MeC{\equiv}CAlMe_2]_2$	187 [a]	192	8.49 [a]	10.28 [a]	2105—2108	54—56

[a] In benzene solution. [b] Melts with decomposition. [c] Concentration based on dimeric $Mg(C{\equiv}CMe)_2$.

Results and discussion

Dimethylpropyn-1-ylaluminum reacts with dipropyn-1-ylberyllium and with dipropyn-1-ylmagnesium in dioxane-1,4 to form tetra-μ-propyn-1-yl(tetramethyl)dialumino-beryllium or -magnesium.

$$[Me_2AlC{\equiv}CMe]_2 + (MeC{\equiv}C)_2M \xrightarrow{\text{Dioxane-1,4}} Me_4(MeC{\equiv}C)_4Al_2M \qquad (1)$$

The products are very soluble in dioxane-1,4, triethylamine, and poorly soluble in tetrahydrofuran. They are involatile at room temperature, even under a vacuum of 10^{-5} Torr. Sublimation is observed at 80°C, but only decomposition products were found. (These were not further investigated.) Cryoscopic measurements, spectral data, melting points and conductivity data for the substrates and complexes are shown in Table 1.

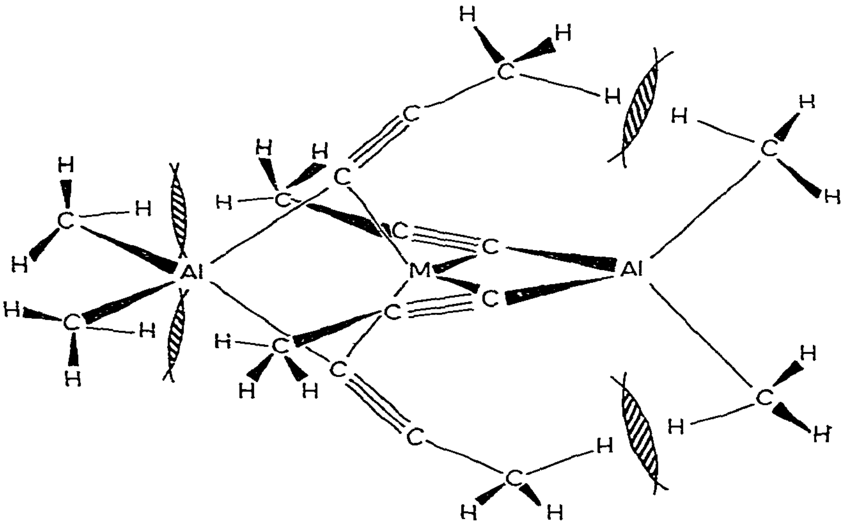
The molecular weight measurements and elemental and gasometric (methane and propyne) analyses agree well with the proposed composition ($Al/M = 2/1$) and structure. They indicate also that dioxane does not coordinate with the complex as it does with the corresponding complexes involving first group metal [1] and $Me_4(MeO)_4Al_2Mg$: (2-diox) [9]. Attempts to obtain alkynyl complexes of 1 : 1 stoichiometry, as in alkylaluminummagnesium compounds were unsuccessful; when the reactants were mixed in 1 : 1 ratio the products contained free dipropynylmagnesium or free dipropynylberyllium compounds observed together with the 1 : 2 complex, as shown by the bands from triple bonds in the IR spectra and by the $CH_3C{\equiv}$ resonance in the ^{1}NMR spectrum. The presence of signals from the reactants in the 1 : 1 mixture indicate that exchange of substituents is slow, if it takes place at all.

The spectral data provide evidence for the formation of the defined complexes but the changes in the positions of the ^{1}HMR signals and IR —C≡C— bands cannot be explained in simple terms. The related complexes of the first group metals shows the same trends [1].

Conductances

Dioxane-1,4			Dioxane-1,4/TEA (1/1)		
C (mol dm^{-3})	$\mathcal{H} \times 10^{-6}$ [Ω^{-1} cm^{-1}]	λ (cm^2 Ω^{-1} mol^{-1})	C (mol dm^{-3})	$\mathcal{H} \times 10^{-6}$ [Ω^{-1} cm^{-1}]	λ (cm^2 Ω^{-1} mol^{-1})
2.437	0.744	3.05×10^{-4}	2.437	0.749	3.06×10^{-4}
0.241	0.157	6.53×10^{-4}	0.240	0.155	6.46×10^{-4}
0.228	0.046	2.01×10^{-4}	0.231	0.45	1.94×10^{-4}
0.225 ^{c}	0.230	1.02×10^{-3}	0.224 ^{c}	7.41	3.31×10^{-2}
0.211	0.192	9.04×10^{-4}	0.212	0.196	9.24×10^{-4}
—	—	—	—	—	—

We considered three possible models for these complexes. Models A and B are shown below. Structure C is intermediate between A and B, and has two alkynyl groups *sp* bonded to the central metal atom and two to each of aluminum atoms. Three assumptions were made, on the basis of the previous investigations [10—12], in constructing these models: (i) there is only a small deviation from the linearity of the —C≡C—R when the complex is formed; (ii) that there are differences in the bridge bond lengths, which is a structural feature unique to organo-beryllium and -aluminum compounds, and (iii) that the alkynyl group has a much stronger bridging ability than alkyl groups *. Model A



A

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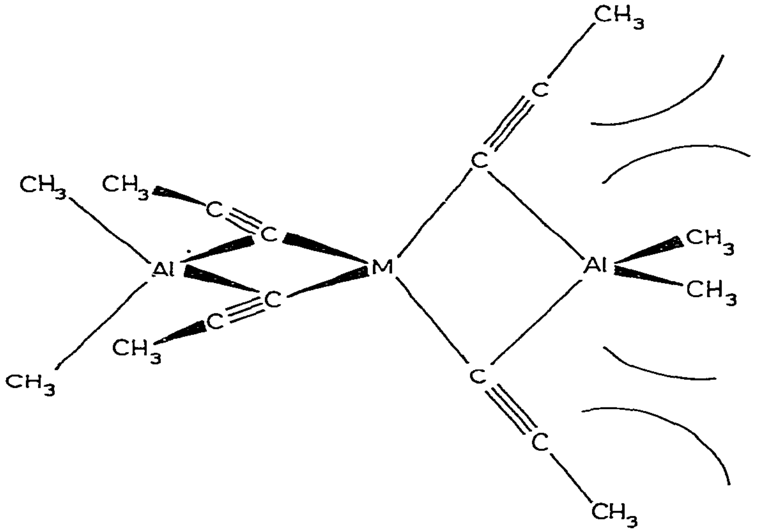
* The oxygen of Et_2O is a much stronger donor than a methyl or even a chlorine substituent in dimeric Me_3Al or Me_2AlCl whereas the —C≡CMe group has a similar donor strength; this follows from the fact that former compounds form stable complexes with ether, whereas ether can be removed from $Me_2AlC{\equiv}CMe \cdot Et_2O$ under vacuum to form back dimeric $Me_2AlC{\equiv}CMe$.



B

was then the only acceptable (for both Be and Mg) when the angle Al—C≡C was less than 140°, and the larger angles formed by alkynyl groups in the beryllium and aluminum compounds suggested that model A is unsatisfactory. In the figure A shows that there are steric interactions between the methyl groups on Al and the methyl groups of propynyl radicals connected to Al, and vice versa. Similar reasoning indicates that the structure C is also improbable. The lower symmetry of the complex and the non-equivalence of the bridging substituents should lead to two IR ν(C≡C) bands for model C. Since there is no fast exchange of substituents, at least three peaks could be expected for C in ^{1}H NMR spectra. But both complexes gave only one ν(C≡C) band and two ^{1}H NMR peaks.

Model B does not involve steric hindrances. The symmetry is high (D_{2h}) and the observed IR and ^{1}H NMR spectra agree well with that predicted. The ^{13}C NMR spectra [7] of all previously investigated alkynylaluminum compounds and their complexes display a large broadening of the signal of the α alkynyl carbon atom due to quadrupole coupling with the aluminum atom. In beryllium and magnesium complexes the coupling is much smaller, and only slight broadening of the signals from the α alkynyl carbon nuclei is observed. Although the observed narrowing can be rationalized in terms of the lower electric field gradient in a molecule of higher symmetry at aluminum *, it can be better explained (in agreement with model B) in terms of a change in the Al—C≡ bonds from sp^3(Al)—sp(C) character to a system of three-centre two electrons plus sp^3(Al)—π(C≡C) interactions. Furthermore, the position of the signal in the ^{13}C NMR spectra is very similar to that from $(RC{\equiv}C)_2Be \cdot$ diox; this suggests that all the ligands are bonded with beryllium or magnesium through sp orbitals of alkynyl groups.

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* In previously published compounds of even higher symmetry at aluminum, $Me_2Al(C{\equiv}CMe)_2$-Li or -Na, the broadening of the α alkynyl carbon signal was similar to that found in $[Me_2AlC{\equiv}CMe]_2$ or $Me_2AlC{\equiv}CMe \cdot$ diox [1,7].

The IR and ^{1}H NMR spectra are very similar for all the propynyl-substituted complexes of the first and second group metals so far examined. Furthermore, the conductances are low in weakly donating solutions, indicating covalent interaction in the bridges. But whereas the first group metal complexes undergo ionisation in dioxane/triethylamine solution, the conductivity of the second group metal complexes remains low, even in this strongly basic solvent. This can be explained in terms of higher electonegativity of beryllium and magnesium, but it also confirms the presence of a covalently bonded central atom as represented in structure B. We do not rule out a contribution from electrostatic interaction to the bridge bonding: it might be as high as 20 kcal/mol [*], but it could not be the dominant contributor to the bridging interaction.

Experimental

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

(1) $[Me_2AlC{\equiv}CMe]_2$ was synthesized as previously described [1].

(2) $Be(C{\equiv}CMe)_2$ was synthesized as described by Coates and Francis [8]. Analysis: Be, found: 5.14, calc.: 5.14%.

(3) $Mg(C{\equiv}CMe)_2$. A solution of 24.9 g (0.136 mol) of magnesium bromide in 70 ml of diethyl ether was added dropwise during 30 min to a vigorously stirred dispersion of 12.5 g (0.273 mol) propynyllithium in 60 ml of diethyl ether. The mixture was stirred for 6 h, then 100 ml of dioxane-1,4 was added and the precipitate was filtered off. The filtrate was evaporated, and the solid residue found still to contain 30% of bromine. The solid was dissolved in 135 ml of dioxane-1,4, and the solution was stirred 1 hour, then filtered. The filtrate was concentrated by vacuum distillation until the turbidity appeared. After 10 h a precipitate separated and the mixture was again filtered. This procedure was repeated 10 times, and finally 1.82 g (8.5%) of dipropynylmagnesium was obtained. Purity 99.5%, m.p. 142—144°C. Analysis: Mg, 11.91%, molecular ratio of Mg/dioxane-1,4 was 1/0.86, and 96% of the expected volume of propyne was obtained in gasometric measurements (calcd. based on magnesium).

(4) $Me_4(MeC{\equiv}C)_4Al_2Be$. A solution of 2.43 g (25.3 mmol) of dimethylpropynylaluminum in 10 ml of dioxane-1,4 was added to 1.1 g (12.6 mmol) of dipropynylberyllium in 17 ml of dioxane-1,4. The mixture was stirred for 4 h at 80°C and 6 h at room temperature, then concentrated to about 4 ml and filtered through a G3 sintered disc. The solid was washed twice with 2 ml of cyclopentane and dried under high vacuum. The yield of the product was 2.98 g (84%). The pale yellow powder is soluble in THF, dioxane-1,4 and triethylamine. It is insoluble in aliphatic and aromatic hydrocarbons. Analysis. Found: Al, 19.11; Be, 3.22. $C_{16}H_{24}Al_2Be$ calcd.: Al, 19.35; Be, 3.22%.

(5) $Me_4(MeC{\equiv}C)_4Al_2Mg$. A solution of 1.69 g (17.6 mmol) of dimethylpro-

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[*] The calculations were based on the values of net charge, for uncomplexed alkynyl group in CpBeCCMe [13] and for the aluminium atom in R_3Al. Bond lengths were taken from the literature [10—12].

pynylaluminum in 6 ml dioxane-1,4 was added to 0.9 g (8.8 mmol) of dipropynylmagnesium in 25 ml of dioxane-1,4. The mixture was stirred for 4 h at 60—65°C and 6 h at room temperature. A small amount of precipitate containing bromide salts was removed by filtration, and the filtrate was concentrated to about 6 ml, then treated with cyclopentane. The precipitate was filtered off and dried under high vacuum. The yield was 1.43 g (55%). The white solid is very soluble in dioxane-1,4, less in THF, scarcely in boiling toluene, and insoluble in aliphatic hydrocarbons. Analysis found: Al, 18.20; Mg, 8.26. $C_{16}H_{24}Al_2Mg$ calcd.: Al, 18.34; Mg, 8.25%.

The analytical methods and apparatus were described in a previous paper [1]

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