

The reaction of trimethylaluminium with 1,2-dihydroxymethylbenzene

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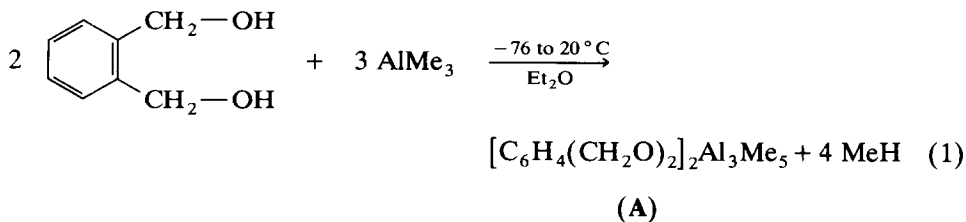
Abstract

The reaction of 1,2-dihydroxymethylbenzene with trimethylaluminium carried out at a 2:3 molar ratio yields the complex $[C_6H_4(CH_2O)_2]_2Al_3Me_5$ (A) possessing one five- and two four-coordinated aluminium atoms.

Trialkylaluminium compounds react easily with monodentate electron donors and usually form simple compounds containing flat 4- or 6-membered rings (Al_2X_2 or Al_3X_3 , X = O, N, S) in the molecule [1]. However when multidentate ligands, for example trisilanol [2], binuclear iridium complex $Ir_2(CNR)_4(dmpm)$ (R = 2,6-Me₂C₆H₃, dmpm = Me₂PCH₂PMe₂) [3], bidentate ligands bis(diphenylphosphinoyl)methane [4] and bis(diphenylthiophosphinoyl)methane [5], 1,4,8,11-tetraazocyclotetradecane [6] are used as the electron donors, complicated aggregates are obtained.

Recently we have reported the synthesis and structure of trimethylaluminium complexes with a multidentate carbosiloxane type ligand [7]. We now turn our attention to the reactions of organoaluminium compounds with diols as bidentate ligands. Here we report the synthesis and structure of $[C_6H_4(CH_2O)_2]_2Al_3Me_5$ isolated from the reaction of trimethylaluminium with 1,2-dihydroxymethylbenzene.

The reaction was carried out according to eq. 1. Two moles of methane per mole of diol are liberated when the reaction is carried out at a molar ratio of diol : AlMe₃ = 2 : 3. A small amount of white amorphous solid precipitates from the



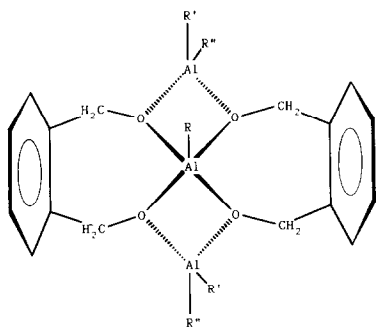


Fig. 1. Structure of the complex $[C_6H_4(CH_2O)_2]_2Al_3R_5$.

reaction mixture. It was defined as a mixture of polymeric compounds, based on elemental analysis and insolubility in organic solvents. A small amount of $AlMe_3$ was also detected in the reaction mixture. The main reaction product **A** was isolated as colourless crystals. Its structure (Fig. 1) is based on 1H , ^{13}C and ^{27}Al NMR spectra and on cryoscopic molecular weight determination.

Compound **A** possesses a central, five-coordinated aluminium atom bonded to four oxygen atoms and to one methyl group R , and two four-coordinated aluminium atoms, each bonded to two oxygen atoms and to two methyl groups R' and R'' .

The 1H NMR spectrum of compound **A** (Fig. 2) has two multiplets of aromatic protons, a degenerate doublet of doublets (type AB) assigned to CH_2 groups and three singlets at -0.38 , -0.48 and -1.36 ppm (integration ratio 2:2:1 respec-

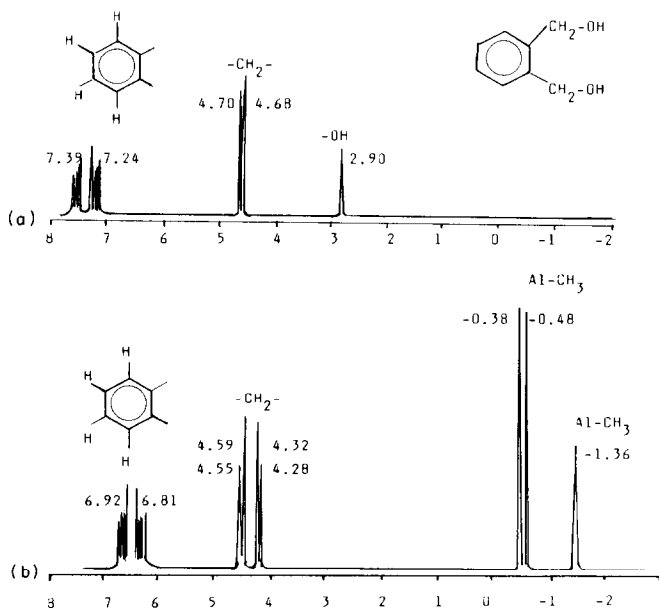


Fig. 2. 1H NMR spectra of: (a) 1,2-dihydroxyethylbenzene in CD_3COCD_3 solution, standard $CD_3COCD_2H = 2.04$ ppm; (b) product **A**, in C_6D_6 solution, standard $C_6D_5H = 7.15$ ppm.

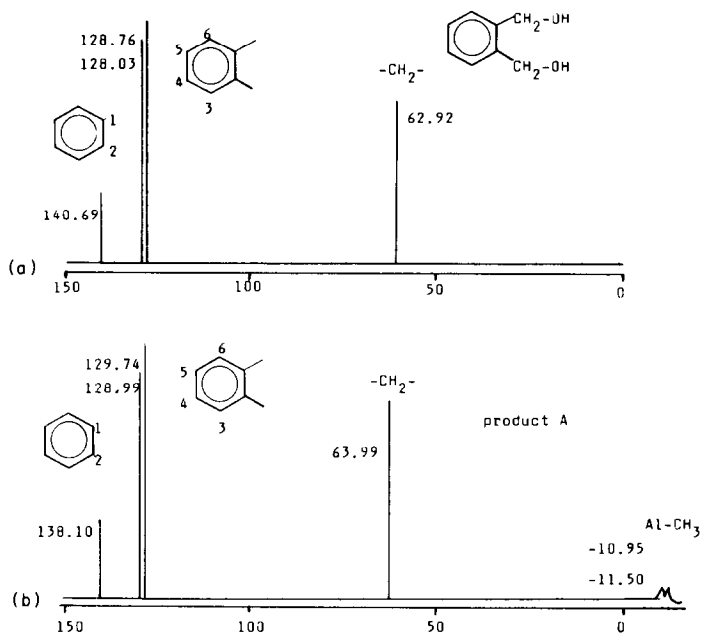


Fig. 3. ^{13}C NMR spectra of: (a) 1,2-dihydroxymethylbenzene in CD_3COCD_3 solution, standard $^{13}\text{CD}_3\text{COCD}_3 = 29.80$ ppm; (b) product A, solv. C_6D_6 standard $^{13}\text{C}_6\text{D}_6 = 128.00$ ppm.

tively) assigned to methyl groups. ^1H NMR spectrum shows that compound A possesses 8 aromatic protons, 4 CH_2 groups and 5 methyl groups $\text{Al}-\text{CH}_3$, one of them (singlet of -1.36 ppm) being very different from the others.

The ^{13}C NMR spectrum (Fig. 3) gives evidence that all CH_2 groups are equal and that compound A has at least 2 kinds of methyl group $\text{Al}-\text{CH}_3$. The spectrum comprises 3 signals of aromatic carbons, one signal of $-\text{CH}_2-$ groups and two low intensity, wide signals of methyl groups $\text{Al}-\text{CH}_3$.

^{27}Al NMR studies show that complex A contains four- and five-coordinated aluminium atoms. Two wide signals in the spectrum at 160.60 ppm and 73.90 ppm were assigned to four- and five-coordinated aluminium atoms respectively.

Cryometric measurements carried out in benzene show the association degree of $[\text{C}_6\text{H}_4(\text{CH}_2\text{O})_2]_2\text{Al}_3\text{Me}_5$ as $n = 1.05$.

Experimental

A solution of 0.81 g (11.3 mmol) of AlMe_3 in 20 cm^3 of diethylether was added dropwise over 1 h into a cooled (-76°C) solution of 1.03 g (7.5 mmol) of 1,2-dihydroxymethylbenzene in 20 cm^3 of diethylether. The reaction mixture was warmed to room temperature over the next 2 h. Evolution of methane was observed during the reaction. A white, amorphous solid (0.25 g), insoluble in benzene and toluene precipitated after 24 h. Elemental analysis of the solid: Al, 14.12%; hydrolyzable methyl groups, -9.04 wt.%. The solvent was partially evaporated from the filtrate and colourless crystals were obtained on cooling the remaining solution to -30°C . Elemental analysis: found: Al, 18.37%; hydrolyz-

able methyl groups, – 18.00 wt.%; $[\text{C}_6\text{H}_4(\text{CH}_2\text{O})_2]_2\text{Al}_3\text{Me}_5$ calc.: Al, 18.93%; Me, 17.5 wt.%.

References

- 1 R. Kumar, M.L. Sierra, V. Srimi, J. de Mel and J.P. Oliver, *Organometallics*, 9 (1990) 484; V. Srimi, J. de Mel, R. Kumar and J.P. Oliver, *Organometallics*, 9 (1990) 1305; M.P.R. van Vliet, G. van Koten, M.S. de Keiper and K. Vrieze, *Organometallics*, 6 (1987) 1652; M.D. Healy, D.A. Wierda and A.R. Barron, *Organometallics*, 7 (1988) 2543; V. Srimi, J. de Mel and J.P. Oliver, *Organometallics*, 8 (1989) 827; J.F. Janik, E.N. Duesler, W.F. McNamara, M. Westerhausen and R.T. Paine, *Organometallics*, 8 (1989) 506; A.P. Shreve, R. Mulhaupt, W. Fultz, J. Calabrese, W. Robins and S.D. Ittel, *Organometallics*, 7 (1988) 409.
- 2 F.J. Feher, T.A. Budzichowski and K.J. Weller, *J. Am. Chem. Soc.*, 111 (1989) 7288.
- 3 J. Wu, P.E. Fanwick and C.P. Kubiak, *J. Am. Chem. Soc.*, 111 (1989) 7812.
- 4 G.H. Robinson, B. Lee, W.T. Pennington and S.A. Sangokoya, *J. Am. Chem. Soc.*, 110 (1988) 6260.
- 5 G.H. Robinson, M.F. Self, W.T. Pennington and S.A. Sangokoya, *Organometallics*, 7 (1988) 2424.
- 6 G.H. Robinson, A.D. Rae, C.F. Campana and S.K. Byram, *Organometallics*, 6 (1987) 1227.
- 7 S. Pasykiewicz and W. Ziemkowska, *J. Organomet. Chem.*, 397 (1990) 269.