

Journal of Organometallic Chemistry, 153 (1978) 123–126
 © Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

BASIC PROPERTIES OF THE OXYGEN ATOM IN THE TETRAETHYLALUMINOXANE—BENZONITRILE COMPLEX

A. PIOTROWSKI, R. KUNICKI and S. PASYNKIEWICZ *

*Institute of Organic Chemistry and Technology, Technical University (Politechnika), ul.
 Koszykowa 75, 00-662 Warszawa (Poland)*

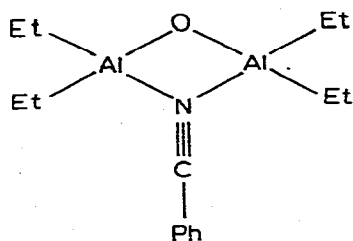
(Received January 10th, 1978)

Summary

The complex of tetraethylaluminumoxane with benzonitrile was found to form complexes with Et_2AlCl and EtAlCl_2 . The structure of these complexes was investigated. The electronegativity of aluminium atoms in these complexes was calculated from the Dailey—Shoolery equation.

Introduction

It was previously reported that in nonpolar solvents, tetraethylaluminumoxane is a cyclic trimer associated through the oxygen atoms [1]. It forms a monomeric complex with benzonitrile in the 1 : 1 molar ratio [2] (I)

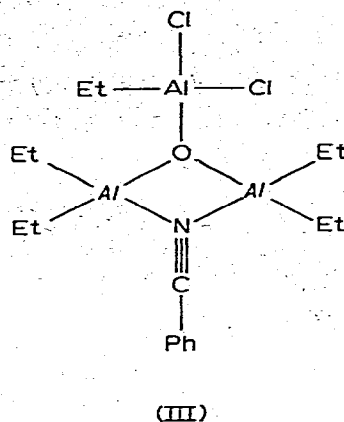
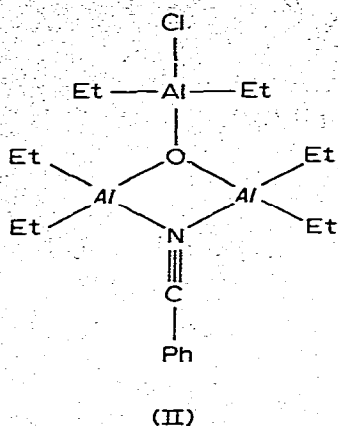


(I)

In this complex the non-bridging oxygen atom may exhibit donor properties toward Lewis acids. We tried to prove this possibility by showing the existence of a donor—acceptor interaction between complex I and the organometallic compounds.

Results and discussion

PMR and IR spectral studies and cryoscopic molecular weight determinations proved the formation of complexes II and III in the reaction of I with organo-aluminium compounds.



In the low temperature PMR spectra of complexes II and III, changes in the chemical shifts and internal chemical shifts of the protons of the ethyl groups were observed (Table 1). A decrease of the internal chemical shifts of protons of the Al ethyl groups from 1.10 to 0.99 in the case of complex II and from 1.10 to 0.94 in the case of complex III was observed. The internal chemical shifts of protons of the Al ethyl groups increased at the same time in these com-

TABLE 1

PMR SPECTRA. CHEMICAL SHIFTS (τ , ppm) OF PROTONS OF THE ETHYL GROUPS OF INVESTIGATED SPECIES. Toluene as internal standard at τ 7.66 ppm, temperature -70°C .

a)

	CH ₃	CH ₂	(Et)
EtAlCl ₂	8.81	9.72	0.91
Et ₂ AlCl	8.50	9.52	1.02
Et ₃ Al	8.46	9.61	1.15
complex I	8.00	9.10	1.10

b) The triple complexes II and III

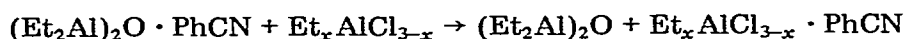
Acceptor	EtAlCl ₂			Et ₂ AlCl			Et ₃ Al		
	CH ₃	CH ₂	δ (Et)	CH ₃	CH ₂	δ (Et)	CH ₃	CH ₂	δ (Et)
Protons of ethyl groups bonded to Al	8.36	9.33	0.97	8.37	9.48	1.11	8.47	9.61	1.14
Protons of ethyl groups bonded to Al	8.13	9.09	0.94	8.09	9.06	0.99	7.99	9.08	1.09

TABLE 2

THE ELECTRONEGATIVITIES OF ALUMINIUM ATOMS: *Al* ALUMINIUM ATOM OF THE ALUMINOXANE IN THE TRIPLE COMPLEX II; *Al*-ALUMINIUM ATOM OF THE ACCEPTOR $\text{Et}_x\text{AlCl}_{3-x}$ ($x = 1, 2, 3$) IN THE TRIPLE COMPLEXES II AND III, AND *Al'*-ALUMINIUM ATOM OF THE FREE ACCEPTOR. THE ELECTRONEGATIVITY OF THE ALUMINIUM ATOM *Al* IN COMPLEX I EQUAL 1.36

Acceptor	EtAlCl_2	Et_2AlCl	Et_3Al
<i>Al</i>	1.49	1.46	1.39
<i>Al</i>	1.47	1.38	1.36
<i>Al'</i>	1.50	1.44	1.36

plexes. The signals of protons of the ethyl groups of free aluminosane were not observed, which shows that the exchange of benzonitrile between complex I and $\text{Et}_x\text{AlCl}_{3-x}$ ($x = 1, 2$) does not take place.



The electronegativities of aluminium atoms in the triple complexes II and III were calculated according to the modified Dailey—Shoolery equation [4,5] (Table 2). An increase in the *Al* electronegativity with increasing acidity of organoaluminium compounds added was found. Simultaneously a decrease in the *Al* electronegativity in complexes II and III occurred (Table 2). The changes in electronegativities observed were caused by the donor effect of the oxygen atom towards the *Al* atoms. The *Al* atoms became more acidic, and this was confirmed by IR spectra. In the IR spectra of I the band at 2270 cm^{-1} was assigned to the vibrations of the $\text{C}\equiv\text{N}$ groups of complexed benzonitrile. The addition of Et_2AlCl or EtAlCl_2 to the solution of I with a 1 : 1 molar ratio caused a shift of the $\text{C}\equiv\text{N}$ band to higher frequencies: by 4 cm^{-1} and 6 cm^{-1} respectively. When Et_3Al was added such a shift was not observed. Since the PMR spectra excluded the formation of a complex between $\text{Et}_x\text{AlCl}_{3-x}$ ($x = 1, 2$) and benzonitrile in these conditions (see equation), the shift of the $\text{C}\equiv\text{N}$ band was caused by the formation of the triple complexes II and III (Table 3). An increase of the molecular weight in the mixture of I and the organoaluminium compound was observed, which is possible only when II and III are formed. In the case of Et_2Zn and Me_2Zn such an increase was not observed. The molecular weight was an average between that of the organozinc compound and I.

The aluminosane oxygen atom in the systems investigated exhibits donor properties only towards the acceptor metal atoms, the acidity of which is higher

TABLE 3

CRYOSCOPIC MOLECULAR WEIGHT MEASUREMENTS OF THE MIXTURE OF I WITH AN ACCEPTOR (MOLAR RATIO 1 : 1) IN BENZENE AS SOLVENT. MOLECULAR WEIGHT OF COMPLEX I EQUALS 289

Acceptor	Me_2Zn	Et_2Zn	Et_3Al	Et_2AlCl	EtAlCl_2
Molecular weight	190	210	336	340	360
Molar participation of the triple complex	0	0	0.50	0.80	0.85

than the acidity of the aluminium atom in I (Table 2). The lower acidity of the zinc atom in the organozinc compounds may be the reason why these compounds do not form triple complexes. According to the cryoscopic molecular weight determinations, the formation of the triple complex in the case of Et_3Al could be suggested. However, the acidity of the aluminium atom in Et_3Al is similar to that in I and is too weak to cause the electron transfer along the Al—O bond. The acidity of the aluminium atom in Et_2AlCl or EtAlCl_2 is higher than in I, and is sufficient to cause the electron transfer along the Al—O bond.

References

- 1 A. Storr, K. Jones and A.W. Laubengayer, *J. Amer. Chem. Soc.*, **90** (1968) 3173.
- 2 M. Boleslawski, S. Pasynkiewicz, A. Kunicki and J. Serwatowski, *J. Organometal. Chem.*, **128** (1977) 21.
- 3 J. Florjańczyk, Ph.D. Thesis, Technical University (Politechnika) Warsaw, Poland, 1974.
- 4 B.P. Dailey and J.N. Shoolery, *J. Amer. Chem. Soc.*, **77** (1955) 3977.
- 5 P.T. Narasimhan and M.T. Rogers, *J. Amer. Chem. Soc.*, **82** (1960) 5983.
- 6 T. Takeshita and W.E. Frankle, *Tetrahedron Lett.*, **56** (1968) 5913.