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^{13}C NMR SPECTRA OF ORGANOALUMINUM COMPOUNDS: EVIDENCE FOR AN OXYGEN—ALUMINUM π-INTERACTION

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Summary

The ^{13}C NMR spectra of some trialkylaluminum compounds and a series of alkoxy-bridged and amido-bridged organoaluminum compounds are reported and discussed. In the alkoxy-bridged compounds the O—C resonance is sensitive to substitution at the aluminum atom and the degree of oligomerization. In the amido-bridged compounds the analogous carbon (N—C) resonance shows no variation upon changes of substituents at the aluminum. These observations are used as evidence for the existence of an oxygen to aluminum $p_\pi—d_\pi$ dative bond in the alkoxy-bridged compounds.

Introduction

Although ^{13}C NMR has been shown to be a useful structural probe in organometallic chemistry there have been few reports of ^{13}C NMR studies of organoaluminum compounds [2—4]. In this paper the ^{13}C NMR spectra of some trialkylaluminum compounds, some alkoxy-bridged organoaluminum compounds and some amido-bridged species will be reported and discussed. This paper represents a preliminary investigation to establish ^{13}C spectral characteristics of acido-bridged species so that an investigation of the more complex aminoethoxy derivatives could be undertaken. The results of the aminoethoxy compounds will be presented in a subsequent paper.

The trigonal geometry about the oxygen atom observed in all structural investigations of dimer and trimer alkoxy-bridged organoaluminum compounds [5—8] (Fig. 1) has led to postulation of an oxygen to aluminum $p_\pi—d_\pi$ dative bond in these species [6,7]. Recent ab initio molecular orbital calculations on $(H_2AlOH)_2$ and related species suggest that the oxygen is trigonal as the result of intramolecular Van der Waal's repulsions [9]. It is interesting to note that in

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* Taken in part from the Ph. D. Thesis [1].

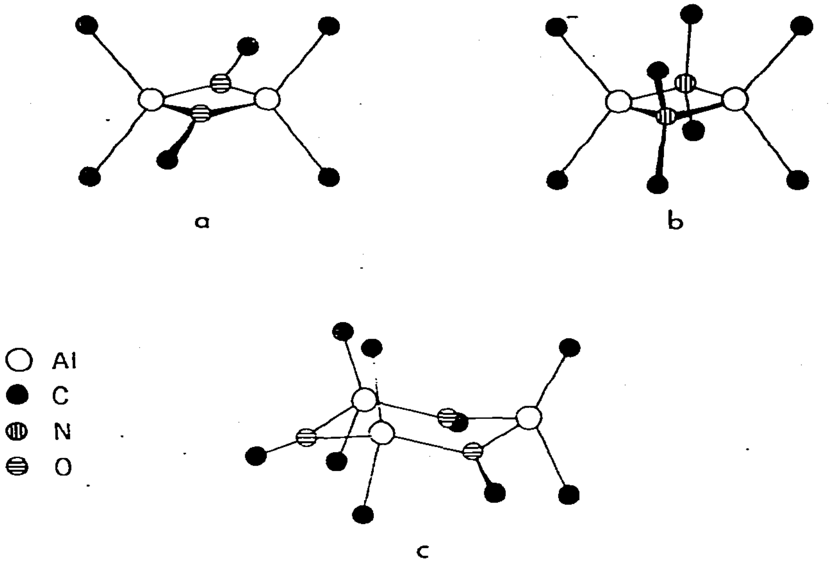

Fig. 1. Molecular structures of (a) dimeric dialkylaluminum alkoxides, (b) dimeric dialkylaluminum dialkylamides, and (c) trimeric dialkylaluminum alkoxides.

$(Me_2AlSMe)_2$, where intramolecular Van der Waal's repulsions should be of the same order of magnitude as those in oxygen-bridged species and where the sulfur would not be expected to π-bond, the sulfur atom displays pyramidal geometry [10]. The ^{13}C NMR data presented in this paper have been interpreted as supporting evidence for the existence of an oxygen to aluminum p_π—d_π dative bond in alkoxy-bridged organoaluminum compounds.

Experimental

Instrumentation. ^{13}C NMR spectra were obtained with a Bruker HX-90E NMR Spectrometer operating in the Fourier transform mode at 22.63 MHz. Transients were accumulated by a Nicolet B-NC-12 computer. Spectra were routinely obtained with broad-band proton decoupling and 500—2000 transients were usually sufficient to obtain well resolved spectra. The 25° C spectra were obtained using the solvent n-heptane except in the cases of methylchloroaluminum methoxide and all of the dichloroaluminum derivatives which for solubility enhancement were studied in *o*-dichlorobenzene. Both of these solvents were used with 20% benzene-d_6 as a lock and 5% TMS as an internal reference. Toluene was used as a solvent for the low temperature spectrum of trimethylaluminum with toluene-d_8 as a lock and 5% TMS as an internal reference. Chemical shifts downfield from TMS are reported as positive.

Aluminum alkyls. These compounds were obtained from Texas Alkyls and used without further purification.

Alkoxy-bridged compounds. These compounds were prepared according to reported techniques [11]. Their purities were confirmed by comparison of their ^1H NMR and infrared spectra with the reported spectra.

Amido-bridged compounds. These compounds were prepared according to

TABLE 1

^{13}C CHEMICAL SHIFTS OF TRIALKYLALUMINUM COMPOUNDS

Compound	Temperature (°C)	C(1)[a]	C(2)[a]
Me_3Al	25	−7.28	
Me_3Al	−75		
bridging		−5.34	
terminal		−8.09	
Et_3Al	25	0.75	8.74

[a] values listed are chemical shifts relative to internal TMS.

TABLE 2

^{13}C CHEMICAL SHIFTS OF SOME NITROGEN-BRIDGED ALUMINUM COMPOUNDS

Compounds	C(1)[a]	C(2)[a]	C(3)[a]	C(4)[a]
$(Me_2AlNEt_2)_2$	~11		39.87	11.82
$(Et_2AlNEt_2)_2$	~0	9.60	39.92	12.41
$(EtClAlNEt_2)_2$		8.47	39.86	12.24
$HNEt_2$ [b]			44.1	15.4
$(Me_2AlNMe_2)_2$			41.91	
$(Et_2AlNMe_2)_2$		9.22	41.75	
$(MeClAlNMe_2)_2$			41.97	
$(Cl_2AlNMe_2)_2$			42.07	
$HNMe_2$			39.02	

[a] Values listed are chemical shifts relative to internal TMS at 25°C. [b] Taken from ref. 21.

TABLE 3

^{13}C CHEMICAL SHIFTS OF ALKOXY-BRIDGED ALUMINUM COMPOUNDS

Compound	C(1)[a]	C(2)[a]	C(3)[a]	C(4)[a]
$(Me_2AlOMe)_3$			50.76	
$(Et_2AlOMe)_3$	~1	8.95	51.41	
$(Et_2AlOMe)_2$		8.63	50.00	
$(MeClAlOMe)_3$			53.51 [b] 53.00 [b]	
$(EtClAlOMe)_3$	~1	8.09	53.81 [b] 53.99 [b]	
$(EtClAlOMe)_2$		8.01	52.81	
$(Cl_2AlOMe)_3$			57.12	
HOMe [c]			49.3	
$(Me_2AlOEt)_3$			60.30	
$(Me_2AlOEt)_2$			58.74	18.34
$(Et_2AlOEt)_2$	~0	8.79	59.34	18.45
$(MeClAlOEt)_3$			63.97 [b] 63.81 [b]	17.64
$(MeClAlOEt)_2$			61.12	17.85
$(EtClAlOEt)_3$		8.20	64.03 [b] 64.24 [b]	17.69
$(EtClAlOEt)_2$		8.20	61.33	17.69
$(Cl_2AlOEt)_3$			66.78	17.10
$(Cl_2AlOEt)_2$			62.14	17.96
HOEt [c]			57.3	17.9

[a] Values listed are chemical shifts relative to internal TMS at 25°C. [b] trans-Isomer. Most intense peak listed first. [c] Taken from ref. 20.

reported techniques [12] and their purities were confirmed by ^{1}H NMR and infrared spectroscopy.

Results

The ^{13}C chemical shifts of trimethyl- and triethyl-aluminum are listed in Table 1. The chemical shifts of the amido-bridged compounds RR'AlNR$_2''$ (RR' = Me$_2$, Et$_2$, EtCl; R'' = Et: RR' = Et$_2$; Me$_2$, MeCl, Cl$_2$; R'' = Me; Me = CH$_3$; Et = C$_2$H$_5$) are listed in Table 2. The chemical shifts of the alkoxides (RR'AlOR'')$_n$ (RR' = Me$_2$, Et$_2$, MeCl, EtCl, Cl$_2$; R'' = Me, Et, n = 2, 3) are listed in Table 3.

Discussion

In discussing spectral features carbon atoms will be numbered according to the following scheme.

C—C—Al—O(N)—C—C
2 1 3 4

Trialkylaluminum compounds. The spectra of trimethyl- and triethylaluminum at room temperature show resonances characteristic of only one alkyl group, consistent with exchanging bridging and terminal alkyl groups [3,13—18]. Thus trimethylaluminum shows one resonance at —7.28 ppm and triethylaluminum shows one C(1) resonance at 0.75 ppm and one C(2) resonance at 8.74 ppm. The low temperature spectrum (—75°C) of trimethylaluminum shows two resonances for C(1), assigned by relative intensities to the bridging C(1) at —5.34 and the terminal C(1) at —8.09 ppm. Similar results have been observed in the low temperature ^{13}C NMR spectra of triethylaluminum and tri-n-propylaluminum [3] and in the low temperature ^{1}H NMR spectrum of trimethylaluminum [19]. In both trimethyl- and triethylaluminum the C(1) resonance is relatively sharp at 25°C. These are the only cases observed in this study where C(1) was sharp. For all other compounds C(1) is observed to be extremely broad apparently due to quadrupolar coupling of C(1) to the ^{27}Al nucleus ($I = 5/2$).

Amido-bridged and alkoxy-bridged compounds. In the amido-bridged compounds the C(1) resonance was observed to be extremely broad and usually not resolvable. For these compounds the data in Table 2 indicate the C(2), C(3) and C(4) resonances show relatively small variations among the derivatives. In the case of the NEt derivatives the C(3) values are within 0.10 ppm of each other, while the C(2) and C(4) values have ranges of 1.1 ppm and 0.6 ppm respectively.

Most of the alkoxy-bridged compounds studied exist in dimer—trimer equilibrium in hydrocarbon solvents [11]. The ^{13}C chemical shifts for the observed dimer and trimer species are found in Table 3. To assign the dimer and trimer resonances, spectra were recorded at several temperatures ranging from 25—70°C. Peaks increasing in intensity with increasing temperature were assigned to the dimer species. As in the amido-bridged compounds C(1) was broad and generally not resolvable in all of the alkoxy-bridged compounds. As can be seen in Table 3, only the C(3) resonance exhibits a high sensitivity to substitution at the aluminum and to the degree of oligomerization. The C(3) resonance is shifted downfield in the series $R_2Al < RClAl < Cl_2Al$ in both the dimer and trimer oligomers of the observed methoxy- and ethoxy-bridged compounds.

The effect observed in going from RClAl derivatives to Cl_2Al derivatives may be due in part to aromatic solvent effects since the latter were studied in o-dichlorobenzene. In studies of related acido-bridged organoaluminum compounds we have observed no solvent effects in the ^{13}C resonance of C(3).

The trends in the C(3) chemical shifts can be accounted for by considering the inductive effects of the non-bridging aluminum substituents. If a mechanism prevails for transmission of these effects to C(3) it should be expected that successive replacement of alkyl groups by chloride would result in downfield shifts of the C(3) resonance. Indeed relatively large shifts in the C(3) resonance (2.0—4.5 ppm) of the alkoxy-bridged compounds accompanying each chloride substitution are observed. Corresponding substitutions in the amido-bridged compounds, however, result in shifts of the C(3) resonance position no larger than 0.1 ppm with each chloride substitution. This suggests that the mechanism which is transmitting inductive effects from aluminum to C(3) in the alkoxy compounds is not operative in the amido compounds.

There is no obvious reason to believe that differences in the σ-bonding systems of the amido- and alkoxy-bridged compounds are sufficiently large to account for the striking differences in the effects of substituent variation at aluminum. Since only the alkoxy compounds have non-bonding electrons on the bridging atom and thus the possibility of a p_π—d_π dative bond, it is proposed that a π-bonding system is responsible for the observed transmission of substituent effects.

The C(3) resonances of all trimeric alkoxy compounds studied are downfield from those of the corresponding dimers by at least 1.1 ppm. If the proposed p_π—d_π dative bond is present in both oligomers this observation suggests a stronger π-bond in the trimer. The infrared data reported for these compounds [11] are consistent with this model in that the trimeric species always have lower C—O stretching frequencies than the corresponding dimers.

In all alkoxy derivatives the C(3) resonance is downfield from that of the corresponding carbon in the parent alcohol (see Table 3). This observation is consistent with any mechanism which removes electron density from the bridging oxygen including a p_π—d_π dative bond. In the amido derivatives the C(3) resonance is upfield from that of the parent amine (see Table 2). This indicates the prevalence of a shielding mechanism which exceeds any deshielding arising from negative inductive effects through the Al—N σ-bonding system. It is generally accepted that hydrogens on carbons separated by two intervening carbons, if in the proper spatial orientation, can interact to give rise to upfield shifts of the carbon resonance (this is the so-called γ-effect or steric shift) [20—22]. The C(3) carbon and the substituent on aluminum are separated by two atoms in both the alkoxy- and amido-bridged compounds. In dimeric amido-bridged species with a planar Al—N ring [23] (Fig. 1) the aluminum and nitrogen substituent would be "locked" into the proper spatial orientation to give an upfield shift. This may account for the upfield shift in the amido-bridged species relative to parent amine. Although the same effect could be proposed for the alkoxy-bridged species calculations using the expression derived by Cheney and Grant [22] show that in these compounds there is no basis for expecting a steric shift.

In conclusion this study indicates that as a probe for studying the nature of the aluminum atom in organoaluminum compounds the C(1) and C(2) resonances are generally insensitive to variations in the inductive effect of other substituents on aluminum. Indeed the C(1) resonance is generally inaccessible. The requirements for a useful ^{13}C NMR probe of the electronic properties of aluminum are a carbon atom sufficiently remote to preclude quadrupolar relaxation by ^{27}Al but sufficiently interactive with the electronic system of the aluminum atom to detect the effects of substituent variation. These requirements are met by C(3) in the case of alkoxy-bridged species where a p_π—d_π dative bond appears to furnish the mechanism for transmission of the electronic effects. The existence of this π-interaction is further supported by the lack of sensitivity of C(3) to substituent variation at aluminum in the amido-bridged species where there can be no π-interactions.

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References

1 L. Cocco, Ph. D. Thesis, University of Iowa, 1975.
2 L. Zetta and G. Gatti, Org. Mag. Res., 4 (1972) 585.
3 O. Yamamoto, K. Hayamiza and M. Yamagisawa, J. Organometal. Chem., 73 (1974) 17.
4 M. Uetsuki and Y. Fujiwara, Bull. Chem. Soc. Japan, 50 (1977) 673.
5 M. Bonamico and G. Dessy, J. Chem. Soc., (1968) 291.
6 A. Haaland and O. Stokkeland, J. Organometal. Chem., 94 (1975) 345.
7 D.A. Drew, A. Haaland and J. Weidleim, Z. Anorg. Allg. Chem., 398 (1973) 241.
8 M. Bonamico and G. Dessy, J. Chem. Soc., (1967) 1786.
9 O. Gropen, R. Johnson, A. Haaland and O. Stokkeland, J. Organometal. Chem., 92 (1975) 197.
10 A. Haaland and O. Stokkeland, J. Organometal. Chem., 94 (1975) 353.
11 W.E. Rhine and D.P. Eyman, Inorg. Chem., to be submitted.
12 E. Howell, Ph. D. Thesis, The University of Iowa, Iowa City, Iowa, 1970.
13 N. Muller and D.E. Pritchard, J. Amer. Chem. Soc., 82 (1960) 248.
14 E.G. Hoffmann, Trans. Faraday Soc., 58 (1962) 642.
15 K.C. Ramey, J.F. O'Brien, I. Hasegawa and A.E. Borchest, J. Phys. Chem., 69 (1965) 3418.
16 M.P. Groenewege, J. Smidt and H. De Vries, J. Amer. Chem. Soc., 82 (1960) 4425.
17 K.C. Williams and T.L. Brown, J. Amer. Chem. Soc., 88 (1966) 5460.
18 E.A. Jeffery and T. Mole, Australian J. Chem., 22 (1969) 1129.
19 E.G. Hoffmann, Bull. Chim. Soc. France, 7 (1963) 1467.
20 J.B. Stothers, 'Carbon-13 NMR Spectroscopy', Academic Press, New York, 1972.
21 G.C. Levy and G.L. Nelson, Carbon-13 Nuclear Magnetic Resonance for Organic Chemists, Wiley-Interscience, New York, 1972.
22 D.M. Grant and B.V. Cheney, J. Amer. Chem. Soc., 89 (1967) 5315.
23 H. Hess, A. Hinderer, and S. Steinhauser, Z. Anorg. Allg. Chem., 377 (1970) 1.