^{13}C NMR spectra and electronic structure of alkenylalanes

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The parameters of ^{13}C NMR spectra of linear and cyclic alkenylalanes synthesized from mono- and disubstituted acetylene and the simplest alkylalanes have been obtained. A strong paramagnetic effect of the aluminum atom on shielding of α- and β-carbon atoms at the double bond has been observed for the dimeric form of organoaluminum compounds (OAC) in inert solvents, unlike that for the monomeric form solvated in electron-donor solvents (Et_2O, THF, and Et_3N). The results were interpreted in terms of the model of the electron density redistribution on going from the dimeric structure of OAC to the monomeric one. The PM3 method describes most adequately (as compared to MNDO and AM1) the equilibrium geometry of cyclic dimers of OAC.

Key words: ^{13}C NMR spectroscopy, electronic structure, alkenylalanes, quantum-chemical calculations.

Previously,[1—3] we have described the parameters of the ^{13}C NMR spectra of several higher OAC, including tris(4-*Z*-hexenyl)aluminum[1] in which the intramolecular π—p-interaction between the multiple bond of the hexenyl substituent and vacant p-orbital of the Al atom was assumed to be similar to that in tris(4-pentyl)aluminum.[4]

In this work, we obtained the parameters of the ^{13}C NMR spectra of new linear and cyclic alkenylalanes and performed the comparative analysis of their electronic structure established by the semiempirical MNDO,[5] AM1,[6] and PM3 [7] methods.

Experimental

Synthesis of compounds 1—4 was carried out by a known procedure.[8] Compounds **5—9** were obtained according to previously developed methods.[9,10] Samples were purified by prolonged pumping at 60 °C.

^{13}C NMR spectra were recorded on JEOL FX-90Q (22.5 MHz) and Bruker AM-300 (75.5 MHz) spectrometers with external and internal (C_6D_6) stabilization of the signal of the deuterated solvent. The spectra were recorded with complete proton decoupling and in the absence of the latter with the retention of the Overhauser effect (Gated Decoupling). Spectra of samples containing no traces of solvents, starting organoaluminum compounds (OAC), and oxidation products were considered. The dehydrated solvents added were injected by a syringe through a rubber plug to a sealed NMR ampule. Solutions of OAC (30%) were used for recording spectra.

Quantum-chemical calculations were performed by the AMPAC 2.1 program.[11]

Results and Discussion

The parameters of the ^{13}C NMR spectra of alken-1-yl-1-dialkylalanes **1—9** obtained in inert and electron-donor solvents and without solvent are presented in Table 1.

The spectral parameters of the saturated carbon atoms of the alkenyl substituents and phenyl groups agree with the values for normal hydrocarbons[12] and the corresponding products of deuterolysis **10—14**. Anomalous downfield chemical shifts are observed for the α- and β-carbon atoms at the multiple bond of alkenylalanes, which are evidence for their efficient deshielding. Unlike the ^{13}C NMR spectra of alkenylalanes recorded in the absence of solvents or in an inert solvent, the spectra of OAC recorded in Et_2O or Et_3N (for compound **9**) exhibit deshielding of the α-carbon atom (+28.20 ppm in compound **9**) and weakening of the deshielding effect on the β-carbon atom (−43.37 ppm in compound **3**). The direct spin-spin coupling constants (J_{CH}) also tend to decrease on going from nonpolar to polar solvents.

The observed effects of changing the chemical shifts (CS) were interpreted in terms of the known model of formation of the dimeric form (**A**) of the OAC studied with the bridging α-carbon atom at the double bond[13] in inert solvents and the monomeric form (**B**) with a solvent molecule involved in the coordination sphere of the Al atom (Scheme 1).

For studying the decomposition of the dimer in more detail, experiments with the fractional addition of elec-

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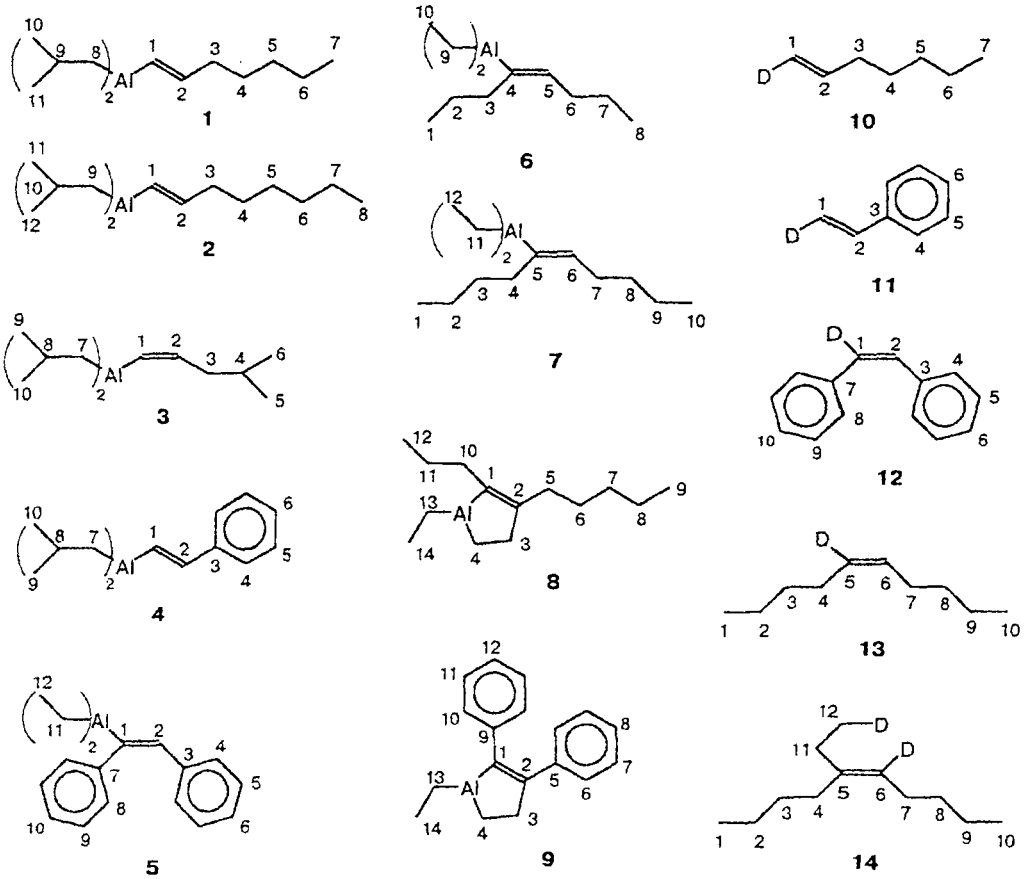
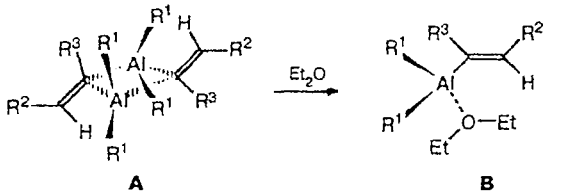
Table 1. ^{13}C NMR spectra of alkenyl organoaluminum compounds ($SiMe_4$)

Compound	Solvent (T/°C)	δ ($^1J_{C-H}$/Hz)													
		C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)	C(10)	C(11)	C(12)	C(13)	C(14)
1	— (20)	127.30 d	186.30 d	41.50 t	28.52 t	32.46 t	22.75 t	14.28 q	23.94 t	26.36 d	28.31 q	28.31q			
	Et_2O (20)	140.49 d (117.7)	149.07 d (140.0)	39.69 t (129.5)	29.53 t	31.62 t	23.13 t	14.30 q	23.42 t	26.15 t	28.71 q	28.62 q			
	C_6D_6 (20)	126.60 d (124.3)	186.01 d (143.9)	40.60 t (127.1)	28.59 t	31.61 t	22.62 t	14.00 q	24.67 t	26.42 t	28.08 q	28.08 q			
	C_6D_6 (70)	127.32	185.75	40.64	28.57	31.71	22.63	13.86	24.60	26.41	28.27	28.27			
2	— (20)	126.71 d (124.5)	185.42 d (151.3)	40.54 t	27.22 t	29.05 t	31.87 t	22.59 t	14.03 q	24.35 t (119.6)	26.44 d (125.0)	28.13 q (124.1)	28.13 q (124.1)		
	Et_2O (20)	140.15 d (119.0)	148.70 d (145.4)	39.36 t (126.8)	29.11 t	29.54 t	32.12 t	22.91 t	14.36 q	23.55 t	26.70 d	28.53 q	28.53 q		
3	— (20)	127.16 d (124.3)	184.79 d (147.1)	47.58 t (126.5)	28.00 d	22.52 q	22.52 q	23.83 t	26.24 d	28.00 q	28.00 q				
	Et_2O (20)	140.15 d (119.3)	141.52 d (141.2)	46.09 t (126.5)	29.18 d	22.65 q	22.65 q	24.20 t	26.57 d	28.53 q	28.53 q				
4	— (20)	126.12 d	179.70 d (152.4)	136.43 s	128.79 d	128.47 d	133.43 d	21.41 t	26.31 d	28.00 q	28.00 q				
5	C_6D_6 (20)	145.63 s	162.08 d (152.3)	136.49 s	128.99 d	127.68 d	126.90 d	144.79 s	130.88 d	127.94 d	125.92 d	1.89 t	9.20 q		
6	— (20)	15.08 q	23.70 t	34.08 t (123.5)	140.48 s	177.48 d (154.4)	35.45 t (125.1)	22.32 t	14.30 q	1.04 t	9.01 q				
	Et_2O (20)	14.25 q	24.41 t	35.31 t	152.81 s	140.93 d	30.68 t	23.76 t	14.95 q	0.64 t	9.03 q				
7	— (20)	13.90 q	22.85 t	32.51 t	28.00 t	141.52 s	176.57 d (145.6)	27.81 t	30.61 t	22.0 t	13.90 q	23.63 t	26.50 d	28.53 q	28.53 q
	Et_2O (20)	13.71 q	22.13 t	32.51 t	33.55 t	152.55 s	151.45 d (150.8)	32.70 t	31.66 t	22.13 t	14.29 q	23.63 t	26.70 d	28.83 q	28.83 q
8	— (20)	131.30 s	192.30 s	36.04 t	5.36 t	32.96 t	28.73 t	32.56 t	22.85 t	14.23 q	35.18 t	22.43 t	14.95 q	1.24 t	9.04 q
	Et_2O (20)	159.28 s	151.18 s	36.19 t	4.18 t	35.06 t	29.53 t	31.79 t	23.11 t	14.36 q	35.32 t	22.57 t	14.82 q	2.06 t	9.60 q
9	— (20)	130.29 s	194.59 s	38.32 t	6.01 t (116.2)	141.39 d	128.88 d	127.56 d	126.70 d	148.05 s	130.29 d	127.55 d	124.48 d	2.75 t	9.50 q
	Et_3N (20)	158.49 s	154.19 s	37.66 t (125.0)	3.07 t (116.2)	145.11 s	127.55 d	127.55 d	125.33 d	145.80 s	128.90 d	126.72 d	122.58 d	2.15 t (117.7)	10.05 q (123.5)



Scheme 1



A B

R^1 = alkyl; R^2 = alkyl, aryl; R^3 = H, alkyl, aryl

Table 2. Calculated charges (q) on C_α/C_β atoms for alkenylalane molecule **1**, its complex with Et_2O (**1** · Et_2O), and cyclic dimer (**1** · **1**)

Method of calculation	$q(C_\alpha)/q(C_\beta)$		
	1	**1** · Et_2O	**1** · **1**
MNDO	−0.29/−0.08	−0.24/−0.10	−0.38/+0.11
AM1	−0.36/−0.14	−0.29/−0.16	−0.40/+0.03
PM3	−0.37/−0.07	−0.36/−0.14	−0.43/+0.09

tron-donor solvents to an NMR tube with individual OAC were carried out. When additions of Et_2O were introduced into an NMR tube with OAC **1**, the signals of the C atoms at the double bond are broadened and disappear when the composition approaches the equimolar Et_2O : OAC ratio. When the ratio is 1 : 1, the signals of the C atoms at the double bond of OAC appear, whose CS correspond to those presented in Table 1 for monomeric ether complexes **B**. The disappearance of the signals of the C atoms at the double bond attests to the dimer–monomer equilibrium in an excess of OAC. In an excess of Et_2O, the equilibrium is shifted to the formation of complex **B**. A similar situation is observed for acyclic OAC **5** and cyclic OAC **9**.

Quantum-chemical semiempirical MNDO, AM1, and PM3 calculations were used to estimate the electronic effects on going from the dimeric to solvated monomeric forms and to analyze the shielding effects in the ^{13}C NMR spectra of the OAC under study. It is shown (Table 2) that in the case of alkenylalane **1**, all methods give a similar pattern of the electron density redistribution on the C atoms at the double bond on going from **A** (**1** · **1**) to **B** (**1** · Et_2O).

The results obtained agree qualitatively with the data in Table 1. For example, on going from **A** to **B**, the shift of the signal by +12 ppm corresponds to the decrease in the electron density on the α-carbon atoms in compound **1** by +0.06 electron charge units (PM3), and the shift by −36 ppm corresponds to the increase in shielding of the C_β nucleus by −0.23 electron charge units.

As can be seen from Table 1, the effect of changing CS is observed for alkenylalanes obtained from both

Table 3. Comparative parameters of trimethylaluminum and (3,3-dimethyl-1-buten-1-yl)(diisobutyl)alane dimers in MNDO/AM1/PM3 approximations (experimental values from the XDA data[15,16])

Parameter	Trimethylaluminum dimer	Di(μ-*trans*-3,3-dimethyl-1-buten-1-yl)-(tetraisobutyl)dialane
	Distance/Å	
Al—C_{br}	2.05/2.78/2.27 (2.15)	2.00/1.96/2.02 (2.11)
Al—C_{nonbr}	1.85/1.79/1.94 (1.96)	1.90/1.82/2.03 (—)
Al—Al	2.51/2.55/2.57 (2.60)	2.65/2.58/2.61 (2.68)
	Angle/deg	
Al—C_{br}—Al	75.8/54.4/69.2 (74.7)	82.7/82.4/80.4 (79.0)
	ΔH^*/kcal mol^{-1}	
	−37.9/−17.2/−0.1	−34.3/−19.7/−39.1

* Enthalpy of dissociation to monomers.

terminal (**1**—**4**) and internal acetylenes (**5**—**7**) and alumacyclopentenes (**8**, **9**). According to the calculations, the change in the charges on the C_α and C_β atoms in compound **6** on going from the dimeric form to its complex with Et_2O is close to a similar change for compound **1**.

The study has shown that the PM3 method describes most adequately (as compared to MNDO and AM1) the equilibrium geometry of cyclic dimers of trimethylaluminum and (3,3-dimethyl-1-buten-1-yl)(diisobutyl)alane (Table 3). Unsatisfactory results on the calculation of the dimerization energy of monomeric OAC are explained by the underestimation of the stability of the three-centered bond inherent in the MNDO method.[14]

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