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MODIFICATION OF OLEFIN POLYMERIZATION CATALYSTS

II *. A ^{29}Si NMR STUDY ON THE COMPLEXATION OF SILYL ETHERS WITH TRIETHYLALUMINIUM

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Summary

The effect of complexation with a Lewis acid, $AlEt_3$, and alkylation on the chemical shift of silyl ethers has been studied using ^{29}Si NMR spectroscopy. The substitution of a methoxy group for an ethyl group shifts the ^{29}Si signal on an average by 36.9 ppm to lower field, and the signal for the complexed silyl ether is usually shifted to lower field compared with that for the uncomplexed ether, the shift varying between -1.4 and 18.1 ppm. Dynamic processes have been observed for some of the spectra; this is interpreted in terms of competition of Al acceptors for the several silyl ethers simultaneous present.

Introduction

Aluminium alkyls are widely used as cocatalysts with $TiCl_3$ in Ziegler–Natta catalysts. In order to combine a high activity with a good stereoselectivity the cocatalyst contains a complex of trialkylaluminium (AlR_3) and an electron donor (ED). A wide range of O, N, S and P donors such as ethers, esters, and amines have been claimed to be effective [1,2].

Trialkylaluminium compounds tend to react chemically with these Lewis base donors especially at elevated temperatures and high concentrations of AlR_3; the products are aldehydes, ketones and primary alkoxy derivatives. The formation and stability of these complexes and reaction products have been studied by ^{1}H, ^{13}C NMR, IR and UV spectroscopic methods [3–5].

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There are no reports of NMR studies on the interactions of silyl ethers with AlR_3. Silyl ethers were considered to be good candidates for the NMR studies because the sensitivity of the ^{29}Si shifts to the structural changes greatly assists structure elucidation. The ^{29}Si resonance frequency, in particular, depends strongly on the number of oxygen atoms bonded to the silicon strongly [6].

However, in spite of intensive research on silicon compounds since the advent of FT NMR method the chemical shift data for silyl compounds are still quite incomplete. This is especially true for silyl ethers of the type $RR'_nSi(OR'')_{3-n}$. Similarly, no data are available for the effects of complexation of silyl ethers with Lewis acids. There are, however, some empirical and semi-empirical models for interpretation and prediction of the chemical shifts [6]; these models are based on additive substituent effects or mutual interaction approach, but they have not given very satisfactory results.

Experimental

All manipulations of the reagents were carried out under dry, oxygen free nitrogen (99.998%).

Materials

Triethylaluminium (Schering) (TEA) was stored in a dry box (Vacuum Atmospheres Co.) and used without purification. The silyl ethers, $RSi(OMe)_3$ ($R = Et$, n-Bu, Ph), $Ph_2Si(OMe)_2$ and $Si(OMe)_4$, were purchased from Petrarch. They were dried over 4Å molecular sieves and degassed with nitrogen before use. $PhEtSiCl_2$ and Ph_3SiCl were obtained from Petrarch and Aldrich, respectively.

$PhEtSi(OMe)_2$ and Ph_3SiOMe were prepared from the corresponding chloro compounds by treatment with methanol in benzene in the presence of pyridine in 70–73% yield [7]. $PhEtSi(OMe)_2$ was obtained as a colorless liquid: ^{13}C NMR (C_6D_6) δ 134.8, 133.6, 130.3, 128.2 (C_6H_5Si), 50.3 (SiOMe), 6.6 ($SiCH_2CH_3$), 4.6 ($SiCH_2$); ^{29}Si NMR (C_6D_6) δ -15.8. Ph_3SiOMe was recrystallized from hexane, Mp. 55 °C, ^{13}C NMR (C_6D_6) δ 135.8, 134.6, 130.2, 128.2 (C_6H_5Si), 51.6 ($SiOCH_3$); ^{29}Si NMR (C_6D_6) δ -11.1

$PhEt_2SiOMe$ was made from $PhEtSi(OMe)_2$ by a Grignard reaction [8]. The reaction was carried out in anhydrous diethyl ether. After 15 h reflux at 45 °C the mixture was treated with 10% aqueous HCl. The products were extracted with diethyl ether and evaporation of the extract yielded a yellow oil, which was vacuum distilled to give $PhEt_2SiOMe$ (B.p. 94–99 °C/9 mmHg). The yield was 32%. ^{13}C NMR (C_6D_6) δ 136.2, 134.3, 129.7, 128.1 (C_6H_5Si), 50.7 ($SiOCH_3$), 6.9 ($SiCH_2CH_3$), 5.0 ($SiCH_2$); ^{29}Si NMR (C_6D_6) δ 9.2.

NMR methods

The samples were examined in C_6D_6 (99% isotopic purity, Aldrich-Chemie) containing tetramethylsilane as reference. The procedure for the preparation of the NMR samples has been described elsewhere [9]. The spectra were measured on a Bruker AM-250 spectrometer operating at 62.9 MHz for ^{13}C and at 49.7 MHz for ^{29}Si.

The proton-decoupled ^{13}C and ^{29}Si spectra were obtained with the gated decoupling technique. The ^{13}C fids were recorded with a delay of 100 s and 10 kHz spectral width using quadrature detection and 64 k of memory. A delay of 600 s was used for ^{29}Si. Exponential weighting with line broadening of 1.8 and 1.5 Hz was employed for ^{13}C and ^{29}Si, respectively. The ^{13}C lines were referenced to the central line of C_6D_6 with δ 128.0 ppm. The ^{29}Si shifts are given in ppm relative to tetramethylsilane with shifts to lower field positive. The assignments of ^{13}C resonances were carried out by use of coupled spectra. The coupled ^{29}Si spectra were obtained using a polarization transfer technique; DEPT (recycling time 10 s, σ (^1H) 0.12 π and delay time $1/2J = 0.067–0.12$).

Results and discussion

The complexation between silyl ethers and triethylaluminium was studied in benzene solution at 25–75°C with variation of the molar ratio of the components and the heating time [9]. The starting compounds and/or the products can be arranged to form five series (n varies from 1 to 3 or 4):

$$\begin{array}{ccc} Ph_{4-n}Si(OMe)_n & PhSiEt_{3-n}(OMe)_n & Ph_{3-n}SiEt(OMe)_n \\ (I) & (II) & (III) \\ SiEt_{4-n}(OMe)_n & n\text{-}BuSiEt_{3-n}(OMe)_n & \\ (IV) & (V) & \end{array}$$

The products were identified by using ^{29}Si and ^{13}C NMR spectra. For the trimethoxyphenylsilane series, I, the products were also independently synthesized. In some cases the products could be assigned only as complexes with TEA, the chemical shift of the free compound remaining unknown.

From detailed spectral analyses and the synthesis of some of the suggested intermediates, we proposed the following scheme for the complexation and ethylation [9].

SCHEME 1

$$R_{4-n}Si(OMe)_n + 1/2(AlEt_3)_2 \rightarrow R_{4-n}Si(OMe)_n{}^{\star}AlEt_3 \rightarrow R_{4-n}SiEt(OMe)_{n-1} + AlOMeEt_2$$

$$\xrightarrow{1/2(AlEt_3)_2} R_{4-n}SiEt(OMe)_{n-1}{}^{\star}AlEt_3 \rightarrow$$

$$R_{4-n}SiEt_2(OMe)_{n-2} + AlOMeEt_2 \xrightarrow{1/2(AlEt_3)_2} R_{4-n}SiEt_2(OMe)_{n-2}{}^{\star}AlEt_3, \text{ etc.}$$

The ether can be alkylated $n-1$ times and the reaction is complete when only one methoxy group is left. Hydride formation is also observed.

The ^{29}Si chemical shifts for the free and complexed ethers are presented in Table 1 along with the chemical shift differences between the complexed and free silanes and the change in shift in successive ethylation steps.

The effect of alkylation and complexation on the ^{29}Si chemical shift is depicted in Fig. 1. A smooth curve is obtained except for deviations for Ph_4Si (δ -13.98 ppm [10]) in series I and Et_4Si (δ 7.10 ppm [11]) in series IV. These tetraorgano species are not, however, expected to complex or react with TEA. Consecutive steps on replacing a methoxy group by a less electronegative phenyl or ethyl group shift the silicon resonance almost regularly towards lower field. Silyl ethers with only one ether linkage (except Ph_3SiOMe) have a positive chemical shift.

There is a clear correlation between the chemical shift and the degree of alkylation of a methoxy group: the introduction of a methoxy group in place of an

TABLE 1

^{29}Si CHEMICAL SHIFTS FOR SOME SILYL ETHERS AND THEIR COMPLEXES WITH $AlEt_3$ (TEA)

	$\delta(^{29}Si)$ [a]		$\Delta\delta$(Compl. free) [c]	$\Delta\delta$(Ethylation) [c] $OMe_{n-1} - OMe_n$
	free	complexed [b]		
$PhSiOMe_3$	−54.6	−51.3	3.3	
				38.8
$PhSiEtOMe_2$	−15.8	−3.4	12.4	
				26.2
$PhSiEt_2OMe$	10.4	27.3	18.1	
$PhSiEt_2H$	−4.6 [e]			
Ph_2SiOMe_2	−29.0	−19.9	9.1	
				35.0 [d]
$Ph_2SiEtOMe$		15.1		
Ph_2SiEtH	−11.5 [f]			
Ph_3SiOMe	−11.0	2.7	13.8	
Ph_3SiH	−17.6 [g]			
$SiOMe_4$	−78.2	−79.5	−1.4	
				36.7
$EtSiOMe_3$	−41.5	−36.4	5.1	
				48.0 [d]
Et_2SiOMe_2		11.6		
Et_3SiOMe	22.6	39.7	17.1	
Et_3SiH	0.4 [h]			
n-$BuSiOMe_3$	−41.8	−34.1	7.9	
				55.8 [d]
n-$BuSiEtOMe_2$		21.7		
				17.5 [d]
n-BuSiEtOMe		39.2		

[a] C_6D_6 solutions with respect to TMS at 49.7 MHz for ^{29}Si. [b] Average value, depending on the molar ratio, temperature, and heating time with TEA. [c] Average value. [d] Calculated from the complexed values. [e] ^1J(Si-H) 198.2 Hz. [f] ^1J(Si-H) 191.0 Hz. [g] ^1J(Si-H) 183.4 Hz. [h] ^1J(Si-H) 117.8 Hz, ^2J(Si-H) 6.9 Hz.

ethyl group shifts the ^{29}Si signal about 36 ppm to lower field, i.e. alkylation has a deshielding effect. The same is true for the complexation: the complexed silyl ether resonance is shifted to lower field compared to the free ether. The shift varies between −1.4 and 18.1 ppm. On complexation with $AlEt_3$ the shielding at silicon is diminished due to the electron withdrawing effect of aluminium via the oxygen. However, $SiOMe_4$ is an exception, in this case the complexation shields the silicon nucleus by −1.4 ppm, the deshielding effect of aluminium presumably being offset by the back donation from the methoxy groups.

The change in the chemical shift on complexation is largest when the molecule has only one methoxy group (see series $Ph_{4-n}Si(OMe)_n$, $PhSiEt_{3-n}(OMe)_n$ and $Et_{4-n}Si(OMe)_n$). It decreases with the increasing number of methoxy groups. This could be accounted for by assuming that the complexation of TEA with the donor occurs via the oxygen atom and involves a rapid exchange process. When the donor contains more than one methoxy group, the aluminium alkyl molecule can move between the equivalent coordination sites, and thus the change in the average chemical shift is smaller.

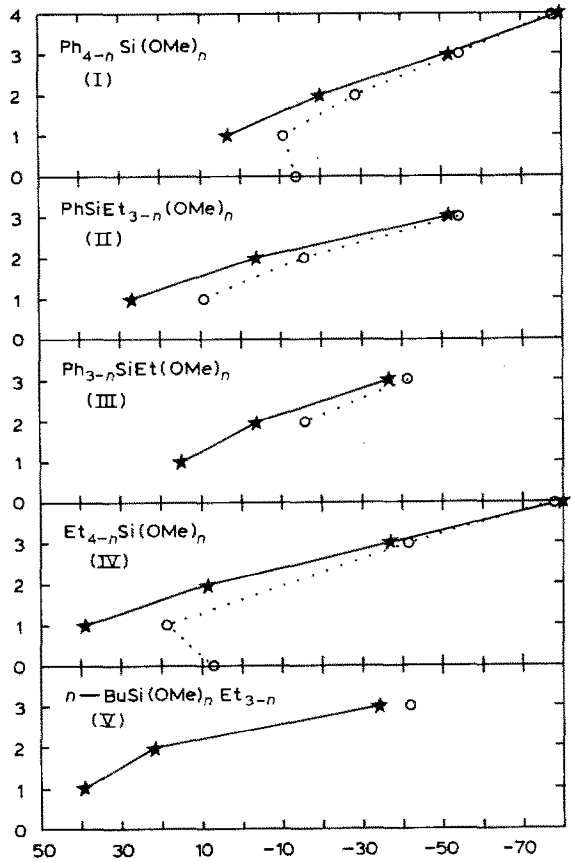


Fig. 1. The ^{29}Si chemical shifts for the free compounds (○) and complexes (★) of the series I–V. The values for the chemical shifts of Ph_4Si and Et_4Si are taken from refs. 10 and 11, respectively.

A small diamagnetic shift is observed after prolonged heating, when the compounds have undergone further reaction. This is also a general trend for other complexes, and can be attributed to the fall in the concentration of triethylaluminium arising from the alkylation reactions (see below).

Dynamic processes can also be observed in some spectra. The linewidths of the complexes are usually about the same as for the free compounds (2–3 Hz), but for two monomethoxy complexes this is not the case. When $PhEt_2SiOMe$*TEA is formed in the NMR tube from $PhSi(OMe)_3$ and TEA, the linewidth is 37.6 Hz (measured at room temperature after heating at 75°C for 120 h with an Al/donor ratio of 3/1). When $PhEt_2SiOMe$ was synthesized separately and then complexed with TEA, the half-width under same conditions was only 5.09 Hz. No broadening is observed when the Al donor ratio is 10/1. When the ratio was 3/1, the reactions of $PhSi(OMe)_3$ with TEA consumed all the aluminium alkyl to give aluminium monoalkoxides, $(AlEt_2OMe)_n$($n = 2,3$). These also form donor–acceptor complexes with Lewis bases but with great difficulty because of the strong Al–O–Al bridge bonds in the R_2AlOR autocomplexes [12]. Free $PhSiEt_2OMe$ is now also present

TABLE 2

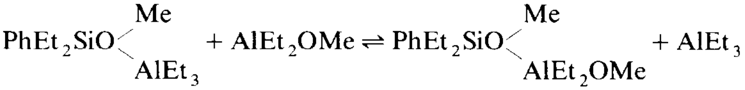
THE CHEMICAL SHIFT AND HALF-WIDTH OF THE ^{29}Si SIGNAL OF THE $PhSiEt_2OMe$*TEA COMPLEX [a]

Heating time (h)	Temp. (Measd.) (°C)	$\delta(^{29}Si)$ [b]	$\nu_{1/2}$ [c]
22	RT	27.1	1.8
60	RT	25.9	12.2
120	RT	24.9	28.2
120	50	24.4	6.1
120	5	25.6	81
120	−5	c.27	102

[a] 75°C, Al/donor = 3/1. The sample also contains also 1-hexene to prevent freezing of C_6D_6 at the lower measurement temperatures, molar ratio Al/hexene 1/0.5. [b] In ppm, reference TMS. [c] In Hz, TMS has a linewidth of about 1.8–4 Hz.

alongside the complexed species ($\nu_{1/2}$ 3.8 Hz). The linewidth of the resonance of the first alkylation product, $PhSiEt(OMe)_2$*TEA, is also broadened ($\nu_{1/2}$ 7.4 Hz under the same conditions as above), whereas that for the original complex, $PhSi(OMe)_3$*TEA, remains unchanged ($\nu_{1/2}$ 2.8 Hz, for TMS 4.3 Hz). This suggests that there is competition, being Al-acceptors from several reaction products present at the same time. The changes observed in the ^{29}Si spectra are presumed to be due to the fast exchange depicted in Scheme 2. This is the case also for the $Et_{4-n}Si(OMe)_n$ series, where marked broadening of the $Et_3Si(OMe)_n$*TEA complex can be observed after prolonged heating (130 h at 75°C, Al/donor = 3/1). Some data for $PhSiEt_2OMe$*TEA is presented in Table 2.

SCHEME 2



$$PhEt_2SiO\begin{matrix}^{\diagup Me}\\_{\diagdown AlEt_3}\end{matrix} + AlEt_2OMe \rightleftharpoons PhEt_2SiO\begin{matrix}^{\diagup Me}\\_{\diagdown AlEt_2OMe}\end{matrix} + AlEt_3$$

Due to the above-mentioned deviations from and non-linearity of the curves in Fig. 1, attempts fit the chemical shifts to some additive substituent effect model or to a mutual interaction approach are not successful. But it is reasonable to assume that the missing chemical shifts for the free silanes could be evaluated with fair accuracy from Fig. 1.

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