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Preliminary communication

NMR evidence of methyl group exchange between tetramethyltitanium and trimethylaluminum

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Alkyl group exchange between polymeric alkyltitanium compounds and excess alkylaluminum compounds is currently assumed to be the main transfer process in Ziegler–Natta olefin polymerization[1]. This view, however, is supported only by indirect evidence, *e.g.*, the decrease in the polymer molecular weight at higher alkylaluminum concentrations[2]. The NMR technique served as an effective tool for a direct demonstration of the methyl group exchange between alkyltitanium and alkylaluminum.

To avoid interference from the solvent signals and to follow the methyl-group transfers we used perdeuterated organometallic compounds dissolved in conventional protonated compounds in this study. The ^{2}D NMR spectra were recorded with a Bruker Spectrospin HX-90 instrument at 13.81 MHz. A 1/1 v/v mixture of perfluorobenzene and perdeuterobenzene (external reference) was applied for ^{19}F external lock at room temperature. In the low temperature experiments (to −80°) the perfluoromethyl signal of the CF_3–CF_2–$COOCH_3$ served the same purpose.

All precautions commonly applied in the study of organometallic compounds were taken here. Samples for the recording of spectra were sealed in glass tubes.

$(CD_3)MgI$ solution in $(C_2H_5)_2O$ was prepared from CD_3I by a standard procedure. $Ti(CD_3)_4$ was obtained by treating (at −40°) the $TiCl_4$ solution in n-hexane with the perdeuteromethylmagnesium iodide solution followed by distillation of the $Ti(CD_3)_4$ etherate under reduced pressure[3]. Most of the ethyl ether was subsequently removed *in vacuo* from the mixed hexane/ether solvent. The concentration of $Ti(CD_3)_4$ reached 0.1–0.2 mol/l as measured by EDTA titration. The ^{1}H NMR spectrum of the solution revealed that it contained n-C_6H_{14} and $(C_2H_5)_2O$ in 10/1 molar ratio. $Al_2(CD_3)_6$ was prepared from CD_3I by a slightly modified Grosse and Mavity method[4].

The ^{2}D and ^{1}H chemical shifts of substances under investigation are given in Table 1. The resonance of the perdeuterobenzene used for internal reference was arbitrarily assigned a value of 2.63 ppm in order to approach the ^{2}D chemical shift scale to that of the protons. The references for ^{1}H chemical shifts are quoted in brackets. The

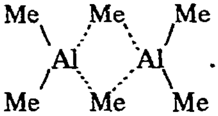
TABLE 1

^2D AND ^1H CHEMICAL SHIFTS CORRELATION

Compound	*Solvent*	*^2D Internal standard*	*Chemical Shifts (ppm)*	
			$CD_3{}^a$	*$\tau(CH_3)$*
MeMgI	$(C_2H_5)_2O$	$C_6D_5CD_3$	11.4	11.3(5)
Al_2Me_6	$C_6H_5CH_3$, 20°	$C_6D_5CD_3$	10.29	10.14(6)
	$C_6H_5CH_3$, –75°	$C_6D_5CD_3$	9.56; 10.58	9.72; 10.28(6)
$AlMe_3 \cdot Et_2O$	$C_6H_{14}/(C_2H_5)_2O$, 10/1	C_6D_6	10.8	
	$C_6H_5CH_3+(C_2H_5)_2O$		–	10.35(7)
$TiMe_4$	$C_6H_{14}/(C_2H_5)_2O$, 10/1		8.5	–
Methane	$C_6H_{14}/(C_2H_5)_2O$, 10/1	C_6H_6	9.8	–
	CCl_4		–	9.77(8)

[a] $\delta(C_6D_6) + 2.63$ or $\delta(CD_3Ph) + 7.68$. Accuracy ± 1 Hz.

^2D data agree reasonably well with the values of proton chemical shifts. In conformity with ^1H NMR studies on Al_2Me_6[6], the resonance line of perdeuterated trimethylaluminum in toluene at –75° divided in two lines with relative intensities 2/1 corresponding respectively to terminal and bridging methyls in the dimer



. The spectrum of $Ti(CD_3)_4$ in a 10/1 hexane/ethyl ether mixture in the

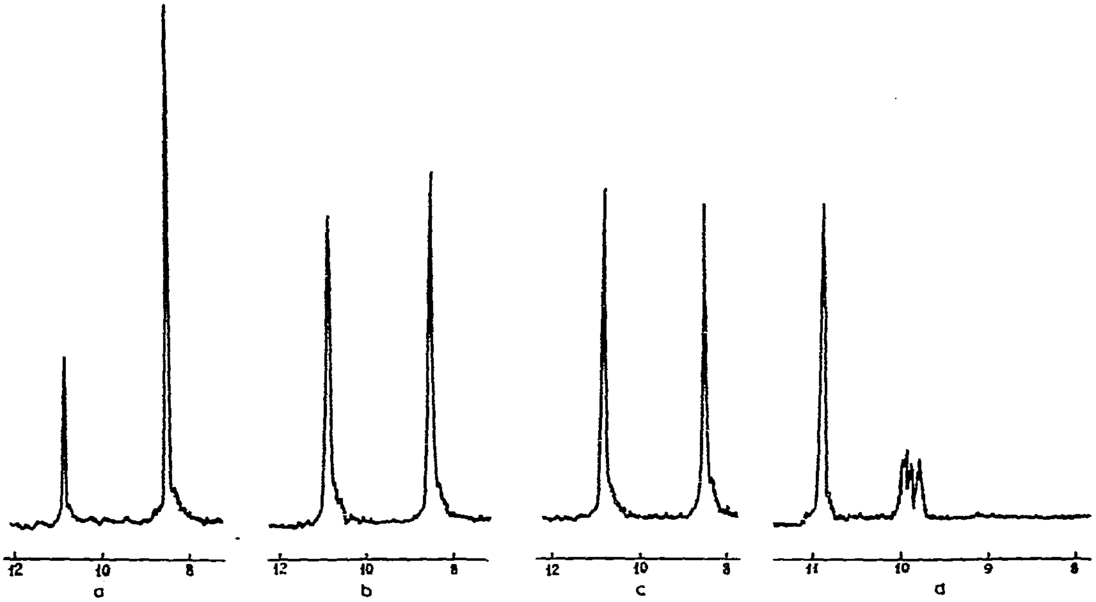


Fig. 1. ^2D NMR spectra of the reaction mixture $Ti(CD_3)_4/Al(CH_3)_3$ recorded at 13.81 MHz (Solvent $n\text{-}C_6H_{14}/C_6H_5CH_3/(C_2H_5)_2O$ in 10/5/1 molar ratio); trimethylaluminum concn. 0.2 *M*; tetramethyltitanium concn. 0.15 *M*; internal reference C_6D_6. (a) 20 min of exchange at –75°; (b) 95 min, –70°; (c) 112 min, –30°; (d) after 12 h at room temperature.

temperature range −80° to −40° contained a single line at 8.5 ppm. At room temperature rapid decomposition occurred accompanied by precipitation of black titanium metal and titanium carbides[9] and formation of methane. The latter appeared in the ^2D NMR spectra as a very sharp line at 9.8 ppm.

The methyl group exchange between tetramethyltitanium and trimethylaluminum was observed on adding $Al_2(CH_3)_6$ toluene solution to the solution of $Ti(CD_3)_4$ at −75°. The exchange is slow on the NMR scale since the $Ti{-}CD_3$ absorption line retained its position and the $Al{-}CD_3$ resonance appeared at 10.8 ppm. However after 20 min at −75° already 25% of CD_3 groups were transferred to the alkylaluminum (*cf.* Fig. 1). The exchange actually occurred between the etherates since the $CD_3{-}Al$ signal appeared as a single line at 10.8 ppm even at −80°.

Additional proof of the exchange was obtained on decomposition of the above reaction mixture at room temperature. The $Al{-}CD_3$ line remained intact but instead of a sharp perdeuteromethane line, a broad signal split into three appeared at 9.8 ppm apparently due to the species CD_4, CD_3H and CDH_3 originating from $Ti(CH_3)_n(CD_3)_{4-n}$ ($n \leqslant 4$). The results give additional support to the assumption[9] that in the course of $TiMe_4$ decomposition, methane is predominantly formed by intramolecular hydrogen abstraction.

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