

## Preliminary communication

### Reaction of dicyclopentadienylzirconium dihydride with trimethylaluminium. Formation of a novel hydride containing both Zr—H—Zr and Zr—H—Al

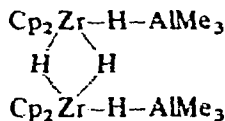
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(Received July 31st, 1972)

The importance of complexes between alkylaluminiums and compounds of titanium in Ziegler–Natta catalysis prompts us to report some preliminary findings on the reaction of  $\text{Cp}_2\text{ZrH}_2$  with alkylaluminiums, in particular  $\text{AlMe}_3$  ( $\text{Cp} = \pi$ -cyclopentadienyl).

On dropwise addition of trimethylaluminium in stoichiometric amounts to a stirred slurry of  $\text{Cp}_2\text{ZrH}_2$  in benzene at room temperature\*, a ready reaction ensued to give a clear pale violet solution from which the faintly blue compound



was isolated in almost quantitative yields\*\*. The  $\text{C}_5\text{H}_5$  and  $\text{CH}_3$  protons showed chemical shifts\*\*\* of  $\delta = 5.50$  and  $-0.41$  ppm respectively in the  $^1\text{H}$  NMR spectrum (see Fig.1) with relative intensities in accord with the structure assigned to the complex. The hydridic hydrogens, which are coupled in the NMR spectrum but do not exchange, give rise to bands, also with the appropriate relative intensity, at  $\delta = -0.92$  and  $-2.92$  ppm. The triplet nature of these bands is consistent with the proposed structure. Assignment of the peak at  $\delta = -0.92$  to the Zr—H—Al hydride can be made on two counts. Firstly, this multiplet is broadened and less well defined than that at higher field, a consequence of coupling with the aluminium. Then, since the chemical shift of the hydride hydrogen in compounds such as diisobutylaluminium hydride<sup>1</sup> and diphenylaluminium hydride<sup>2</sup> lies between  $\delta = 2$  and 5 ppm, it would seem that the low field band at  $\delta = -0.92$  is more likely to be associated with the hydride attached to the aluminium.

\* Reaction at  $5^\circ$  is very slow.

\*\* Satisfactory C, H and total ash analyses were obtained.

\*\*\* Relative to internal standard hexamethyldisiloxane.

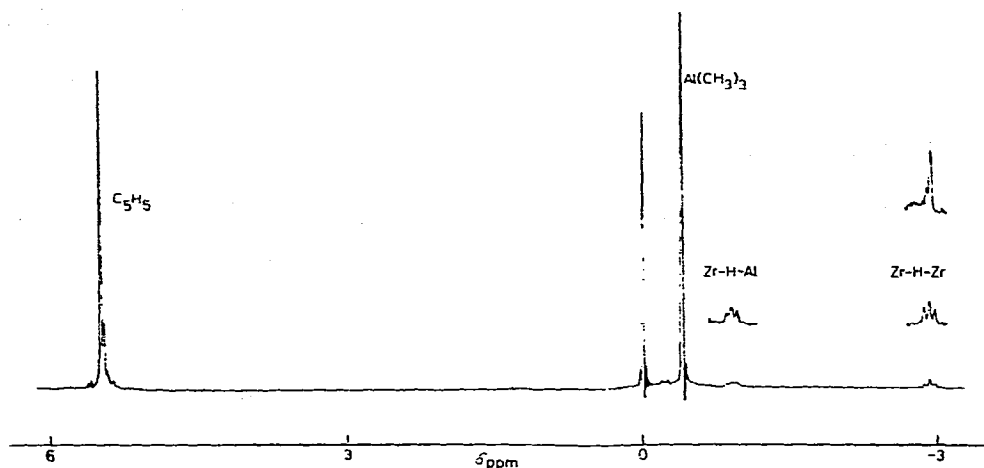
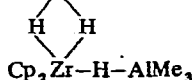


Fig.1. The  $^1\text{H}$  NMR spectrum of  $\text{Cp}_2\text{Zr-H-AlMe}_3$ , including the decoupled Zr-H-Zr absorption



in benzene- $d_6$ , on an HA-100 spectrometer using hexamethyldisiloxane as internal standard and benzene as lock signal.

That the methyl  $^1\text{H}$  NMR peak remains a singlet down to  $-60^\circ$  (in toluene- $d_8$ ) tends to negate the possibility of methyl exchange, a process expected if bridging methyl groups were present.

Although the possibility of coupling between the hydrides and the  $\text{C}_5\text{H}_5$  protons does exist, no evidence of any interaction between these groups was detected. In the compounds  $\text{Cp}_2\text{MF}_2$ ,  $\text{M} = \text{Ti, Zr or Hf}$ , it was found<sup>3</sup> that the  $\text{C}_5\text{H}_5$  hydrogens were not NMR

TABLE I

INFRARED FREQUENCIES ( $\text{cm}^{-1}$ ) OF SOME DICYCLOPENTADIENYLZIRCONIUM HYDRIDES AND DEUTERIDES

	Assignment	Hydride	Deuteride	Reference
$\text{Cp}_2\text{Zr-H-AlMe}_3$				
$\begin{array}{c} \text{H} \quad \text{H} \\ \diagdown \quad \diagup \\ \text{Cp}_2\text{Zr-H-AlMe}_3 \end{array}$	Zr-H-Zr	1350	980	This work
$\text{Cp}_2\text{Zr-H-AlMe}_3$	Zr-H-Al	1780	1290	
$\text{Cp}_2\text{Zr(H)AlH}_4$	Zr-H-Zr	1425	1055	4
	$\text{AlH}_4$	1790, 1700	1310, 1260	
$\text{Cp}_2\text{Zr(H)BH}_4$	Zr-H	1945		5
$\text{Cp}_2\text{ZrH}_2$	Zr-H-Zr	1520, 1300	1100, 960	4
$\text{Cp}_2\text{Zr(H)Cl}$	Zr-H-Zr	1390	1020	4
$\text{Cp}_2\text{Zr(H)CH}_3$	Zr-H-Zr	1500	1090, 965	4

equivalent (triplet,  $J = 1.7$  Hz) in the case of the titanium compound, but were equivalent in the case of  $M = \text{Zr}$  or  $\text{Hf}$ .

The infrared spectra of this compound and its deuterido analogue have been measured in nujol and halocarbon oil (see Table 1). Reaction with  $\text{KBr}$  prevented the use of this material as a support. All of the hydrido and deuterido adsorptions were broad and the ratio  $\gamma(\text{M-H})/\gamma(\text{M-D})$  was 1.38 for both types of hydrido groups.

The compound is thermally unstable decomposing even at room temperature to a crimson compound with the evolution of methane and hydrogen. The methyl groups react here with a bridging hydride rather than abstracting a proton from the cyclopentadienyl ring since on warming the deuterido compound,  $\text{CH}_3\text{D}$  was detected in the gaseous decomposition products. Its low thermal stability would also account for the low (found 376, calc. 591.0) dimer molecular weight observed ebulliometrically in benzene. Cryoscopically, in the same solvent, the value determined was 510. Dimerization through  $\text{Zr-H-Zr}$  bridges may be expected since this behaviour occurs in the parent compound<sup>4</sup>

$\text{Cp}_2\text{Zr(H)Cl}$  also reacts with aluminium trimethyl, but the products are unstable at room temperature.

#### REFERENCES

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