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THE REACTIONS OF DICYCLOPENTADIENYLTITANIUM WITH ALUMINIUM ALKYLS

P. C. WAILES AND H. WEIGOLD

Division of Applied Chemistry, Chemical Research Laboratories, Box 4331, G.P.O., Melbourne, Victoria, 3001 (Australia)

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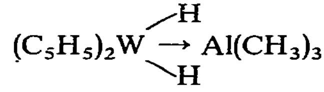
SUMMARY

When dicyclopentadienyltitanium (titanocene) is warmed with triethylaluminium, ethane is eliminated and a red diamagnetic complex is obtained. It is believed to be identical with the compound $[C_5H_5TiC_5H_4Al(C_2H_5)_2]_2$ isolated by Natta and co-workers from the reaction between $(C_5H_5)_2TiCl$ and $Al_2(C_2H_5)_6$. The corresponding methyl derivative has also been isolated.

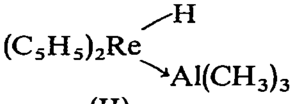
INTRODUCTION

Certain dicyclopentadienylmetal compounds with non-bonding electrons have been shown to form donor–acceptor complexes with electron-deficient compounds. Examples of such complexes are (I)[1], (II)[1] and (III)[2] in which transition metal derivatives form donor bonds with compounds of Group III elements.



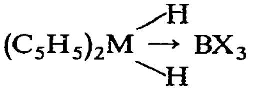
$$(C_5H_5)_2W\underset{\searrow H}{\overset{\nearrow H}{\longrightarrow}}Al(CH_3)_3$$

(I)



$$(C_5H_5)_2Re\begin{matrix}\nearrow H\\ \searrow Al(CH_3)_3\end{matrix}$$

(II)



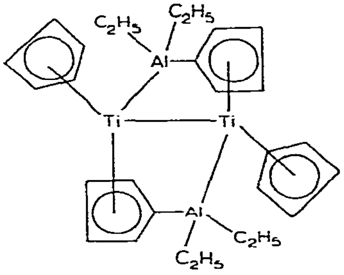
$$(C_5H_5)_2M\underset{\searrow H}{\overset{\nearrow H}{\longrightarrow}}BX_3$$

$M = W, Mo; X = F, Cl$

(III)

RESULTS AND DISCUSSION

In exploring the possible donor properties of dicyclopentadienyltitanium (titanocene), its reactions with aluminium alkyls were examined. Instead of donor–acceptor compounds being obtained, an alkane was eliminated and crimson coloured diamagnetic complexes were isolated. On the basis of analyses, molecular weight determination and hydrolysis experiments, the product from triethylaluminium and dicyclopentadienyltitanium fits closely a formula like $[(C_5H_5)_2TiAl(C_2H_5)_2]_2$. In all of its physical properties this compound appears to be identical with that isolated by Natta and co-workers[3] from the reaction between $(\pi\text{-}C_5H_5)_2TiCl$ and $Al_2(C_2H_5)_6$. An X-ray crystal structure determination of Natta's compound by Corradini and Sirigu[4] confirmed structure (IV), in which the aluminium atoms are bonded to titanium and also to one of the cyclopentadienyl ligands on the neighbouring titanium atom.



(IV)

The ethane obtained in the reaction now described is no doubt evolved when the Al–C_5H_4 bond is formed. It is interesting to note that this begins at room temperature. The formula of the complex should be amended therefore to $[C_5H_5TiC_5H_4Al(C_2H_5)_2]_2$.

From dicyclopentadienyltitanium and trimethylaluminium a similar diamagnetic complex was isolated after evolution of methane. This compound is red-brown in colour, dimeric in benzene and somewhat less soluble than the corresponding ethyl derivative. It is assumed to be the methyl analogue of (IV).

The corresponding reactions with dicyclopentadienylzirconium (zirconocene) were not so well defined. With triethyl- or -trimethylaluminium and dicyclopentadienylzirconium in both cases a mixture of a red and a green product was obtained, together with the corresponding alkane. The red compounds were found to be approximately trimeric in boiling benzene whereas the green derivatives were too insoluble for molecular weight determinations.

EXPERIMENTAL

General remarks

All solid materials were handled in a nitrogen-filled glovebox. Dicyclopentadienyltitanium[4] and -zirconium[6] were prepared by the method of Watt and collaborators. Aluminium alkyls were used without purification and were syringed into the reaction tube under purified argon. All solvents were purified by distillation under nitrogen from $LiAlH_4$. M.p.'s were determined in evacuated capillaries and are uncorrected. Molecular weights were measured ebulliometrically in benzene. Hydrolysis of the products to give a quantitative yield of alkane was carried out with methanol followed by acid, to avoid the formation of hydrogen and alkenes.[7]

Dicyclopentadienyltitanium with triethylaluminium

Triethylaluminium (3.0 ml, 20 mmole) was added to a suspension of dicyclopentadienyltitanium (3.6 g, 20 mmole) in toluene (8 ml) contained in a reaction tube topped by a Fischer and Porter threaded valve. A purple colour developed almost immediately. The valve was sealed with the Teflon stem and the tube was then heated to 70° for several days. The course of the reaction was followed by measuring periodically the gas evolved by pumping it into a calibrated volume on a vacuum line using a Töpler pump. At 70° the reaction was 50% complete after 1 day; at 100° the reaction was complete in 20 h. Gas evolved (432 ml at N.T.P., 19.4 mmole) was condensable and showed an IR spectrum identical with that of ethane. After removal of solvent from the tube the residue was continuously extracted with benzene under argon for 1–2 h, giving a purple-red product in near-quantitative yield, m.p. 172–173°. Natta *et al.*[3] found m.p. 169–170°. [Found: ash ($TiO_2 + 0.5Al_2O_3$), 50.1; ethane (by hydrol.), 40.6 mmole); mol.wt., 496. $C_{28}H_{38}Al_2Ti_2$ calcd.: ash, 49.9%; ethane (by hydrol.), 40.0 mmole; mol.wt., 524.] The compound is essentially diamagnetic, having a T.I.P. of 150–250 cgs units between room temperature and 85° K.

Dicyclopentadienyltitanium with trimethylaluminium

From $(C_5H_5)_2Ti$ (20 mmole) and $Al_2(C_2H_5)_6$ (20 mmole) heated in toluene as above, a red-brown product was obtained, m.p. >320°, with evolution of methane (20 mmole). (Found: ash, 55.5; mol.wt., 481. $C_{24}H_{30}Al_2Ti_2$ calcd.: ash, 55.85%; mol.wt., 468.)

The compound is diamagnetic, with a T.I.P. of 70–80 cgs units between room temperature and 85° K.

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