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### Oligomerization of acetylenes by titanium complexes

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*Document Version*

Publisher's PDF, also known as Version of record

*Publication date:*  
1978

[Link to publication in University of Groningen/UMCG research database](#)

*Citation for published version (APA):*

Veldman, M. E. E. (1978). Oligomerization of acetylenes by titanium complexes. s.n.

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## S U M M A R Y

In this thesis reactions of titanium complexes with substituted acetylenes are described. They were performed to get more insight into the mechanism of the oligomerization reactions of acetylenes in the presence of early transition metals.

In Chapter 1 a short literature survey is given of reactions of titanium complexes with acetylenes and of relevant trimerization reactions.

Reactions of  $(C_8H_8TiCl_1\cdot THF)_2$  with several acetylenes  $RC_2R'$  ( $R = R' = Ph$ ;  $R = R' = To$  (p-tolyl);  $R = Ph$ ,  $R' = Me$ ) are described in Chapter 2. They afford binuclear complexes  $(C_8H_8TiRC_2R')_2$ , containing two acetylene units. The spectra of these compounds are in keeping with the preliminary results of a structure determination performed by Van der Wal and indicate that one of the titanium atoms is part of a titanacyclopentadiene ring and the other is  $\pi$ -bonded to this ring. To each titanium atom a planar cyclooctatetraene ring is octahapto coordinated. The NMR spectra of these complexes can be explained by a fluxional behaviour in solution. These binuclear complexes are converted into the much more stable sandwich complexes  $C_8H_8TiC_4R_2R'_2$  on heating.

If the thermolysis of the binuclear complexes is performed in the presence of excess of free acetylene hexasubstituted benzenes are formed in addition to sandwich complexes. This is described in Chapter 3. Reactions were performed of  $(C_8H_8TiPhC_2Ph)_2$  with the acetylenes  $RC_2R'$  ( $R = R' = Ph$ ;  $R = R' = To$ ;  $R = Ph$ ,  $R' = To$ ;  $R = Ph$ ,  $R' = Me$ ). From the results a mechanism for the oligomerization reactions was derived. It implies that during the thermolysis two active fragments " $C_8H_8TiPhC_2Ph$ " are formed. These can coordinate an acetylene giving " $C_8H_8Ti(PhC_2Ph)(RC_2R')$ ", which can be converted into a sandwich complex  $C_8H_8TiC_4Ph_2RR'$ . If the latter process does not happen, a third acetylene is coordinated to the titanium atom. The three acetylene units combine and leave the metal in a concerted

process. The remaining " $C_8H_8Ti$ " fragment decomposes.

In Chapter 4 reactions of titanium chlorides with acetylenes  $RC_2R$  ( $R = Ph$ ;  $R = Me$ ) in the presence of  $i\text{-PrMgCl}$  are discussed. One of the reaction products is  $C_4Ph_4TiMg_2Cl_6 \cdot 6\text{THF}$ , an organometallic complex containing two different metals and a tetraphenylcyclobutadiene ring. This complex is inactive in the formation of hexaphenylbenzene. To explain the formation of the trimerization products a mechanism similar to that described in Chapter 3 is proposed. In both cases the active species contain divalent titanium.

In Chapter 5 details of the experimental work related to the foregoing Chapters are given.