Journal of Organometallic Chemistry, 260 (1984) 199–205
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

CYCLOTRIMERIZATION OF SUBSTITUTED ACETYLENES TO ARENES BY TITANIUM COMPLEXES

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(Received September 9th, 1983)

Summary

Cyclotrimerization experiments of substituted acetylenes to arenes with (*a*) C_8H_8Ti complexes and with (*b*) $TiCl_3$ are reported. A cyclotrimerization mechanism is proposed which involves the concerted trimerization of three acetylenes coordinated to a divalent titanium centre. The organometallic compounds isolated from the reaction mixtures, viz. $(C_8H_8TiPhC_2Ph)_2$, $C_8H_8TiC_4Ph_4$ in (*a*) and $[C_4Ph_4TiCl_3]^-$ $[Mg_2Cl_3 \cdot 6THF]^+$ in (*b*) are shown not to be intermediates in the cyclotrimerization.

Introduction

Cyclotrimerization of substituted acetylenes to arenes by transition metal complexes has been studied rather extensively for a number of cases [1]. Several mechanisms have been proposed [2]: for instance, for Ni [3] the mechanism comprises the concerted trimerization of three acetylenes coordinated to a metal centre. For Co [4], first two acetylenes condense to a metallacyclopentadiene ring; then, insertion of a third alkyne into the ring yields the arene. For Nb [5] a similar reaction pathway has been proposed via a cyclobutadiene metal complex. Finally, a stepwise *cis*-insertion of coordinated acetylenes into metal–carbon bonds, followed by ring closure is proposed for Pd [6].

To date, not much is known about the activity of titanium complexes in cyclotrimerization reactions. Some years ago, it was reported that reaction of tetraphenyltitanium with diphenylacetylene followed by quenching with hydrogen chloride, yielded, among other products, hexaphenylbenzene [7]. Probably the arene was formed in a concerted process. Details of the mechanism were not given. Also, in our studies of reactions of titanium complexes with substituted acetylenes, the formation of hexa-substituted benzenes in varying amounts has been noticed; for instance in the synthesis of the complexes $(C_8H_8TiRC_2R')_2$ [8], which contain a titanacyclopentadiene ring, and in the synthesis of the complexes $C_8H_8TiC_4R_2R'_2$ [9]

0022-328X/84/$03.00

and $[C_4Ph_4TiCl_3]^-$ $[Mg_2Cl_3 \cdot 6THF]^+$ [10] which both contain a cyclobutadiene ring. Since the latter complexes might be intermediates in the cyclotrimerization, reactions leading to and with these complexes were studied in more detail in order to clarify the cyclotrimerization of acetylenes with titanium compounds.

Results and discussion

Reaction of $TiCl_3 \cdot 3THF$, cyclooctatetraene and diphenylacetylene in the presence of i-PrMgBr yielded the titanacyclopentadiene compound $(C_8H_8TiPhC_2Ph)_2$, the sandwich compound $C_8H_8TiC_4Ph_4$, and a substantial amount of hexaphenylbenzene [9,11].

To find out whether cyclooctatetraenetitanium complexes were intermediates in the trimerization of acetylenes, the following experiments were performed.

Reaction of 1 mol of $(C_8H_8TiCl \cdot THF)_2$ with 2 or 4 mol of diphenylacetylene in the presence of i-PrMgCl gave $(C_8H_8TiPhC_2Ph)_2$, but only trace amounts of hexaphenylbenzene. Thermal conversion of $(C_8H_8TiPhC_2Ph)_2$ gave $C_8H_8TiC_4Ph_4$ but no hexaphenylbenzene. Also $C_8H_8TiC_4Ph_4$ gave, at room temperature and even on thermolysis with diphenylacetylene, no hexaphenylbenzene, neither did diphenylacetylene, as such, under the same reaction conditions. Only when $(C_8H_8TiPhC_2Ph)_2$ was thermolysed in the presence of diphenylacetylene were considerable amounts of the trimerization product formed.

These results exclude both the cyclobutadiene compound, $C_8H_8TiC_4Ph_4$, and the metallacyclopentadiene compound, $(C_8H_8TiPhC_2Ph_2)$, as intermediates in the formation of hexaphenylbenzene in the reaction of $TiCl_3 \cdot 3THF$, cyclooctatetraene and diphenylacetylene in the presence of i-PrMgBr, since this reaction proceeds at low temperature. Omitting C_8H_8 from the reaction mixture i.e. reaction of $TiCl_3 \cdot 3THF$ with one equivalent of i-PrMgCl and an excess of diphenylacetylene in THF, gave 10–20% hexaphenylbenzene, together with the blue cyclobutadiene compound $[C_4Ph_4TiCl_3]^-$ $[Mg_2Cl_3 \cdot 6THF]^+$ [10]. To check whether the latter complex was an intermediate, it was allowed to react with diphenylacetylene in THF at room temperature and under reflux. In both cases no diphenylacetylene was consumed and no hexaphenylbenzene was formed. Both active systems, viz. $TiCl_3 \cdot 3THF$, diphenylacetylene and i-PrMgHal, and the thermolysis of $(C_8H_8TiPhC_2Ph)_2$ in the presence of diphenylacetylene, were studied in more detail. Most attention was given to the latter reaction, since the reaction products were more stable and could be better characterized.

$(C_8H_8TiPhC_2Ph)_2$ was heated with an excess of disubstituted acetylene during 5 h at 160°C. The reaction products were separated and analysed as quantitatively as possible with the aid of column chromatography, IR, NMR and MS. The principal results are given in Table 1. In the experiments 2–4 about 80% of the acetylene units are recovered, which is quite satisfactory considering the complicated working-up procedure.

In the four reactions mentioned, more than one mol of $C_8H_8TiC_4Ph_xR_{4-x}$ is formed per mol of $(C_8H_8TiPhC_2Ph)_2$. This indicates that both "C_8H_8Ti" fragments are essentially able to form the sandwich product.

In the reactions 3 and 4 some diphenylacetylene was found, in addition to di-*p*-tolylacetylene, C_2To_2. From UV, MS and NMR data it could be deduced that the phenyl/tolyl ratio in the hexasubstituted benzenes is approximately 1/5, indicat-

TABLE 1

RESULTS [a] OF THE REACTION OF $(C_8H_8TiPhC_2Ph)_2$ WITH SOME SUBSTITUTED ACETYLENES C_2R_2

R	$(C_8H_8TiPhC_2Ph)_2$	$+RC_2R \rightarrow$	$\Delta C_8H_8TiC_4Ph_xR_{4-x}$	$+C_6Ph_yR_{6-y}$	$+C_2R_2$
1. Ph	1	8.4	1.1	1.0	1.8
2. Ph	1	13.0	1.1	0.9	7.6
3. To	1	10.8	1.6 [b]	0.3 [c]	6.2
4. To	1	7.6	1.6 [b]	0.3 [c]	3.0

[a] In moles. [b] $x = 0, 2, 4$. [c] $y = 0, 2, 4, 6$.

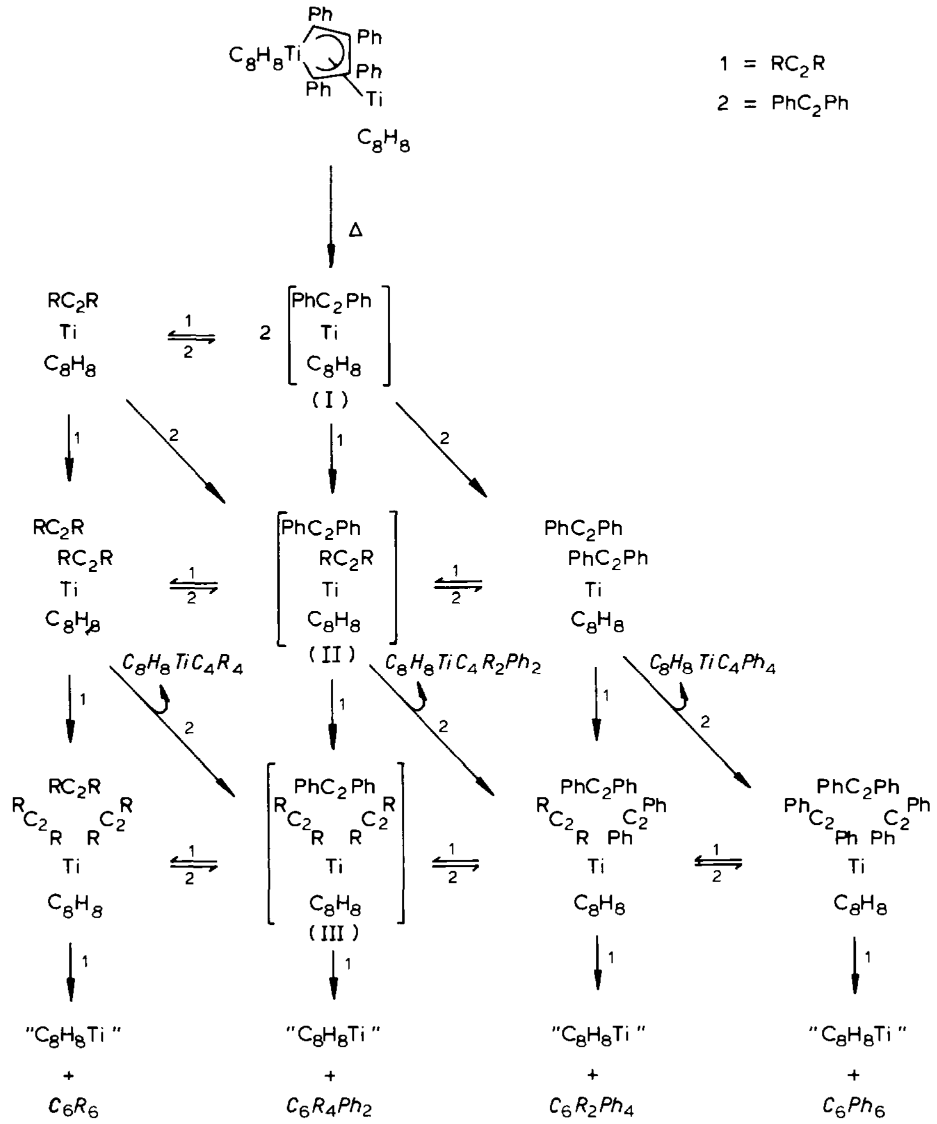
ing a product ratio like $C_6To_6/C_6To_4Ph_2/C_6To_2Ph_4 = 6/3/1$. The absence of products with an odd number of *p*-tolyl substituents in the mass spectrum of the crude reaction product excludes the occurrence of metathesis reactions. NMR and mass spectra indicate that $C_8H_8TiC_4To_2Ph_2$ is somewhat more abundant than $C_8H_8TiC_4To_4$. Only a small amount of $C_8H_8TiC_4Ph_4$ is present. The yield of hexa-substituted benzenes in the reactions 3 and 4 is much lower than in the reactions 1 and 2. It is not clear whether this is due to steric or electronic factors. The occurrence of products like $C_8H_8TiC_4Ph_2To_2$ and $C_6Ph_2To_4$ strongly indicates the possibility of fragmentation of the C_4Ph_4 unit of $(C_8H_8TiPhC_2Ph)_2$ into two C_2Ph_2 units.

Thermolysis of $(C_8H_8TiPhC_2Ph)_2$ was also carried out in the presence of methylphenylacetylene or phenyl-*p*-tolylacetylene. In neither case could separation of the reaction products be achieved. The mass spectrum of the crude product of the first reaction indicates a very low amount of sandwich compounds compared with that of trimerization products. This is in agreement with the assumption that acetylenes with one large (phenyl) and one small (methyl) substituent preferentially convert to trimerization products, while acetylenes with two large substituents give rise to both dimerization and trimerization products [6]. The product distribution found from the mass spectra of the products of both reactions is in good agreement with those described above.

The results so far, exclude not only the sandwich compound $C_8H_8TiC_4Ph_4$ from being an intermediate in the cyclotrimerization process but also the starting compound $(C_8H_8TiPhC_2Ph)_2$ as such; activity arises only at or above decomposition temperature. The metallacyclic part of the molecule $(C_8H_8TiPhC_2Ph)_2$ does not play a role either. In our experiments with $(C_8H_8TiPhC_2Ph)_2$ and di-*p*-tolylacetylene, a cyclotrimerization via the metallacyclic system would result in formation of mainly $C_6Ph_4R_2$, which is definitely not the case. The results also differ from the findings of Brintzinger for $CpCoC_4Me_4CoCp$ [12]. In a reaction with diphenylacetylene he only found $CpCoC_4Ph_4$ and C_6Ph_6; no hexasubstituted benzenes containing one or more MeC_2Me units were mentioned.

Our results are best explained by supposing that the cleavage of $(C_8H_8TiPhC_2Ph)_2$ into two equal parts "$C_8H_8TiPhC_2Ph$" (I), (Scheme 1), occurs as a first step. This cleavage is strongly indicated among others by the mass spectrum of $(C_8H_8TiPhC_2Ph)_2$, in which the ion $(C_8H_8TiPhC_2Ph)^+$ has a high abundance, by the formation of products like $C_8H_8TiC_4R_2Ph_2$ and $C_6R_4Ph_2$, and by the low yield of

SCHEME 1



$C_8H_8TiC_4Ph_4$. Through this cleavage, divalent titanium centres are formed. Both centres are equally active since from the reactions with diphenylacetylene and di-*p*-tolylacetylene it appears that there is a correlation between the quantities of sandwich products and substituted benzenes obtained. Together they amount to approximately 2 mol per mol of titanium complex $(C_8H_8TiPhC_2Ph)_2$, or 1 mol per titanium, in both cases (see Table 1).

The second step involves the coordination of free RC_2R to "$C_8H_8TiPhC_2Ph$", with formation of a diacetylene intermediate "$C_8H_8Ti(RC_2R)(PhC_2Ph)$" (II). II can either form a sandwich complex $C_8H_8TiC_4Ph_2R_2$ or coordinate another acetylene,

TABLE 2

YIELDS OF HEXAPHENYLBENZENE (BASED ON TITANIUM) FROM REACTIONS OF $TiCl_n$ WITH i-PrMgX AND PhC_2Ph

Compound	i-PrMgX (equivalents)	PhC_2Ph (added) (equivalents)	C_6Ph_6 (found) (%)
$TiCl_4$	–	6	–
$TiCl_3 \cdot 3THF$	–	6	–
$TiCl_3 \cdot 3THF$	1	6	10–20
$TiCl_3 \cdot 3THF$	2	6	10–20
$TiCl_3 \cdot 3THF$	3	6	10–20

giving the triacetylene complex "$C_8H_8Ti(RC_2R)_2PhC_2Ph$" (III) as a third intermediate. Cyclotrimerization of the acetylenes in a concerted process forms the arene. Since (cyclooctatetraene)(arene)titanium complexes seem to be unstable [9a], the $C_6Ph_2R_4$ unit leaves the titanium atom. The remaining "C_8H_8Ti" fragment is not active and probably decomposes.

Exchange of the acetylenes in the complexes I, II and III with free acetylenes can explain the other products like C_6R_6, $C_6Ph_4R_2$ and $C_8H_8TiC_4Ph_4$. Since RC_2R was always present in excess, formation of C_6R_6 and $C_8H_8TiC_4R_4$ was strongly favoured.

A similar reaction scheme can be constructed for reactions of $TiCl_3 \cdot 3THF$ with diphenylacetylene in the presence of i-PrMgCl. The results of some preliminary reactions are summarized in Table 2. They show that the titanium atom has first to be reduced to Ti^{II} before reaction takes place. Then the acetylenes are coordinated, leading to an organometallic complex with two acetylene units, $[C_4Ph_4TiCl_3]^-$ $[Mg_2Cl_3 \cdot 6THF]^+$, or to arenes (C_6Ph_6). Reaction of $TiCl_3 \cdot 3THF$ with one equivalent of i-PrMgCl and an excess of 2-butyne afforded about 1 mol of hexamethylbenzene per mole of $TiCl_3$. In this case there is no tendency to form dimerization products, so the arene can be formed in 100% yield.

In conclusion, the mechanism proposed for these reactions involves a stepwise coordination of acetylene groups to a divalent titanium centre. After the addition of two acetylenes, either stable organotitanium complexes containing two acetylene units are formed, or a third acetylene is coordinated. The latter coordination takes place in particular if the acetylenes have small substituents. In a concerted process the substituted benzene ring is formed and splitt off.

Experimental

All experiments were carried out under purified nitrogen. Solvents were dried and made free of oxygen before use. Diphenylacetylene (Aldrich) and $TiCl_3$ (K&K) were used without purification. Cyclooctatetraene (Fluka) and 2-butyne (Aldrich) were distilled before use; i-PrMgCl was prepared in ether using i-propyl chloride (Aldrich) and an excess of Mg (Fluka). Methylphenylacetylene [8], phenyl-*p*-tolylacetylene [13], di-*p*-tolylacetylene [14], $C_8H_8TiCl \cdot THF$ [15], $(C_8H_8TiPhC_2Ph)_2$ [8], and $[C_4Ph_4TiCl_3]^-$ $[Mg_2Cl_3 \cdot 6THF]^+$ [10], were prepared according to published procedures.

UV-Vis spectra were recorded on a Perkin–Elmer EPS-3T spectrophotometer. ^1H

NMR spectra were run on a JEOL C-60 HL instrument using TMS as an internal standard. ^{13}C NMR spectra were recorded on a Bruker WH-270, for $[C_4Ph_4TiCl_3]^-[Mg_2Cl_3 \cdot 6THF]^+$, or a Varian XL-100/15 spectrometer. Mass spectra were run on an AEI MS9 mass spectrometer; operating conditions: energy 70 eV, resolution 1000, accelerating voltage 8 kV. The samples were introduced directly into the ion source using a metal probe.

Elemental analyses were carried out at the Analytical Department of the Chemical Laboratories of this University under supervision of Mr. A.F. Hamminga.

Quantitative UV measurements

The quantitative analysis of hexa-substituted benzenes, sandwich complexes $C_8H_8TiC_4R_4$, diphenylacetylene and di-*p*-tolylacetylene was performed by UV spectroscopy.

The UV spectra of the hexa-substituted benzenes were recorded in 1,2-dichloroethane (Merck). It was assumed, that ϵ in the absorption maximum (247–253 nm) was about the same for all the compounds viz. 56.8×10^3 cm^2 mmol^{-1} [16].

The UV-Vis spectra of the sandwich complexes were recorded in hexane; the amounts were calculated from the values found for a pure sample of $C_8H_8TiC_4Ph_4$: $\epsilon_{451} = 6.8 \times 10^3$; $\epsilon_{780} = 1.2 \times 10^3$.

The amounts of diphenylacetylene and di-*p*-tolylacetylene were calculated from spectra in ethanol (90%,· Uvasol, Merck), based on $\epsilon_{280} = 30.4 \times 10^3$ [17] and $\epsilon_{304} = 30 \times 10^3$ (for an authentic sample), respectively.

Thermolysis of $(C_8H_8TiPhC_2Ph)_2$ in the presence of diphenylacetylene

$(C_8H_8TiPhC_2Ph)_2$ (110 mg, 0.166 mmol) and diphenylacetylene (386 mg, 2.17 mmol, 13.1 equivalents) were heated together at 180°C in a closed Schlenk tube for 5 h. The dark green reaction mixture was first extracted with pentane (100 ml). After concentration this solution was run through an alumina column (Act. 2–3) with pentane. Diphenylacetylene (170 mg, determined by UV spectroscopy), minor amounts of *trans*-stilbene and some other unidentified products were found. The residue was extracted with hexane. An intensely green solution was obtained, containing 94.4 mg of $C_8H_8TiC_4Ph_4$ (1.1 equivalents) and another 55 mg of diphenylacetylene. The remaining white compound was dissolved in 1,2-dichloroethane; in this solution 80 mg (0.9 equivalents) of hexaphenylbenzene were detected.

The other thermolyses were performed in a similar way.

Reactions of titanium chlorides with diphenylacetylene and i-PrMgCl

$TiCl_3$ (91 mg, 0.591 mmol) was converted to $TiCl_3 \cdot 3THF$ by refluxing in THF for 6 h. After being cooled to −20°C, 1 equivalent of i-PrMgCl was added. The reaction mixture was allowed to warm to 20°C and PhC_2Ph (727 mg, 4.08 mmol) was added. Refluxing the mixture for 4 h yielded a deep blue solution. Evaporation of the THF, and subsequent extraction with benzene, gave a blue residue. This residue could be recrystallized from THF/pentane, giving pure $[C_4Ph_4TiCl_3]^-[Mg_2Cl_3 \cdot 6THF]^+$. The extract was concentrated and run through an alumina column with benzene. Hexaphenylbenzene was found in 15% yield, based on titanium, in addition to the excess of diphenylacetylene.

The other reactions were carried out in an analogous fashion.

Acknowledgements

The authors thank Dr.Ir. C.J. Groenenboom for recording the NMR spectra of $[C_4Ph_4TiCl_3]^- [Mg_2Cl_3 \cdot 6THF]^+$. This investigation was supported by the Netherlands Foundation for Chemical Research (SON), with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO).

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