A Reinvestigation of the Thermal Decomposition of $(C_5H_5)_2TiPh_2$

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Summary The formation of benzene during the thermal decomposition of $(C_5H_5)_2TiPh_2$ in hydrocarbon solvents is shown to be the result of a phenyl group abstracting a proton from another co-ordinated group on the titanium complex.

As part of a study of the thermal chemistry of organometallic compounds, we have been reinvestigating the mode of benzene formation in the thermal decomposition of bis-(π-cyclopentadienyl)diphenyltitanium(IV), (I). Razuvaev and his co-workers carried out the thermal decomposition of (I) in various hydrocarbon solvents.[1–3] In each case benzene was the major product. The authors suggested a free radical mechanism for the thermal decomposition of (I) (Scheme 1).

$$(C_5H_5)_2TiPh_2 \xrightarrow{70\text{—}90^\circ} (C_5H_5)_2TiPh + Ph\bullet$$

$$(C_5H_5)_2TiPh \xrightarrow{70\text{—}90^\circ} (C_5H_5)_2Ti + Ph\bullet$$

SCHEME 1

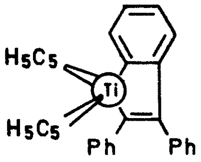
The phenyl radicals were then supposed to abstract hydrogen from the solvent giving the observed benzene. Summers and Uloth, who first prepared (I), observed that the pyrolysis of (I) at 105° under N_2 gave benzene not biphenyl.[4] We repeated the thermal decomposition of (I) in benzene and did not detect biphenyl, the expected product of phenyl radical attack on benzene.[5] The ready formation of benzene in the decomposition of (I) prompted us to attempt to determine the origin of the hydrogen in the evolved aromatic hydrocarbon.

As a preliminary experiment, (I) was heated under reflux in hexadeuteriobenzene for 5 hr. and the benzene distillate analysed by mass spectrometry. Apart from C_6D_6 the only product found was C_6H_6, not the expected radical product C_6H_5D.

To determine whether the proton had been abstracted from the cyclopentadienyl or from another group, $(C_5H_5)_2$-$Ti(C_6D_5)_2$, (II) was prepared. When (II) was heated under reflux in C_6H_6 for 24 hr. and the resultant benzene solution distilled, mass spectral analysis showed that approximately one mole of C_6D_6 per mole of (II) was liberated. Consequently, a co-ordinated phenyl abstracts a proton from another co-ordinated phenyl group.

In order to determine the nature of the generated titanium complex, (II) was heated under reflux for 2 hr. in benzene and then anhydrous HCl was bubbled through the solution. In addition to C_6D_5H from unreacted (II), the mass spectral data of the benzene distillate showed only two other benzenes, C_6D_6 and $C_6D_4H_2$, and these were present in equal concentration. Thus a phenylene titanium complex was produced for each C_6D_6 formed.

As a result of a recent publication of the reaction of (I) with diphenylacetylene (III), the proton abstracted is felt to be an *o*-proton.[6] Here (I) was heated under reflux in benzene in the presence of (III) to give 1, 1-di-π-cyclopentadienyl-2,3-diphenyl-1-titanaindene. Interpreting their results in the light of the generally accepted radical decomposition of (I) the authors suggest that this compound is formed *via* the reaction of (III) with the Ti^{III} intermediate of Scheme 1. Our work has shown that under these conditions a phenylene titanium complex is generated which then reacts with (III) to form the observed product, (IV). This reaction can be simply visualized as the insertion product of (III) into a titanium carbon bond, according to Scheme 2.



(IV)

Although the occurrence of aryne type intermediates of low-valent titanium compounds has been postulated to explain the products of the reduction of diphenyltitanocene with an excess of phenyl-lithium, the nature of the $(C_5H_5)_2$-TiC_6H_4 intermediate is not immediately apparent.[7,8]

The above results dismiss a radical mechanism in the thermal decomposition of $(C_5H_5)_2TiPh_2$. The solvent merely provides a medium and is not involved in the reaction. Rather, the thermal decomposition follows an internal pathway, with hydrogen being abstracted by co-ordinated phenyl groups from other co-ordinated groups.

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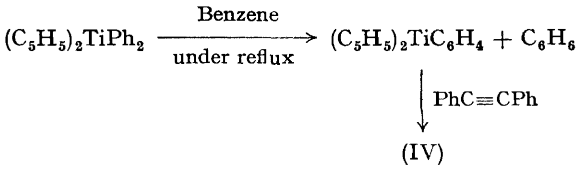

$$\begin{tikzcd}(C_5H_5)_2TiPh_2 \arrow[r, "\text{Benzene}", "\text{under reflux}"'] & (C_5H_5)_2TiC_6H_4 + C_6H_6 \arrow[d, "PhC\equiv CPh"] \\ & \text{(IV)}\end{tikzcd}$$

SCHEME 2

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