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THE REACTION OF INTERMEDIATE ZIRCONOCENE—ARYNE COMPLEXES WITH C—H BONDS IN THE THERMOLYSIS OF DIARYLZIRCONOCENES

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Summary

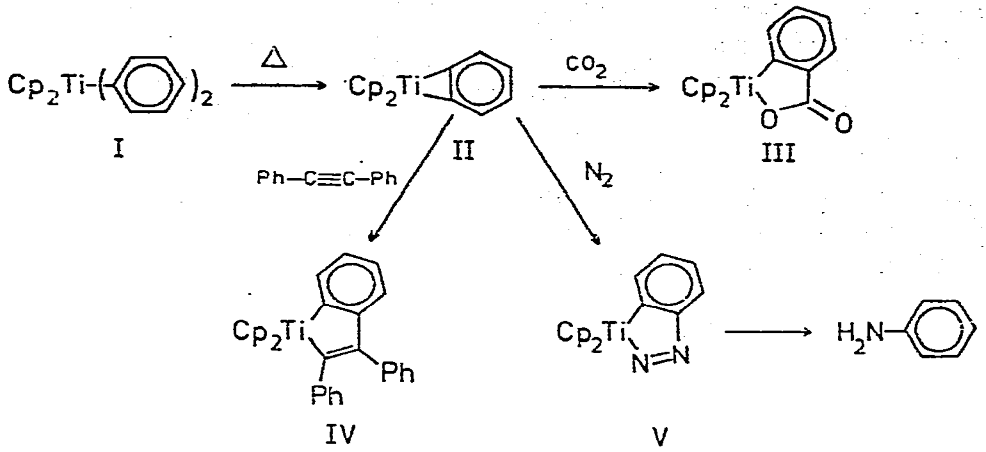
Upon thermolysis in aromatic hydrocarbon solvents diarylzirconocenes undergo successive replacement of their σ-bonded ligands by aryl groups from the solvent. Analysis of the product mixture by photochemical degradation to biphenyls reveals that intermediate aryne zirconocene complexes are formed which then react with the solvent with C—H bond fission and formation of new Zr—C bonds. A β-hydride elimination process can be excluded for the formation of the aryne complexes and it is suggested that they are formed via abstraction of an *ortho* proton from one of the aryl ligands by the other σ-bonded group.

Introduction

Activation of C—H bonds in hydrocarbons has been much studied in recent years. Numerous transition metal complexes have been shown to be able to cleave such bonds with formation of metal—carbon bonds [1]. Because of the strength of the C—H bond, only reactive transition metal complexes are expected to enter this reaction.

As substrates we chose symmetrical diarylzirconocenes, which are potential precursors of aryne complexes. The first 1,2-didehydrobenzene complexes of transition metals have recently been isolated [2a] and proposed as reactive intermediates [2b]. Thus diphenyltitanocene (I) was reported to undergo thermolysis to give the aryne complex 1,2-didehydrobenzenetitanocene (II) [3], which could be trapped by carbon dioxide, ketones, or acetylenes. The benzyne complex II, though not isolated, is even suggested to be the reactive species in nitrogen fixation of I at elevated temperatures [4] (Scheme 1). Though II shows a remarkable reactivity towards multiple bonds, no reaction of such species with C—H bonds has been reported. It has been stated that hydrocarbons in the thermolysis of I and related systems do "merely act as solvents and do not

SCHEME 1. Reactions of 1,2-didehydrobenzenetitanocene (II).



participate in the reaction" [3a]. We have tested the validity of this statement by thermolysis of diarylzirconocenes in hydrocarbon solvents.

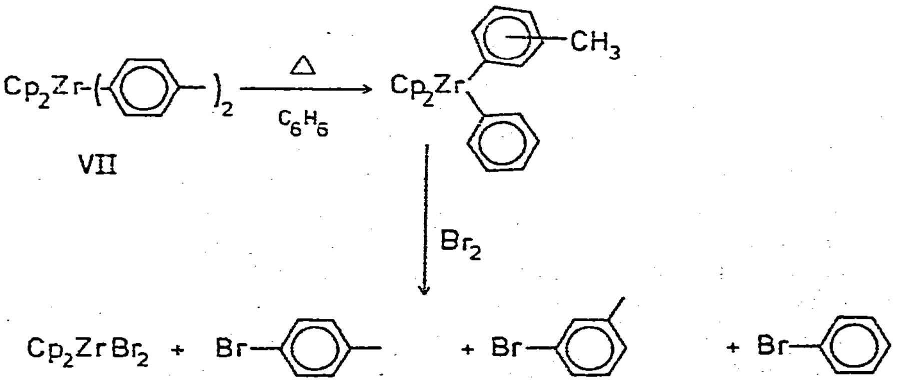
Starting materials

The compounds, diphenylzirconocene (VI), di-*p*-tolylzirconocene (VII), and di-*m*-tolylzirconocene (VIII) have been prepared by treating zirconocene dichloride with the appropriate aryllithium reagent [5]. Recrystallisation from ether at low temperature gives the complexes as white solids, which are moderately soluble in aromatic solvents and slightly soluble in saturated hydrocarbons.

Results

Initially a solution of VII in degassed absolute benzene (0.1 *M*) was thermolyzed under argon (70°C, 3 h). Treatment of the mixture with bromine gave zirconocene dibromide and *p*-bromotoluene, as expected, plus much *m*-bromotoluene and bromobenzene (Scheme 2). Similar mixtures were obtained from

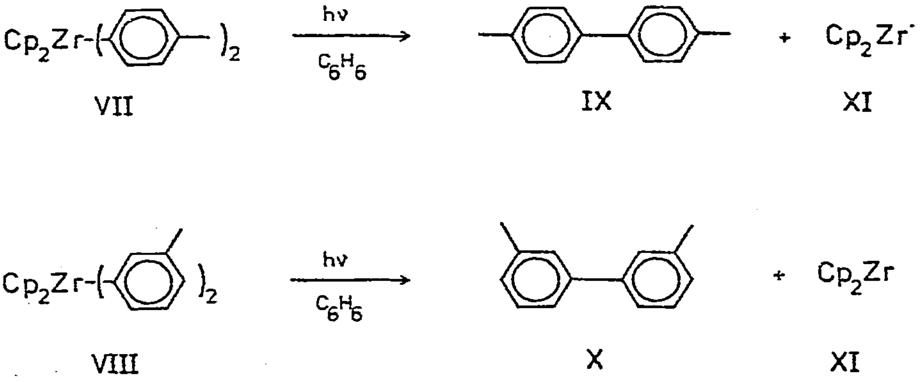
SCHEME 2. Products obtained after thermolysis of VII in benzene and subsequent treatment with bromine.



VI and VIII, respectively. No biphenyls were formed *. Since it is known that electrophilic reagents can cleave transition metal to carbon σ-bonds [7], it seemed that the solvent had reacted by fission of C—H bonds and formation of Zr—C bonds.

Having failed to separate the mixture of σ-complexes formed by thermolysis, we achieved a complete analysis by photochemical degradation of the products. Photolysis (Philips HPK 125, Pyrex filter) does not affect the h^5-cyclopentadienyl ligands but selectively couples the σ-bonded aryl groups to form biphenyls. For example, photolysis of VII at 20°C in benzene (or ether) produces a deep blue-brown solution from which an almost quantitative yield of 4,4'-dimethylbiphenyl (IX) can be isolated. This solution is spontaneously decolorized by added bromine, and zircononcene dibromide is obtained. We thus suggest that this deeply colored species is zirconocene (XI) [8]. Photolysis of VI and VIII gave analogous results, the σ-bonded aryl ligands undergo stereospecific coupling to biphenyls upon photolysis (Scheme 3).

SCHEME 3. Photochemical decomposition of diarylzirconocenes.



Having developed this method of coupling the two σ-aryl ligands bonded to the same zirconium atom without affecting the label, we thermolyzed solutions of VI in toluene, and VII and VIII in benzene (0.1 *M*), respectively, in sealed ampules under argon. After subsequent photolysis we obtained solutions which consisted only of the organic products benzene, toluene, and a mixture of biphenyls, all of which could be separated by GLC.

At low temperatures and short reaction times (e.g. 70°C, up to 10 h) thermal decomposition of VII, which can be described by a first order rate expression ($k = 2.8 \pm 0.2 \times 10^{-5}$ sec^{-1} at 70°C), produces three new diarylzirconocenes. By photochemical degradation to biphenyls their structures have been shown to be *m*-tolylphenylzirconocene (XIII), *p*-tolylphenylzirconocene (XIV), and diphenylzirconocene (VI). As can be seen from Table 1, which gives typical product ratios obtained from VII, formation of VI occurs only after an induction period. The "mixed" tolylphenylcomplexes XIII and XIV are formed in comparable amounts; their ratio, however, never becomes constant, and shows a considerable

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* Formation of biphenyls would not be unprecedented since several σ-bonded ligands form coupling products upon thermolysis [6].

TABLE 1

PRODUCT COMPOSITIONS (in %) OBTAINED IN THE THERMOLYSIS OF VII, VIII, AND XVI IN BENZENE AT 70°C [a]

Starting compound	Thermolysis time (sec)	Products after thermolysis					
		VII	VIII	XVI	XIII	XIV	VI
VII	1800	93.9			1.8	4.3	—
VII	3600	89.1			3.5	7.0	0.4
VII	7200	79.9			7.5	10.9	1.7
VII	10800	71.2			10.4	15.1	3.3
VII	32400	31.7			21.3	23.8	23.2
VIII	7200		67.1		21.8	7.9	3.2
VIII	16200		43.3		33.4	13.0	10.3
VIII	25600		29.0		37.0	15.0	19.0
VIII	32400		22.0		37.4	15.0	25.6
XVI	0			68.8	24.1	—	7.1
XVI	600			24.3	68.5	—	7.2
XVI	1800			6.0	86.7	—	7.3
XVI	3600			3.1	87.6	0.9	8.4
XVI	10800			0.4	74.2	3.7	21.7

[a] All product ratios were obtained by GLC analysis after photochemical degradation of the diarylzirconocenes to the corresponding biphenyls.

time dependence. Analogous results were obtained from VI in toluene as well as from VIII in benzene (rate constants at 70°C: $3.0 \pm 0.1 \times 10^{-5}$ and $4.2 \pm 0.2 \times 10^{-5}$ sec^{-1}). From VIII the same primary products XIII and XIV are formed (Table 1). Their ratio, again, is time dependent but quite different from the ratio of these products in the thermolysis of VII, in this case XIII is formed predominantly. Diphenylzirconocene (VI) is observed after prolonged thermolysis. Almost equimolar amounts of XIII and XIV are formed first from VI in toluene (Table 2). Of the six possible ditolyl isomers, the complexes VII, VIII, and *m,p'*-ditolylzirconocene (XV) are observed after longer reaction times.

To complete this series we needed di-*o*-tolylzirconocene (XII). We were unable to make it by reaction of *o*-tolyllithium with zirconocene dichloride in

TABLE 2

PRODUCT COMPOSITIONS (in %) OBTAINED IN THE THERMOLYSIS OF DIPHENYLZIRCONOCENE VI IN TOLUENE AT 70°C [a]

Thermolysis time (sec)	Products after thermolysis					
	VI	XIII	XIV	VIII	XV	VII
3600	88.0	5.7	6.3	—	—	—
7200	80.9	8.5	10.6	—	—	—
10800	70.0	12.6	15.4	0.4	1.1	0.5
18000	55.3	21.0	19.0	1.2	2.2	1.3
28800	40.2	23.7	24.0	3.3	5.2	3.6

[a] After photochemical degradation to biphenyls.

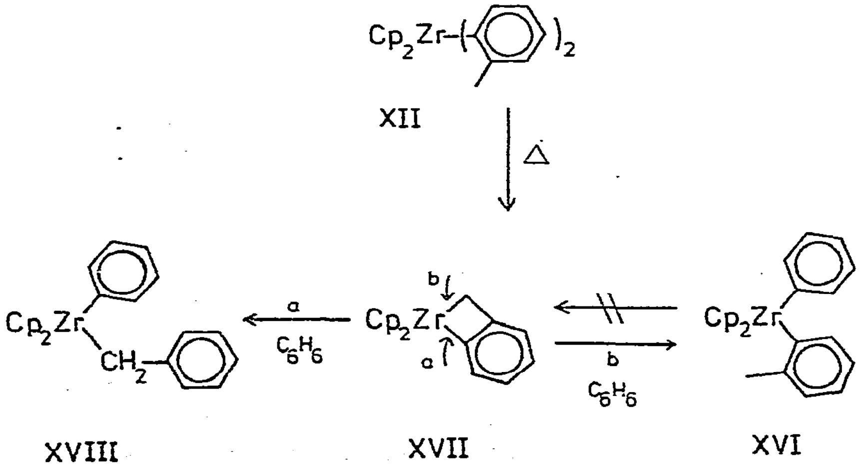
ether, but performing the reaction in an ether/benzene mixture, we obtained a mixture of diarylzirconocenes, which, by photochemical degradation was shown to consist of *o*-tolylphenylzirconocene (XVI, 69%), *m*-tolylphenylzirconocene (XIII, 24%), and diphenylzirconocene (VI, 7%). Apparently XII is too unstable to be isolated even at low temperature. Even XVI is much more reactive than all other diarylzirconocenes studied. It decomposes in benzene in a first order reaction ($k = 1.3 \pm 0.2 \times 10^{-3}$ sec^{-1} at 70°C) to produce XIII and VI, the former being the main product (Table 1). After prolonged thermolysis small amounts of XIV are formed (up to 3.7% after 4 h at 70°C).

In all these thermolyses the solutions of diarylzirconocenes remain clear and colorless throughout the reaction. At higher temperatures (>90°C) or longer reaction times (>10 h), however, the solutions become dark green, and the kinetics are no longer first order. In all the thermolyses no changes in rates or product compositions were observed when the concentrations of the starting materials were changed by a factor of 50.

Discussion

Since tolyl groups from the solvent become bound to the metal during the thermolysis of VI, any mechanism in which loss of a methyl group from the starting material VII or VIII is a consequence of a direct participation of this group in the reaction can be excluded. The situation is not so clear for the decomposition of the complexes XII and XVI, in which C—H bonds of the methyl groups in the *o*-tolyl ligands might be attacked by the other aryl ligand [9] (Scheme 4). However, for two reasons we believe that such a process which would explain the remarkable rate enhancement observed for XVI as well as XII, is improbable. First, as can be seen from Scheme 4, the intermediate XVII must be prone to two modes of attack by the benzene solvent, leading to XVI and benzylphenylzirconocene (XVIII). Since XVIII would not have escaped

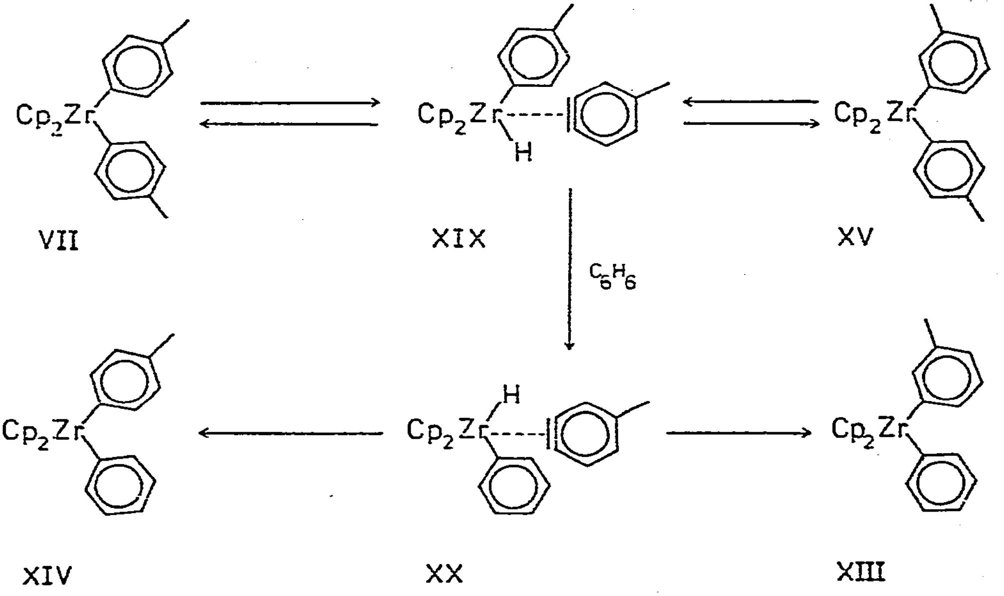
SCHEME 4. Consequences of the formation of dicyclopentadienylzirconabenzocyclobutene (XVII) as an intermediate in the thermolyses of diarylzirconocenes (XII and XVI) in benzene.



detection *, one would have to postulate that this intermediate forms products by route b only, and this seems unreasonable. Second, we can definitely exclude this mode of decomposition in the thermolysis of *o*-tolyl-phenylzirconocene (XVI), since the product, *m*-tolylphenylzirconocene (XIII), could not be formed via XVII.

Tolyl groups are successively exchanged for phenyl groups in VII and VIII. From the time dependence of the product ratio it is obvious that mixed tolylphenylzirconocenes are the initial products, and subsequently give diphenylzirconocene. The fact that a mixture of XIII and XIV is obtained from VII shows that at some time during the reaction the 4- and 3-positions of one of the σ-bonded tolyl groups become equivalent. The intermediate that leads to this equivalence (and that of the 2- and 3-positions of the tolyl groups in XVI and XII, respectively), must be an aryne, in this case complexed by the metal. As has been suggested such an intermediate [3] could have been formed by β-hydride elimination [11] to give the hydride complex XIX. This in turn could react with benzene solvent to produce XX, which would form the mixed products XIII and XIV in the reverse reaction (Scheme 5).

SCHEME 5. Formation of products in the thermolysis of diarylzirconocenes via a β-hydride elimination mechanism.



That this attractive scheme, which involves only well established mechanisms [12] and known reactions [13], cannot apply to the ligand exchange of diarylzirconocenes is shown by the fact that no isomerized *m,p'*-ditolylzirconocene (XV) is formed in the reactions starting from VII, VIII, or XII.

We suggest that the Scheme presented in Fig. 1 presents the explanation of

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[*] The σ-bonded ligands in dibenzylzirconocene are coupled to give 1,2-diphenylethane upon photolysis under these conditions [10].

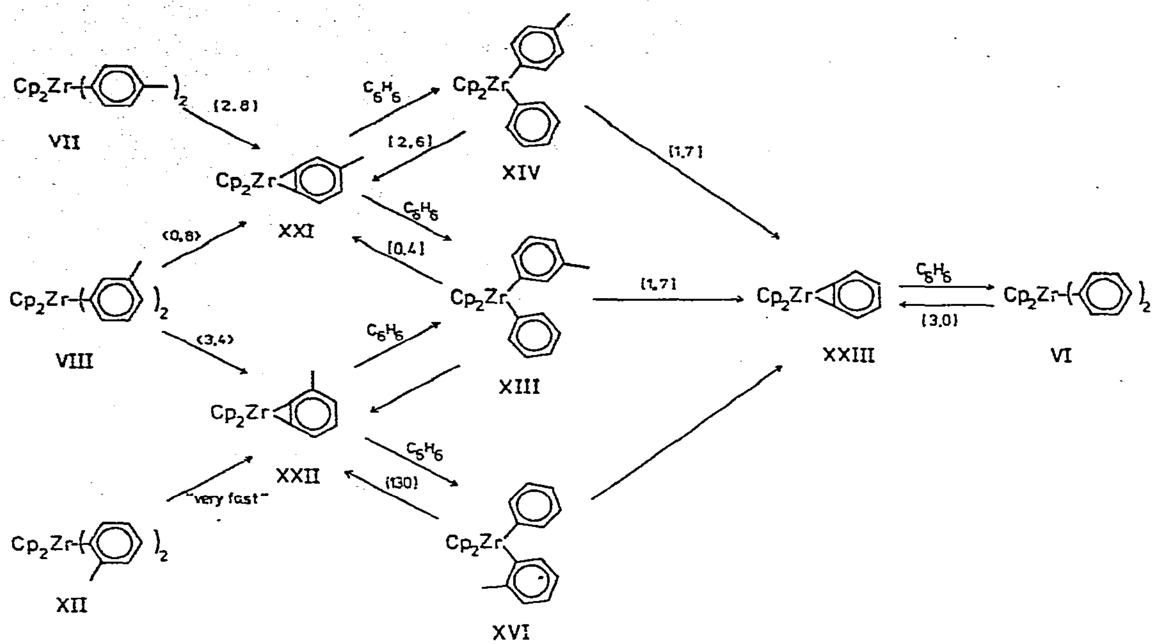

Fig. 1. Reaction scheme for the thermolysis of diarylzirconocenes in benzene. The rate constants ($k \times 10^5$ sec^{-1}) at 70°C have been measured ( ), calculated [ ], or recalculated using calculated and measured values < >.

our results. The aryne complex XXI is formed from VII. This intermediate reacts with the benzene to form XIII and XIV. Consequently XXII is formed from XII, and in turn gives XIII and XVI by attack on the solvent. Each of these primary products XIII, XIV, and XVI, however, can form aryne complexes, namely XXI and XXIII from XIV, XXII and XXIII from XVI, and all three from XIII. Thus the formation of XIV and VI must be consecutive reactions starting from XII, a fact that is verified by the time dependence of the observed product distribution in the thermolysis starting from XVI. On the other hand XVI and VI must be consecutive products in the thermolysis of VII. This can be shown to be true for VI. In this case XVI cannot be observed at all because its reverse reaction to XIII via XXII (and, though less important, to VI via XXIII) is too fast. This, of course, is also the reason why XVI cannot be observed in the thermolysis of VIII, which should be able to form both XXI and XXII.

That this explanation can also account quantitatively for the observed results was shown by a computer simulation of the reaction for this kinetic scheme using the measured *k*-values and the observed product distributions. We were able to show that this scheme with a single set of rate constants fits the behaviour starting from VII or VIII. Figure 2 shows the relation of calculated and experimental product compositions in the thermolysis of VII and VIII in benzene at 70°C. Since the ratio XIV/XIII is >1 starting from VII but <1 starting from VIII, there is only one set of rate constants that produces the observed product distributions. The calculated *k*-values are given in Fig. 1.

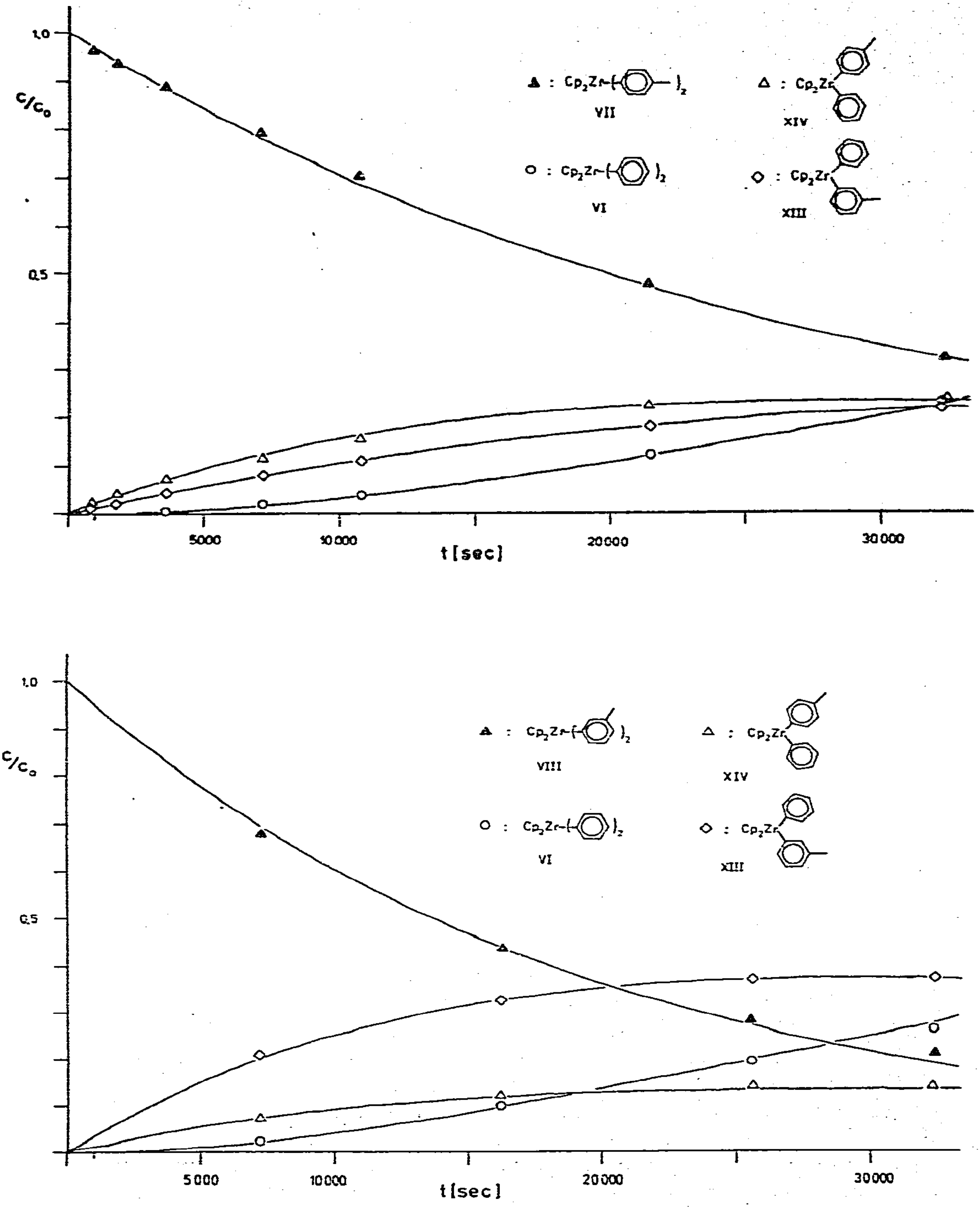

Fig. 2. Time dependent product compositions in the thermolysis of di-*p*-tolylzirconocene (VII) and di-*m*-tolylzirconocene (VIII) at 70°C in benzene. (Solid lines represent ratios obtained from the computer simulation; the measured values are marked.)

Conclusion

There is ample evidence for the intermediacy of aryne complexes in the thermolysis of diarylzirconocenes. Since formation of these dehydrobenzene complexes, by β-hydride elimination can be excluded, we assume that the abstraction of an *ortho* proton from one of the σ-bonded aryl ligands by the other aryl ligand directly leads to the intermediate *, which reacts with the C—H bonds of aromatic hydrocarbons. This type of reaction also would explain why at elevated temperatures another parallel reaction occurs, leading to two equivalents of toluene from VII and VIII as the only isolable products. Obviously at higher temperatures the h^5-cyclopentadienyl ligands serve more effectively as proton donors in this abstraction reaction [3]. Further studies of this reaction and of the way in which the aryne complexes react with C—H bonds are under investigation in our laboratory.

Experimental

All reactions were carried out in Schlenck type glassware under argon. Ethyl ether and tetrahydrofuran were distilled from lithium aluminum hydride. Benzene, toluene, chloroform, and pentane were distilled from P_4O_{10}. All solvents were saturated with argon before use. Zirconocene dichloride was synthesized from zirconium tetrachloride (Merck—Schuchardt) procedures [15]; a yield of 80% was obtained using dry tetrahydrofuran instead of dimethoxyethane. Aryllithium compounds were obtained by reaction of lithium metal with the appropriate aryl bromide or chloride in ether.

NMR spectra were recorded on a Varian A60-D spectrometer. Deuterochloroform and hexadeuterobenzene were distilled from P_4O_{10}. All solutions of organometallic compounds were introduced into the sample tube under argon.

GLC analyses were performed on a Hewlett Packard 5750 FID. Preparative GLC separations were carried out on a Varian 90-P (H.W.D.). Three types of column materials were used: A, silicone GE SE-30 (Hewlett Packard), 10% on Chromosorb P, 80—100 mesh, AW/DMCS treated; B, 10% Bentone 34 (WGA) and 10% Apiezon L (Hewlett Packard) on Chromosorb W, 80—100 mesh, AW/DMCS treated; and C, 5% tri-2,4-xylenyl phosphate (WGA) on Chromosorb P, 60—80 mesh, AW/DMCS treated.

Elemental analyses were performed by Dornis und Kolbe, Mikroanalytisches Laboratorium, Mülheim/Ruhr.

Diarylzirconocenes

Diarylzirconocenes were prepared by adaption of Rausch's procedure for the preparation of diphenylzirconocene [5] by treating zirconocene dichloride with two equivalents of aryllithium reagent in ether at —40°C. The solution was then allowed to warm to room temperature. The solvent was removed in vacuo. The remaining white solid was washed twice with pentane and dried in vacuo. The organometallics were extracted with benzene or toluene. The aromatic solvent was removed by vacuum distillation, and the crude organometallic

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* We note the similarity between this reaction and the *ortho*-metalation reaction [14].

compounds were dissolved in ether and the small amount of white precipitate was filtered off. Upon concentration of the filtrate and cooling the diarylzirconocenes VI, VII, and VIII were obtained as white crystalline solids (yield 70%).

VII: Analysis: C, 71.18; H, 6.00; Zr, 22.80. $C_{24}H_{24}Zr$ calcd.: C, 71.41; H, 5.99; Zr, 22.60%. NMR ($CDCl_3$, internal standard TMS, ppm, τ scale): 2.6—3.0 (AA'BB', 8H: aromatic protons), 3.85 (s, 10H, is shifted to 4.15 in C_6D_6: Cp), 7.75 (s, 6H: Me-groups). IR (KBr): 3100m, 2950m, 1485m, 1440m, 1375m, 1040s, 1020 and 1015s, 825s, and 810s cm^{-1}.

VIII: Analysis: C, 71.10; H, 5.83; Zr, 23.00 $C_{24}H_{24}Zr$ calcd.: C, 71.41; H, 5.99; Zr, 22.60%. NMR ($CDCl_3$, internal standard TMS, ppm, τ scale): 2.6—3.3 (m, 8H: aromatic protons), 3.85 (s, 10H, is shifted to 4.15 in C_6D_6: Cp), 7.75 (s, 6H: Me-groups). IR (KBr): 3100m, 2950m, 1440m, 1375m, 1095m, 1022 and 1012s, 900m, 815s, and 805s cm^{-1}.

Attempted preparation of di-o-tolylzirconocene (XII)

Zirconocene dichloride was treated as above with two equivalents of *o*-tolyllithium in ether at —40°C. In the workup no organometallic compounds could be extracted with benzene after removal of the solvent in vacuo at room temperature. By carrying out the reaction in an ether/benzene mixture (80/20), however, a white noncrystalline solid was obtained after evaporation of the solvent from the benzene extract. Since this mixture of diarylzirconocenes could not be separated by crystallization or chromatography it was photochemically decomposed to a mixture of biphenyls.

Photochemical decomposition of diarylzirconocenes

A solution of di-*p*-tolylzirconocene (VII) in benzene (ca. 0.1 *M*) was irradiated (Philips HPK 125, pyrex filter) for 16 h. A deep blue-brown solution containing some similarly colored precipitate was obtained. No special care to avoid contact with the atmosphere was taken after completion of the photolysis. The solvent was stripped off and the residue in hexane was passed through alumina. Upon evaporation of the solvent 4,4'-dimethylbiphenyl (IX) crystallized in long needles. Yield: 97%. Analogous results were obtained from VI and VIII.

In a separate experiment the deeply colored solution obtained from photolysis of VIII in benzene was treated with Br_2 in methylene chloride under argon. The resulting clear, slightly yellow solution was concentrated and chromatographed on alumina. Elution with n-hexane gave pure 3,3'-dimethylbiphenyl (X). After removal of all organic material, zirconocene dibromide was obtained by elution with ethyl ether (yield: 40% after recrystallization from benzene).

Thermolysis of diarylzirconocenes in aromatic hydrocarbon solvents

Preparative runs

Thermolysis of diphenylzirconocene (VI) in toluene. 150 ml of a solution of VI in toluene (ca. 0.2 *M*) was thermolyzed under argon for 8 h at 70°C with exclusion of light. The solution was transferred to a photolysis apparatus (Philips HPK 125, Pyrex filter) and photolyzed overnight. The solvent was evaporated, and the hexane solution of the residue was passed through a short alumina column, The colorless solution was concentrated and the biphenyls were separated by preparative GLC. Three fractions were obtained by chromatography on column A at 200°C (Table 3): biphenyl, monomethylbiphenyls, and dimethylbiphenyls. The middle fraction consisted of 4-methylbiphenyl and 3-methylbiphenyl, which were separated on column B at 200°C. The third fraction from column A contained three components, which were separated on column C at 180°C and shown to be 3,3'-dimethylbiphenyl, 3,4'-dimethylbiphenyl, and 4,4'-dimethylbiphenyl. All the components were isolated under the conditions indicated in Table 3, and identified spectroscopically.

The products from thermolysis of VII, VIII, and XVI in benzene and subsequent photolysis were separated analogously on the GLC columns mentioned.

Kinetic runs. 5 ml of 0.1 *M* solutions of VI in toluene, and VII, VIII, as well as the mixture containing XVI in benzene were sealed in argon filled 15 ml pyrex ampoules. The samples were thermolyzed for a given time in a thermostatted oil bath (temperature maintained to within ±0.1°C). After thermolysis the samples were cooled to room temperature and irradiated for 24 h (Philips HPK 125). Then the ampoules were opened and the solution analyzed by GLC. All the biphenyls were separated by use of columns B and C (Table 3).

As is apparent from the photolysis of the diarylzirconocenes, biphenyls were formed quantitatively from the corresponding complexes upon photolysis. We, therefore, defined the sum of all biphenyls found as being 100% and calculated the product distributions given in Tables 1 and 2 on that basis. To justify this definition, and since we could not find an internal standard that did not interfere with the products in the GLC analysis, we conducted the experiment described below.

As can be seen from Table 1 the di-*p*-tolyl complex VII is not formed in the thermolysis of di-*m*-tolylzirconocene (VIII) in benzene (and vice versa), so 4,4'-dimethylbiphenyl was not found after photolysis of the corresponding thermolysis mixture. Therefore, exactly 5 ml of a 0.1 *M* solution of VIII were thermolyzed then photolyzed, and then mixed with exactly 5 ml of a 0.1 *M* solution of VII which had been directly photolyzed. GLC analysis showed that the sum of products derived from VIII was equal to the amount of 4,4'-dimethylbiphenyl within the accuracy of our GLC analysis. The same result was obtained when a weighted amount of 4,4'-dimethylbiphenyl was used as internal standard, or when 3,3'-dimethylbiphenyl derived from photolysis of VIII was increased with the mixture from thermolysis and subsequent photolysis of VII.

Upon thermolysis at higher temperatures or longer reaction times, however, the sum of products was no longer equal relative to this standard but significantly decreased. In these cases the solutions obtained after thermolysis were not clear and colorless but green, and contained varying amounts of a dark green precipitate.

Simulation of the kinetic scheme by analog computer. The simulation of the kinetic scheme given in Fig. 1 was performed on an EAI 380 analog computer. The time dependence of the product composition was simulated for the reactions starting with VII and VIII. Due to the high reactivity of XVI even at room temperature, rates and concentrations in the decomposition of this compound could not be measured as accurately as in the thermolysis of the other diarylzirconocenes, and so we did not carry out the simulation for the reaction of XVI.

TABLE 3

GLC CONDITIONS AND RETENTION TIMES IN THE SEPARATION OF BIPHENYLS OBTAINED FROM DIARYLZIRCONOCENES BY PHOTOCHEMICAL DECOMPOSITION

GLC-conditions				Retention time (min)						
Column material	Column dimensions (m X mm)	Temperature (°C)	Helium flow (ml/min)	2-Methyl-biphenyl	Biphenyl	3-Methyl-biphenyl	4-Methyl-biphenyl	3,3′-Di-methyl-biphenyl	3,4′-Di-methyl-biphenyl	4,4′-Di-methyl-biphenyl
Preparative separations:										
A	2 X 6.35	200	100	5.5	5.5	7.5	7.5	10	10	10
B	2 X 6.35	200	100	7	11	16.5	18	25	28.5	30
C	4 X 6.35	180	80	25	33	50	55	64	71	79
Analytical separations:										
B	2 X 3.175	210	100	5.5	7.2	10.5	11.5	14.5	17.5	17.8
C	3 X 3.175	180	100	9	10.5	15.5	16.5	23	25	27

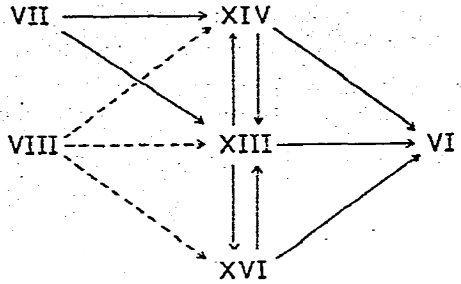

Fig. 3. Simplified kinetic scheme used for the computer simulation of the reactions starting from VII and VIII.

The actual simulation was carried out according to a simplified kinetic scheme (Fig. 3) leaving out products not directly observed. From the obtained k-values the actual rate constants (Fig. 1) could be recalculated by simple mathematical procedures.

Acknowledgement

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