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PHOTOCHEMICAL INVESTIGATIONS OF SOME DI-η^5-CYCLOPENTADIENYLDIARYLTITANIUM COMPOUNDS *,**

MARVIN D. RAUSCH *, WYNDHAM H. BOON and ERIC A. MINTZ

Department of Chemistry, University of Massachusetts, Amherst MA 01003 (U.S.A.)

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Summary

The photolysis of $(\eta^5\text{-}C_5H_5)_2Ti(C_6H_5)_2$ in benzene solution leads to black titanocene and biphenyl. Studies in benzene-d_6 have shown that biphenyl-d_0 and biphenyl-d_5 are produced in ca. equal amounts. Photolysis of $(\eta^5\text{-}C_5H_5)_2Ti(p\text{-}CH_3C_6H_4)_2$ produces black titanocene, toluene, 4-methylbiphenyl and 4,4'-dimethylbiphenyl, while photolysis of $(\eta^5\text{-}C_5H_5)_2Ti(m\text{-}CH_3C_6H_4)_2$ gives titanocene, toluene, 3-methylbiphenyl and 3,3'-dimethylbiphenyl. The above results indicate that the biaryls are formed both by a reductive-elimination process as well as by attack of a radical-like aryl species on the solvent, and not by an *ortho*-phenylene or benzyne-type titanocene intermediate as has been suggested for the thermal decomposition of diaryltitanocenes. Photolysis of $(\eta^5\text{-}C_5H_5)_2Ti(C_6H_5)_2$ in the presence of either CO or PhC≡CPh leads to moderate yields of dicarbonyltitanocene and 1,1-di-η^5-cyclopentadienyl-2,3,4,5-tetraphenyltitanole, respectively. The formation of *cis*- and *trans*-stilbenes as well as *cis,cis*-1,2,3,4-tetraphenyl-1,3-butadiene in the latter reaction is indicative of titanium-hydride intermediates being formed under these photolytic conditions.

Introduction

σ-Bonded organic derivatives of titanium have played an exceedingly significant role in the development of catalysis and chemical technology in recent years. Of fundamental importance to an understanding of the stabilization and catalytic behavior of such compounds are the pathways by which they degrade [1—3]. For example, thermolysis reactions of the diaryltitanocenes, a well-known class of organotitanium compounds in this series, have been extensively

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* Presented in part at a conference [59a] and a meeting [59b].

** Dedicated to Professor Ernst Otto Fischer on the occasion of his 60th birthday on November 10, 1978.

investigated [4—18]. In marked contrast, however, studies relating to photochemically-induced degradations of diaryltitanocenes appear to be limited to a single brief report by Razuvaev et al. in 1961 [5]. These investigators noted that when diphenyltitanocene (I) was photolyzed in chloroform solution for 50—60 h, titanocene dichloride was produced in high yield. In addition, benzene and very small amounts of biphenyl were obtained, however, no chlorobenzene or cyclopentadiene could be detected.

In continuation of our systematic studies on photochemically-induced reactions of σ-bonded derivatives of the transition metals [19—24], we have investigated photochemical reactions of diphenyltitanocene (I), di(*p*-tolyl)titanocene (II) and di(*m*-tolyl)titanocene (III) in benzene solution. Details of these studies are described in this paper.

Results and discussion

When I is irradiated in benzene solution in a Pyrex Schlenk tube ($\lambda > 300$ nm), the reaction mixture rapidly darkens with formation of a greenish-black solution. This photolysis reaction does not appear to be autocatalytic with an induction period, as was previously found for the photolysis of $(\eta^5\text{-}C_5H_5)_2Ti(CH_3)_2$ under similar conditions [23]. Removal of the solvent and organic products left a black residue which analyzed reasonably well for $C_{10}H_{10}Ti$, although an exact empirical formula for the product cannot be assigned with certainty.

The proton NMR spectrum of this product when measured in benzene-d_6 solution exhibited broad resonances between δ 5—6 ppm and δ 0.5—1.5 ppm. The IR spectrum of the product when recorded in Nujol contained sharp, unsplit bands at 790 and 1010 cm^{-1}, and absorptions in the 1220—1230 cm^{-1} region which have commonly been assigned [25,26] to bridging Ti—H—Ti bands in most other forms of titanocene were absent *. The mass spectrum of the photolysis product showed moderately intense peaks at *m/e* 352 $[C_{20}H_{16}Ti_2]^+$, 178 $[C_{10}H_{10}Ti]^+$, 128 $[C_{10}H_8]^+$ and 113 $[C_5H_5Ti]^+$, as well as less intense peaks in the higher mass region at *m/e* 370, 398, 400, 402 and 454 $[(C_5H_5)_4Ti_4]^+$. The product thus has very similar physical and spectral properties to the black, oligomeric form of titanocene produced by the photodegradation of $(\eta^5\text{-}C_5H_5)_2Ti(CH_3)_2$ [19,23], and its chemical properties (vide infra) also closely resemble this material as well. It should be noted, however, that black titanocene produced by the photolysis of I in benzene, while being very air-sensitive, is not pyrophoric in air as is the product derived from the photolysis of $(\eta^5\text{-}C_5H_5)_2Ti(CH_3)_2$.

Earlier studies [4—11] on the thermal degradation of I in hydrocarbon solvents have clearly indicated that benzene is the principal organic product, and that the reaction appears to proceed via the formation of an intermediate organotitianium species of composition $(C_5H_5)_2TiC_6H_4$, which may be regarded either as an *ortho*-phenylene or a benzyne derivative of titanocene [1]. It is

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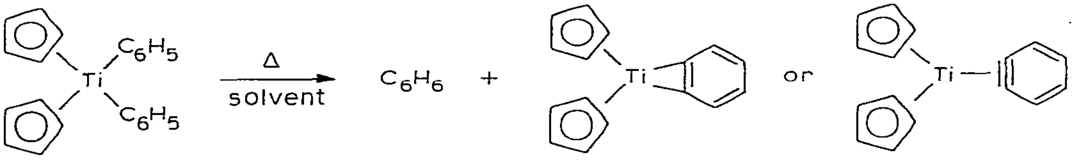
* A very weak band at 1260 cm^{-1} was observed in the IR spectrum of the product derived from the photolysis of II in benzene solution, however.

important to note that biphenyl is not observed to be formed under these thermolytic conditions [4,9,10].



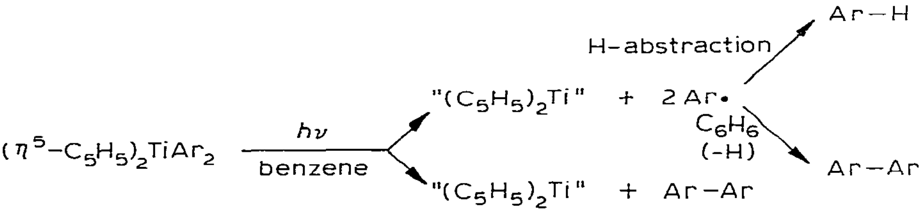
(I)

In contrast, we found that biphenyl was formed as the only detectable product when I was photolyzed in benzene solution. The yield of biphenyl was 121% based on the phenyl groups being derived only from I, or 60.5% based on the phenyl groups reacting independently of one another in the formation of biphenyl. Solvent participation in the formation of biphenyl was therefore clearly evident.

This surprising result lead us to investigate in detail the photolysis of I and the tolyl analogs II and III, in order to learn more about the mechanistic pathways by which biphenyl is formed under these conditions. When I was photolyzed in benzene-d_6 and the biphenyl was analyzed by mass spectrometry, 46% biphenyl-d_0 and 54% biphenyl-d_5 were found to be present. Based on solvent participation as is shown in this experiment, 88% of the phenyl substituents which were originally bonded to titanium can thus be accounted for.

The photolysis of II in benzene solution lead to the formation of black titanocene as well as three organic products which were identified by GLC an GLC-mass spectrometry following several different isolation techniques. These products were shown to be toluene, 4-methylbiphenyl, and 4,4′-dimethylphenyl which were formed in yields of 11%, 11% and 36%, respectively, based on the *p*-tolyl groups of II. It is important to note that neither 3-methylbiphenyl nor 3,3′-dimethylbiphenyl could be detected among the photolysis products. In a related experiment, photolysis of III in benzene solution resulted in the exclusive formation of toluene (35%), 3-methylbiphenyl (35%), and 3,3′-dimethylbiphenyl (21%) as the organic products as evidenced by GLC analysis. Furthermore, 4-methylbiphenyl and 4,4′-dimethylbiphenyl were shown not to be present in this reaction.

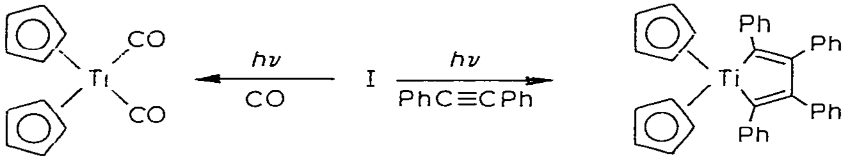
The above data suggest two simultaneous pathways for the photolytic degradation of these diaryltitanocene compounds.



One pathway would involve homolytic cleavage of a titanium—aryl σ-bond and generation of a radical-like intermediate, which could either abstract a hydrogen from the solvent or a cyclopentadienyl group, or undergo homolytic aromatic substitution with the solvent [23,24,27—36]. A second pathway would consist of reductive elimination [2,37—41] with stereospecific coupling of the aryl substituents to form isomerically pure biaryls. Since our studies in this area were completed, this second pathway has been shown to occur in the photodegradation of diarylzirconocene derivatives [42]. Our results also indicate that *ortho*-phenylene or benzyne-type titanium intermediates are not produced during the photolytic decomposition of diaryltitanocenes, since such intermediates would be expected to lead to mixtures of isomeric biphenyls.

The photolysis of I in the presence of anthracene in benzene solution was also studied, since anthracene is a well-known radical-trapping reagent [43,44]. In addition to the anticipated photodimer of anthracene, 9-phenylanthracene and 9,10-dihydro-9-phenylanthracene were obtained in yields of 3% and 2%, respectively. Photolysis of I and anthracene in benzene-d_6 furthermore demonstrated that the phenyl substituents in these products are derived from I and not from the solvent.

The photolyses of I in the presence of several other reactive substrates such as carbon monoxide and diphenylacetylene have likewise been investigated. In these photolyses, black titanocene was not observed, but organotitanium products derived from the monomeric $(\eta^5\text{-}C_5H_5)_2Ti$ unit could be isolated in both cases. Thus, when I was photolyzed in benzene and CO subsequently bubbled through the solution, the mixture turned red-brown immediately, and dicarbonyltitanocene (IV) was isolated in 32% yield. This result is thus analogous to the formation of IV via the photo-carbonylation of $(\eta^5\text{-}C_5H_5)_2Ti(CH_3)_2$ under similar conditions [19,21,23]. GLC analysis indicated that no benzophenone was formed in this photolysis reaction, in contrast to the carbonylation of I under pressure [12].



(IV)

(V)

Photolysis of I or II in the presence of diphenylacetylene produced moderate yields of the titanacycle 1,1-di-(η^5-cyclopentadienyl)-2,3,4,5-tetraphenyltitanole (V) [45]. These results are again in contrast to thermally-induced reactions of diaryltitanocenes in the presence of diphenylacetylene, which invariably lead to the formation of 1,1-di-(η^5-cyclopentadienyl)-2,3-diphenylbenzotitanole via an intermediate *ortho*-phenylene or benzyne-type species such as that described above [9,10,12,18,46].

A detailed analysis of the organic products derived from the photolysis of I or II in the presence of diphenylacetylene was also undertaken, and the results are summarized in Tables 1 and 2, respectively.

In addition, the photolysis of I and diphenylacetylene in benzene-d_6 was studied in order to help determine the origin of the various organic products that were formed. The expected biaryls, biphenyl, biphenyl-d_5, 4-methylbiphenyl, and 4,4′-dimethylbiphenyl were obtained in moderate yields in these reactions, and the results are consistent with those described previously for the photolyses of I or II alone. Both *cis*- and *trans*-stilbenes were obtained in these

TABLE 1

ORGANIC PRODUCTS OBTAINED FROM THE PHOTOLYSIS OF $(\eta^5\text{-}C_5H_5)_2Ti(C_6H_5)_2$ AND DIPHENYLACETYLENE (1/2 RATIO) IN BENZENE AND BENZENE-d_6 SOLUTION

Product	Retention time (min) [a]	Product (mg)	Yield (%)	Isotopic composition [b]
Biphenyl	4.0	240	46	50% d_0; 50% d_5
cis-Stilbene	5.6	50	8.2	75% d_0; 25% d_1
Diphenylacetylene	7.5	160	26	
trans-Stilbene	8.6	10	1.6	[c]
Triphenylethylene	28.4	10	1.2	100% d_0
cis,cis-1,2,3,4-Tetraphenyl-1,3-butadiene		20	3.3	92% d_0; 8% d_1

[a] GLC conditions: OV-101 column; temperature, 150—200°C programmed at 6°C/min; flow rate, 50 ml/min; chart speed, 0.5 cm/min. [b] Reaction run in benzene-d_6; see Experimental. [c] Separation from diphenylacetylene by the gas chromatograph was not adequate for analysis of the mass spectral data.

reactions in 5—10% overall yield. Similar results were obtained involving the photolysis of $(\eta^5\text{-}C_5H_5)_2Ti(CH_3)_2$ and diphenylacetylene, although the yields of *cis*- and *trans*-stilbene in this latter reaction were considerably lower [23]. *cis,cis*-1,2,3,4-Tetraphenyl-1,3-butadiene (VI) was obtained in low yield from the photolysis of either I or II in the presence of diphenylacetylene, and in the former case, a low yield of triphenylethylene was also observed.

The formation of the reduction products, *cis*- and *trans*-stilbene, suggests the presence of titanium hydride intermediates in these reactions, especially since no hydrogen gas could be detected in the headspace of the reaction mixture. The facile lability of ring hydrogens in low-valent titanocene systems is well-known, and their ability to undergo a ring-titanium shift in such activated species has been previously postulated by several groups of investigators [1,47,48]. Such an intermediate, formed during the photolysis of either dimethyl- or diaryl-titanocenes, would be expected to add to diphenylacetylene to form a vinylic-titanium intermediate (VII). The insertion of unsaturated hydrocarbons into transition-metal hydride bonds is likewise well-documented [49—51]. Intermediate VII could subsequently undergo hydrogenolysis to form the stil-

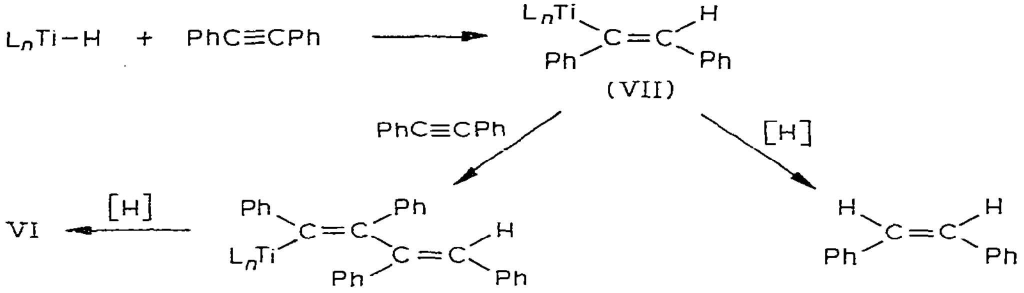
TABLE 2

ORGANIC PRODUCTS OBTAINED FROM THE PHOTOLYSIS OF $(\eta^5\text{-}C_5H_5)_2Ti(p\text{-}CH_3C_6H_4)_2$ AND DIPHENYLACETYLENE (1/2 RATIO) IN BENZENE SOLUTION

Product	Retention time (min) [a]	Product (mg)	Yield (%)
Biphenyl	3.0	0.1	trace
4-Methylbiphenyl	5.0	35	7.5
cis-Stilbene	5.6	19	3.9
4,4′-Dimethylbiphenyl	8.6	100	39
Diphenylacetylene	11.2	350	70
trans-Stilbene	13.3	8.7	1.8
cis,cis-1,2,3,4-Tetraphenyl-1,3-butadiene		33	6.6

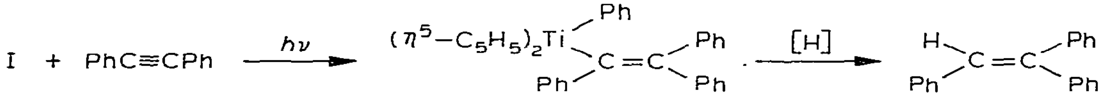
[a] GLC conditions: OV-101 column; temperature 150°C; flow rate, 70 ml/min; chart speed, 0.5 cm/min.

benes, or else could undergo a second insertion reaction with additional diphenylacetylene followed by hydrogenolysis to give VI *.



The pathway suggested for the formation of VI is formally analogous to that postulated for the reactions of $R_3Cr(THF)_3$ and acetylenes [53]. The fact that both *cis-* and *trans*-stilbene were obtained as photolysis products is not significant, since stilbenes are well-known to equilibrate under photolytic conditions, with the *cis*-isomer predominating [32]. Since *cis*-stilbene formed during the photolysis of I and diphenylacetylene in benzene-d_6 was 75% *cis*-stilbene-d_0 and 25% *cis*-stilbene-d_1, the data suggest that both the organotitanium moiety as well as the solvent can participate in the hydrogenolysis step, with the former pathway predominating.

The triphenylethylene formed from the photolysis of I and diphenylacetylene could have arisen from the addition [36,54] of a phenyl radical generated from I to diphenylacetylene, followed by hydrogen abstraction by the resultant vinyl radical to yield this product. An alternative mechanism for the formation of the triphenylethylene might involve insertion of diphenylacetylene into the carbon—titanium σ-bond of I, followed by hydrogenolysis.



Insertion products of this type have previously been isolated in reactions of $(\eta^5\text{-}C_5H_5)_2Ti(CH_3)_2$ with acetylenes under photolytic conditions [22,23]. No evidence for the intermediate formation of such an insertion product could be found in the photolysis of I and diphenylacetylene, however. The fact that the photolysis of I and diphenylacetylene in benzene-d_6 produces exclusively triphenylethylene-d_0 and predominantly *cis,cis*-1,2,3,4-tetraphenyl-1,3-butadiene-d_0 again suggests that the organotitanium moiety serves as the principal hydrogen source for these reduction products.

Experimental

All operations were conducted under argon using Pyrex Schlenk tubes. Argon, solvents and alumina were purified by techniques previously described

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* VI could also possibly be formed by the reduction of titanacycle V under the reaction conditions. When V was photolyzed in benzene for an extended period, a complex mixture of organic products was obtained, but VI was found to be only a very minor product [52].

[23]. Photolyses were conducted by means of a 450 W Hanovia photochemical lamp located in a quartz, water-cooled immersion well, as previously described [23]. Gas chromatographic analyses were performed on a Varian Series 2400 gas chromatograph equipped with a flame ionization detector. Compositions of various samples were also identified by means of a Perkin—Elmer—Hitachi RMU-6L mass spectrometer interfaced with a Perkin—Elmer 990 gas chromatograph. The products were separated on a 6-ft., 4% SE-30 column, and mass spectra were obtained for each component in the sample. Proton NMR spectra were recorded on either a Varian A-60 or a Perkin—Elmer R-12A spectrometer. IR spectra were recorded on either a Beckman IR-10 or a Perkin—Elmer 237B infrared spectrophotometer. Deuterated solvents which were used in reactions were put through four freeze—thaw cycles such that no gas evolved on melting. Deuterated solvents used for NMR spectra were degassed by bubbling argon through them for several min. Toluene-free benzene was prepared by an overnight reflux with basic $KMnO_4$ followed by fractional distillation through an 18 inch column packed with glass helicies. $(\eta^5\text{-}C_5H_5)_2Ti(C_6H_5)_2$ (I), $(\eta^5\text{-}C_5H_5)_2Ti(p\text{-}CH_3C_6H_4)_2$ (II) and $(\eta^5\text{-}C_5H_5)_2Ti(m\text{-}CH_3C_6H_4)_2$ (III) were prepared by literature procedures [4].

Photolysis of $(\eta^5\text{-}C_5H_5)_2Ti(C_6H_5)_2$ in benzene

A. Preparation of titanocene. A solution of $(\eta^5\text{-}C_5H_5)_2Ti(C_6H_5)_2$ (0.50 g, 1.5 mmol) in 250 ml of benzene was irradiated in a Schlenk tube (4 × 30 cm) for 4 h with stirring. The solvent was removed from the resultant dark solution under reduced pressure at room temperature. The organic product was sublimed at 10^{-4} mmHg at room temperature for 60 h, leaving 0.21 g (79%) of a black solid. Found: C, 67.00; H, 5.74; Ti, 26.5. $C_{10}H_{10}Ti$ calcd.: C, 67.44; H, 5.66; Ti, 26.90%. $C_{10}H_9Ti$ calcd.: C, 67.81; H, 5.13; Ti, 27.06%.

B. Isolation of the organic product. A solution of $(\eta^5\text{-}C_5H_5)_2Ti(C_6H_5)_2$ (0.50 g, 1.5 mmol) in 250 ml of benzene was irradiated for 4 h in a Schlenk tube (4 × 30 cm) with stirring. The dark green solution was concentrated to ca. 20 ml under reduced pressure at room temperature. Approximately 2 g of alumina was added and the remainder of the solvent was removed under vacuum. This material was added to a dry-packed alumina column (2 × 40 cm), and the column was eluted with benzene (250 ml) and with ethyl ether (100 ml). The solvents were evaporated to yield biphenyl (285 mg, 1.85 mmol, 61%), m.p. 69—70° C. The product was shown to be biphenyl by mixture m.p., TLC and GLC comparisons with an authentic sample.

Photolysis of $(\eta^5\text{-}C_5H_5)_2Ti(C_6H_5)_2$ in benzene-d_6

A solution of 21 mg (0.063 mmol) of $(\eta^5\text{-}C_5H_5)_2Ti(C_6H_5)_2$ in 10 ml of benzene-d_6 was irradiated for 4 h with frequent swirling in a small Schlenk tube. The solvent was removed under reduced pressure and the residue was extracted with hexane. The extracts were evaporated to dryness and the biphenyl was analyzed by mass spectrometry at both 15 and 80 eV. Peaks were observed at m/e 154 and 159 (equivalent to biphenyl-d_0 and biphenyl-d_5) in an intensity ratio of 46/54, respectively. Several other runs gave similar results.

Photolysis of $(\eta^5\text{-}C_5H_5)_2Ti(p\text{-}CH_3C_6H_4)_2$ in benzene

A. Preparation of titanocene. A benzene solution (250 ml) of $(\eta^5\text{-}C_5H_5)_2Ti$-

$(p\text{-}CH_3C_6H_4)_2$ (0.61 g, 1.7 mmol) was irradiated for 4 h with stirring in a Schlenk tube (4 X 30 cm). Titanocene was isolated in the same manner as is described above, and was shown by spectral measurements to have the same properties as the product obtained from the photolysis of I.

B. Isolation of the organic products via column chromatography. A solution of $(\eta^5\text{-}C_5H_5)_2Ti(p\text{-}CH_3C_6H_4)_2$ (0.53 g, 1.47 mmol) in 250 ml of benzene was irradiated for 4 h with stirring. The dark green solution was then concentrated to 15 ml under reduced pressure at room temperature. Approximately 2 g of alumina was added and the remainder of the solvent was removed with vigorous shaking. This mixture was added to a dry-packed column of alumina (4 X 25 cm) and the column was eluted with 300 ml of benzene. The solvent was evaporated leaving 0.18 g of a mixture of organic compounds. The mixture was analyzed by gas chromatography (12 ft., 10% QF-1 on 80-100 mesh Chromosorb P column, programmed from 80°C to 180°C at 15°C/min) and by GLC-mass spectrometry, and was found to have the following composition: biphenyl (trace), 4-methylbiphenyl (50 mg, 0.30 mmol, 10%), 4,4'-dimethylbiphenyl (129 mg, 0.71 mmol, 48%).

C. Isolation of the organic products by extraction. A solution of $(\eta^5\text{-}C_5H_5)_2$-$Ti(p\text{-}CH_3C_6H_4)_2$ (0.57 g, 1.58 mmol) in 250 ml of benzene was irradiated with stirring for 4 h. The solvent was removed under reduced pressure, and the residue was extracted twice with 40 ml portions of hexane. The extracts were filtered and the solvent evaporated to produce 0.21 g of a solid material. Analysis of this mixture as in the column chromatography workup gave the following results: biphenyl (trace), 4-methylbiphenyl (36 mg, 0.21 mmol, 6.7%), 4,4'-dimethylbiphenyl (170 mg, 0.93 mmol, 59%).

D. Determination of the organic products via gas chromatography. A solution of $(\eta^5\text{-}C_5H_5)_2Ti(p\text{-}CH_3C_6H_4)_2$ (0.64 g, 1.78 mmol) in 250 ml of toluene-free benzene was irradiated for 4 h with stirring. The resulting dark green solution was analyzed by gas chromatography on two different columns (12 ft., 10% QF-1 on 80—100 mesh Chromosorb P column, column temperature programmed from 80°C to 180°C at 15°C/min after the toluene peak; 10 ft., 10% Bentone 34 and 10% Apiezon L on 60-80 mesh Chromosorb W AW/HMDS-treated column, temperature programmed from 160°C to 220°C at 20°C/min after the toluene peak). The following results were obtained: toluene (35 mg, 0.38 mmol, 11%), 4-methylbiphenyl (66 mg, 0.39 mmol, 11%), 4,4'-dimethylbiphenyl (117 mg, 0.64 mmol, 36%).

Photolysis of $(\eta^5\text{-}C_5H_5)_2Ti(m\text{-}CH_3C_6H_4)_2$ in benzene

A solution of $(\eta^5\text{-}C_5H_5)_2Ti(m\text{-}CH_3C_6H_4)_2$ (0.50 g, 1.39 mmol) in 250 ml of toluene-free benzene was irradiated for 4 h with stirring. The resulting dark green solution was analyzed by gas chromatography on a 10 ft., 10% Bentone and 10% Apiezon L on 60-80 mesh Chromosorb W, AW/HDMS-treated column, temperature programmed from 160°C to 220°C at 20°C/min after the toluene peak. The quantities of the products were determined by comparison with known amounts of each respective compound, and the following results were obtained: toluene (90 mg, 0.98 mmol, 35%), 3-methylbiphenyl (164 mg, 0.98 mmol, 35%), 3,3'-dimethylbiphenyl (54 mg, 0.30 mmol, 21%).

Photolysis of $(\eta^5\text{-}C_5H_5)_2Ti(C_6H_5)_2$ *and anthracene in benzene*

$(\eta^5\text{-}C_5H_5)_2Ti(C_6H_5)_2$ (0.48 mmol, 1.45 mmol) and anthracene (1.02 g, 5.7 mmol) were dissolved in 150 ml of benzene in a Schlenk tube (4 × 40 cm), and the solution was irradiated for 4 h with magnetic stirring. A white precipitate which formed was collected and sublimed (185°C, 10^{-3} mmHg) to give 0.70 g (69%) of $\Delta^{9,9'}$-10*H*,10'*H*-bianthracene, m.p. 268—270°C (lit. [55] 272—274°C), mass spectrum, *m/e* 356 (M^+). The solution was concentrated to 15 ml, added to a wet-packed alumina column (2 × 30 cm) and eluted with benzene. A colorless band was collected which produced 0.300 g of product. The composition of this material was determined by gas chromatography and by gas chromatography-mass spectrometry. The quantities were determined by comparison with known amounts of each respective compound, and the following results were obtained: biphenyl (118 mg, 0.77 mmol, 26%), anthracene (138 mg, 0.78 mmol, 14%), 9,10-dihydro-9-phenylanthracene (14 mg, 0.055 mmol, 2%), and 9-phenylanthracene (22 mg, 0.087 mmol, 3%).

Photolysis of $(\eta^5\text{-}C_5H_5)_2Ti(C_6H_5)_2$ *and anthracene in benzene-d_6*

$(\eta^5\text{-}C_5H_5)_2Ti(C_6H_5)_2$ (300 mg, 0.09 mmol) and anthracene (64 mg, 0.36 mmol) were dissolved in 10 ml of benzene-d_6 in a Schlenk tube (1.5 × 9 cm). Two freeze—thaw cycles were performed on this solution, and it was then irradiated for 4 h with periodic swirling. Work-up of the reaction mixture was analogous to the reaction described above using benzene. The anthracene photodimer was obtained in 84% yield. The biphenyl was analyzed by mass spectrometry and peaks at *m/e* 154 and 159 (equivalent to biphenyl-d_0 and biphenyl-d_5) with an intensity ratio of 50/50 were observed. Analysis of the 9,10-dihydro-9-phenylanthracene and the 9-phenylanthracene by mass spectrometry showed the presence of only C_6H_5 groups and no C_6D_5 groups in these products.

Photolysis of $(\eta^5\text{-}C_5H_5)_2Ti(C_6H_5)_2$ *and reaction with carbon monoxide*

$(\eta^5\text{-}C_5H_5)_2Ti(C_6H_5)_2$ (0.48 g, 1.45 mmol) was dissolved in 200 ml of benzene in a Schlenk tube (4 × 25 cm) equipped with a sparge tube. The solution was irradiated for 4 h with magnetic stirring, and CO was then slowly bubbled through the dark green solution for 1 h. The resulting red-brown solution was concentrated to 50 ml under reduced pressure and filtered through a frit packed with 10 cm of silica gel. The silica gel was washed with benzene until the filtrate was colorless. The solvent was removed and the biphenyl sublimed at 10^{-4} mmHg at room temperature for 48 h to leave 0.11 g (32%) of dark red-brown crystals of $(\eta^5\text{-}C_5H_5)_2Ti(CO)_2$. The product was shown to be identical to an authentic sample [56] by spectral comparisons: ν(CO) (hexane) 1980, 1900 cm^{-1}; τ $(\eta^5\text{-}C_5H_5)$ (benzene-d_6) 4.65(s).

Photolysis of $(\eta^5\text{-}C_5H_5)_2Ti(C_6H_5)_2$ *and diphenylacetylene (1/2 ratio) in benzene*

$(\eta^5\text{-}C_5H_5)_2Ti(C_6H_5)_2$ (0.56 g, 1.7 mmol) and diphenylacetylene (0.60 g, 3.4 mmol) were dissolved in 250 ml of benzene in a Schlenk tube (4 × 30 cm). The solution was then irradiated with magnetic stirring for 3.5 h at room temperature, during which time the color changed from golden to dark green. The solution was concentrated to 20 ml under reduced pressure and 2 g of alumina was added. The remainder of the solvent was removed at 10^{-3} mmHg with continuous vigorous agitation, and the resulting residue was added to a dry-packed alumina column (2 × 40 cm). The column was initially eluted with hexane and subsequently with 5/1 hexane/benzene, yielding a colorless band containing 0.46 g of solid. The composition of this material was determined by gas chromatography, products being identified by comparisons with authentic samples, and by gas chromatography-mass spectrometry. The results are summarized in Table 1.

Further elution of the column with 5/1 hexane/benzene yielded predominately *cis,cis*-1,2,3,4-tetraphenyl-1,3-butadiene (0.02 g, 3.3%), mass spectrum m/e 358 (M^+); m.p. 187.0—187.5°C (lit. [57] 182.5—183°C). This product was contaminated with a small amount of triphenylethylene as evidenced by gas chromatography.

Subsequent elution of the column with 1/1 hexane/benzene produced 0.40 g (44%) of 1,1-di-η^5-cyclopentadienyl-2,3,4,5-tetraphenyltitanole, m.p. 157—159°C (lit. [58] m.p. 150°C (dec.)) as dark-green crystals. The product was shown to be identical to an authentic sample [45] by means of IR, proton NMR and mass spectral comparisons.

Photolysis of $(\eta^5\text{-}C_5H_5)_2Ti(C_6H_5)_2$ *and diphenylacetylene (1/1 ratio) in benzene*

A solution of $(\eta^5\text{-}C_5H_5)_2Ti(C_6H_5)_2$ (0.73 g, 2.2 mmol) and diphenylacetylene (0.36 g, 2.0 mmol) in 250 ml of benzene was irradiated for 2 h with stirring. The reaction workup procedure was the same as described above for the 1/2 reactant ratio experiment. The same products were obtained in the following amounts: fraction 1, biphenyl (230 mg, 34%), *cis*-stilbene (57 mg, 16%), diphenylacetylene (17 mg, 5%), *trans*-stilbene (33 mg, 9%), triphenylethylene (14 mg, 2.7%); fraction 2, *cis,cis*-1,2,3,4-tetraphenyl-1,3-butadiene (9 mg, 2.5%); fraction 3, 1,1-di-η^5-cyclopentadienyl-2,3,4,5-tetraphenyltitanole (0.18 g, 34% based on diphenylacetylene); fraction 4, $(\eta^5\text{-}C_5H_5)_2Ti(C_6H_5)_2$ (0.36 g, 49%).

Photolysis of $(\eta^5\text{-}C_5H_5)_2Ti(C_6H_5)_2$ *and diphenylacetylene (1/2 ratio) in benzene-*d_6

A solution of $(\eta^5\text{-}C_5H_5)_2Ti(C_6H_5)_2$ (50 mg, 0.15 mmol) and diphenylacetylene (54 mg, 0.30 mmol) in 8 ml of degassed benzene-d_6 was irradiated for 4 h in a small Schlenk tube with periodic swirling. The solvent was removed from the resultant dark green solution at room temperature and 10^{-3} mmHg. The residue was dissolved in 4 ml of benzene, ca. 50 mg of alumina was added, and the benzene was removed with continuous shaking at reduced pressure. This material was added to a dry-packed alumina column (1 × 16 cm). Elution with hexane and hexane/benzene mixtures gave bands with the same product compositions as were obtained in the reaction run in benzene. All components were analyzed by gas chromatography-mass spectrometry at 18 eV to determine deuterium incorporation. The results are summarized in Table 1.

Photolysis of $(\eta^5\text{-}C_5H_5)_2Ti(p\text{-}CH_3C_6H_4)_2$ *and diphenylacetylene (1/2 ratio) in benzene*

A solution of $(\eta^5\text{-}C_5H_5)_2Ti(p\text{-}CH_3C_6H_4)_2$ (0.51 g, 1.4 mmol) and diphenylacetylene (0.50 g, 2.8 mmol) in 150 ml of benzene was irradiated with stirring for 5 h at room temperature. The dark green solution was concentrated to 20 ml, 2 g of alumina was added, and the remainder of the solvent was removed at reduced pressure with continuous shaking. The mixture was added to a dry-packed alumina column (2 × 40 cm) and the column was eluted with hexane and then with 5/1 hexane/benzene to bring down a colorless band (0.51 g). The composition of this material was determined by gas chromatographic comparisons with authentic samples and by gas chromatography-mass spectrometry. The results are summarized in Table 2.

Further elution with 5/1 hexane/benzene yielded *cis,cis*-1,2,3,4-tetraphenyl-1,3-butadiene (33 mg, 6.6%). Elution with 1/1 hexane/benzene yielded 1,1-di-η^5-cyclopentadienyl-2,3,4,5-tetraphenyltitanole as a dark green band (0.24 g, 32%). Further elution produced no other bands.

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