PHOTOCHEMICAL INVESTIGATIONS OF DI-η5-CYCLOPENTADIENYLDIMETHYLTITANIUM AND DEUTERATED ANALOGS

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Summary

The photolysis of $(\eta^5\text{-}C_5H_5)_2Ti(CH_3)_2$ in hydrocarbon solvents results in cleavage of the carbon—titanium σ-bonds and formation of methane and black titanocene. Deuteration studies have shown that other methyl substituents as well as the cyclopentadienyl rings can serve as the source of hydrogen in the formation of methane. Chemical reactions with HCl, Br_2, and CO, as well as spectroscopic and solution molecular weight studies indicate that photochemically-generated titanocene is probably an oligomeric material, made up of $(\eta^5\text{-}C_5H_5)_2Ti$ and $(\eta^1 : \eta^5\text{-}C_5H_4)Ti_2$ units connected by extended metal—metal bonds. Photolysis of $(\eta^5\text{-}C_5H_5)_2Ti(CH_3)_2$ in the presence of CO leads directly to $(\eta^5\text{-}C_5H_5)_2Ti(CO)_2$ in good yield, whereas photolysis in the presence of diarylacetylenes produces titanacycle analogues along with products derived from insertion of the acetylene into the Ti—CH₃ bond.

Introduction

Photochemically-induced reactions of organotransition metal compounds have been known for 86 years [1,2], but only in the past 20 years have they been explored in any detail. By far the most extensive studies have dealt with photochemistry of the metal carbonyls, in which photo-induced substitution of carbon monoxide by other ligands such as phosphines, amines, olefines, acetylenes, etc., have proved to be of considerable synthetic and mechanistic importance [3—10]. In contrast, however, no systematic studies of photochemically-induced reactions of σ-bonded organic derivatives of the transition metals had been described at the time of our initial communication in this area [11], except

for those of certain σ-alkylcobalt complexes related to Vitamin B_{12} coenzyme models [12—15]. Other photochemical investigations of σ-organotransition metal systems have with few exceptions involved compounds which also contained CO ligands in the coordination sphere of the metal.

In this paper, we present a detailed account of photochemical investigations of di-η^5-cyclopentadienyldimethyltitanium (I) and various deuterated analogs.

Results and discussion

When I is irradiated in hexane in a Pyrex Schlenk tube ($\lambda > 300$ nm), the mixture darkens gradually. After 2—8 h, depending on the relative intensity of the UV-visible light, rapid gas evolution occurs with simultaneous formation of a black precipitate. Gas chromatographic analysis of this gas indicated it to be >99% methane together with traces of ethane and ethylene. The photolysis of I in benzene was very similar, except that while the mixture turned black, no precipitate was evident and the solvent had to be removed to obtain the black titanocene.

In order to gain insight into the source of hydrogen for the formation of methane during the photolysis of I, deuteration studies were undertaken. These involved photolysis of appropriately deuterated materials and analysis of the deuterium content of the methane by mass spectrometry, using low ionizing voltages to minimize fragmentation. The results are summarized in Table 1.

The results indicate that the methane produced in these photolyses derives hydrogen from either a second methyl group or from a cyclopentadienyl group, but not from the solvent. They also suggest that there is a significant deuterium isotope effect in the formation of methane in these systems. Our findings thus parallel to a considerable extent recent results on the thermal degradations of $(\eta^5-C_5H_5)_2TiR_2$ (R = CH_3, $CH_2C_6H_5$, C_6H_5) complexes in the solid state and in solution [16—19].

The abstraction of a hydrogen atom from an adjacent methyl group implies that, if the process is intramolecular, a carbene species II is formed. Although carbene complexes of titanium are unknown, a precedent for II is provided by the recent isolation of a tantalum-methylene complex III [20,21]. Furthermore, it was suggested that the thermal decomposition of III occurred via a doubly methylene bridged dimer IV.

TABLE 1

DEUTERIUM CONTENT OF METHANE DERIVED FROM THE PHOTOLYSIS OF $(\eta^5-C_5H_5)_2Ti(CH_3)_2$ AND SPECIFICALLY DEUTERATED DERIVATIVES

| Compound	Solvent	Deuterium content of methane, ratio				
		CH_4	CH_3D	CH_2D_2	CHD_3	CD_4
$(\eta^5-C_5H_5)_2Ti(CH_3)_2$	C_6D_6	all	—	—	—	—
$(\eta^5-C_5H_5)_2Ti(CD_3)_2$	C_6H_6	—	—	1	6.5	2.5
$(\eta^5-C_5D_5)_2Ti(CH_3)_2$ [a]	C_6H_6	6	3	1	—	—

[a] Ratio corrected to take account of the fact that the cyclopentadienyl rings were only 88% deuterated.

(I)

(II)

(III)

(IV)

(V)

(VI)
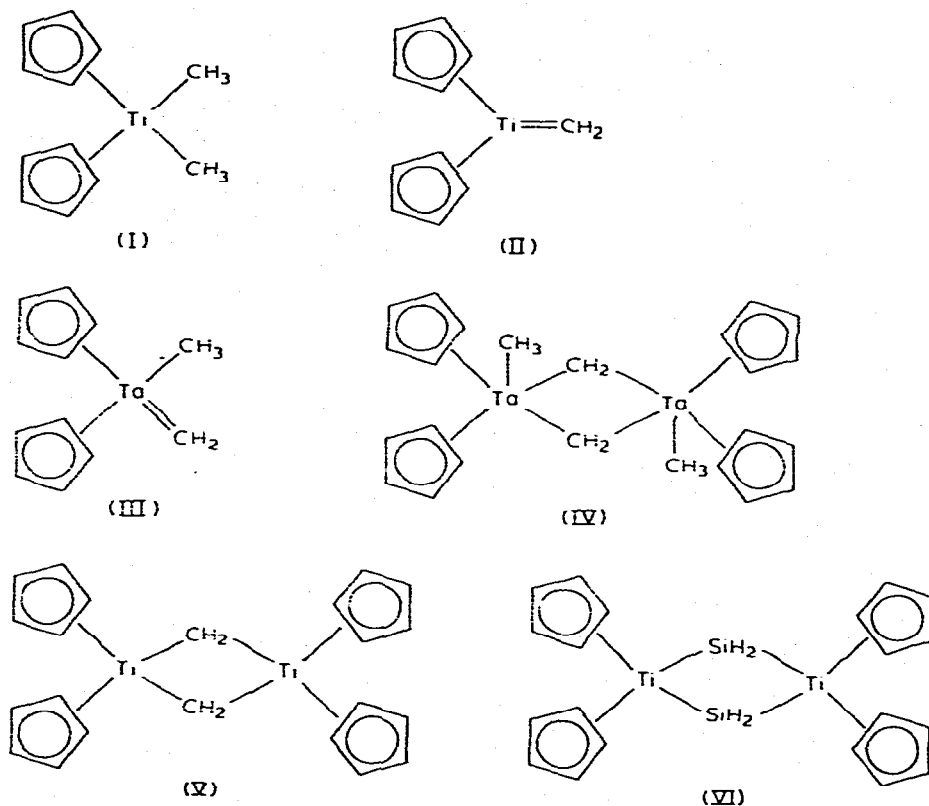
By analogy, the doubly-bridged methylene species V may well be an intermediate in our photolytic studies on I, and could be formed either by dimerization of II or by an intermolecular methyl hydrogen abstraction. Further support for this structure is provided by the recent isolation of the analogous doubly-bridged silylene dimer VI from the reaction of $(\eta^5\text{-}C_5H_5)_2TiCl_2$ and SiH_3K [22].

When the source of hydrogen for methane formation is the cyclopentadienyl ring, several possible intermediates can be postulated. Intramolecular hydrogen abstraction would give an intermediate cyclopentadienylidenetitanium complex VII, whereas a bimolecular process would produce an intermediate such as VIII

(VII)

(VIII)
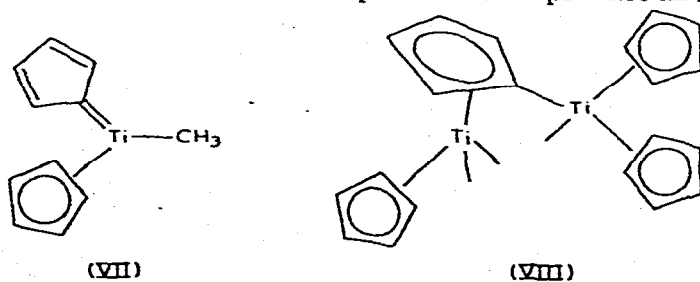
containing a bridging $\eta^1 : \eta^5\text{-}C_5H_4$ unit. Related cyclopentadienylidenemetal complexes have previously been suggested by Marks and Kolb [23] to explain

the rapid intramolecular exchange of hydrogen atoms between C_5H_5 and BH_4 ligands in $(C_5H_5)_2Zr(BH_4)_2$, $(C_5H_5)_2Hf(BH_4)_2$ and $(C_5H_5)_2Zr(H)BH_4$. A similar bimolecular species containing a bridging $\eta^1 : \eta^5$-C_5H_4 ring IX has likewise recently been described by Pez [24].


(IX)   (X)
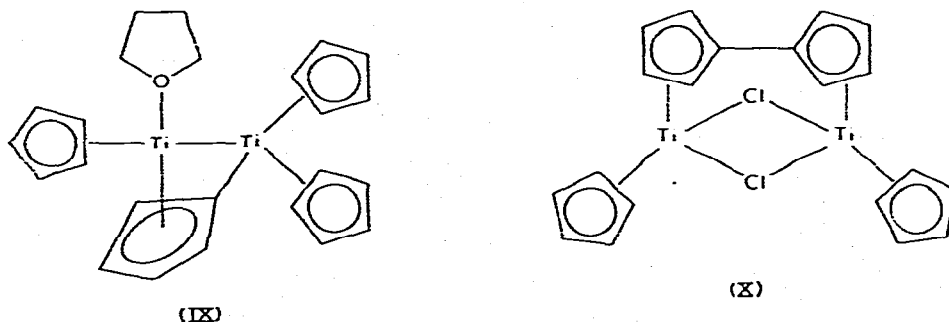
Total elemental analysis of the black organometallic product produced by the photolysis of I indicated it to have the approximate empirical formula $C_{10}H_{9-10}Ti$, and thus to represent a form of titanocene. Since a variety of so-called "titano-cenes", prepared by various chemical reductive methods, have been described in recent years [25], it was of interest to study chemical reactions of our photo-chemically-generated product with reagents which might serve to establish its identity.

Treatment of photochemically-generated titanocene with hydrogen chloride in toluene at $-80°C$ produces an immediate dark purple colour. Several addi-tional colour changes occur on warming the mixture to room temperature, and an NMR spectrum of the mixture indicates that only diamagnetic products are formed. The major product obtained is the well-known $(\eta^5$-$C_5H_5)_2TiCl_2$ (60%) [26,27], together with small amounts of $(\eta^5$-$C_5H_5)TiCl_3$ and a third unidentified product whose mass spectrum contained a major peak at m/e 430 corresponding to an ion of the composition $[(C_5H_4Cl)_3Ti_2Cl]^+$. In contrast, reaction of HCl with titanocene prepared by interaction of I and H_2 [28] produces exclusively $[(C_5H_5)(C_5H_4)TiCl]_2$ [29,30], whose structure in the crystal state has recently been shown to be $[(C_{10}H_8)(C_5H_5)_2Ti_2Cl_2]$ (X) [31]. Titanocene produced by the potassium naphthalene reduction of $(\eta^5$-$C_5H_5)_2TiCl_2$ has been reported under similar conditions to afford a mixture of $(\eta^5$-$C_5H_5)_2TiCl_2$ and the paramagnetic product $[(C_5H_5)_2TiCl]_2$ [24], whereas "metastable" titanocene produced by the decomposition of $[(C_5H_5)_2TiH]_2$ in toluene reacts with HCl to yield $(\eta^5$-$C_5H_5)_2$-$TiCl_2$ as the only apparent organometallic product [32,33].

The reaction of photochemically-generated titanocene with bromine in benzene at room temperature again produced only diamagnetic products as indicable by the NMR spectrum of the reaction mixture. Fractional sublimation afforded $(\eta^5$-$C_5H_5)TiBr_3$ (40%), $(\eta^5$-$C_5H_5)_2TiBr_2$ (30%), and an unidentified third product whose mass spectrum showed peaks at m/e 478 and 414 assign-able to the ions $[(C_5H_5)(C_5H_4Br)_2TiBr]^+$ and $[(C_5H_5)(C_5H_4Br)TiBr_2]^+$, respec-tively.

Photochemically-generated titanocene is also highly reactive towards various neutral molecules such as nitrogen and carbon monoxide [11]. Measurements

have indicated that titanocene produced in this manner reacts almost quantitatively with two equivalents of CO. This reaction can also be carried out on a preparative scale, to give ca. 60% yields of $(\eta^5\text{-}C_5H_5)_2Ti(CO)_2$ (XI) [34]. An X-ray crystallographic investigation of XI has recently been completed which unequivocally establishes the structure of this titanium carbonyl derivative [35]. Titanocene produced by chemical reductive methods is also known to

(XI)   (XII)
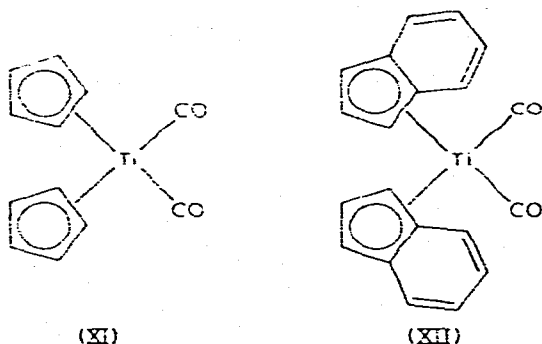
react with CO to form XI, but in much lower yield *.

Photochemically-generated titanocene is reasonably soluble in benzene, and this has allowed us to conduct cryoscopic molecular weight measurements in this solvent. Apparent molecular weight values of ca. 680—710 were obtained in a number of runs, suggesting that the material is an oligomer in solution, the benzene-soluble portion corresponding approximately to a tetramer.

The mass spectrum of photochemically-generated titanocene was similar to the mass spectrum of titanocene [30,36] produced by chemical reductive methods, in that moderately intense peaks at 352 $[C_{20}H_{16}Ti_2]^+$, 128 $(C_{10}H_8)^+$, and 113 $(C_5H_5Ti)^+$ were observed. In addition, an intense peak at m/e 178 was also observed in our product, which can correspond to either $(C_{10}H_{10}Ti)^+$ or $(C_{20}H_{20}Ti_2)^{2+}$. The corresponding singly charged ion $(C_{20}H_{20}Ti_2)^+$ at m/e 356 was not significant in our mass spectrum, however. Furthermore, a series of significant peaks above m/e 356, e.g., m/e 370, 398, 400, 402, 452 $[(C_5H_5)_4Ti_4]^+$, etc., may be indicative of thermal breakdown of oligomers under these conditions (70 eV, 180°C source temperature). Comparative studies have shown that peaks in this higher mass region are not observed in titanocenes generated by non-photolytic methods, and that the latter titanocenes are appreciably more volatile than is our product.

The proton NMR spectrum of photochemically-generated titanocene is not especially informative. When measured in C_6D_6 solution, for example, a broad resonance is observed between δ 5—6 ppm and a series of resonances between δ 0.5—1.5 ppm is also present. While titanocene generated by the earlier chemical reductive methods has been said to exhibit a broad singlet near δ 5.32 ppm [36], the product recently obtained by Pez [24] was reported to show only a broad single resonance at δ 15.0 ppm at 32°C in toluene-d_8. The absorptions found between δ 0.5—1.5 ppm have not been noted previously for other forms

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* So-called "metastable" titanocene has been reported to form XI in quantitative yield, although XI was apparently not isolated as such [33].

of titanocene. We find that they are also observed when $(\eta^5-C_5H_5)_2Ti(CD_3)_2$ is photolyzed in C_6D_6 solution, and therefore must be derived originally from the cyclopentadienyl ring protons.

The visible and near-infrared spectrum of photochemically-generated titanocene in C_6H_6 solution has been recorded. Two maxima are observed at 700 and 826 nm. The data clearly contrasts to similar visible, near-IR absorption data reported recently for other forms of titanocene [24].

The IR spectrum of photochemically-generated titanocene can be recorded in Nujol mulls. The spectrum is very similar to the spectra of the well-known metallocenes ferrocene, nickelocene, titanocene dichloride, etc., in which the η^5-cyclopentadienyl rings are known to be symmetrically bound to the metal atom. Carbon-hydrogen bending vibrations at 800 and 1015 cm^{-1} appear as sharp, unsplit bands, in contrast to $(C_{10}H_8)(C_5H_5)_2H_2Ti_2$ [30], but in analogy with $(C_5H_5)_3(C_5H_4)Ti_2$ [24]. Perhaps most notably, titanocene produced by our photochemical method shows no absorptions in the region near 1220—1230 cm^{-1} which have been commonly assigned to bridging Ti—H—Ti bonds in most other forms of titanocene [24,30]. When photochemically-generated titanocene is heated to reflux in toluene under argon for 12 days, there is essentially no change in the IR spectrum in this region. In contrast, $(C_5H_5)_3(C_5H_4)Ti_2$ is thermally decomposed to give $(C_{10}H_8)(C_5H_5)_2H_2Ti_2$ under these conditions [24].

The photolysis of I in the presence of several reactive substrates such as carbon monoxide and diarylacetylenes has also been investigated. In these photo-induced reactions, black titanocene is not observed, but other organotitanium products derived from the monomeric $(\eta^5-C_5H_5)_2Ti$ unit can be isolated. Thus, when I is photolyzed in pentane while CO is bubbled through the solution, the mixture turns red-brown, and XI can be isolated in 50—60% yield. Di-η^5-indenyldicarbonyltitanium (XII) can likewise be produced by similar photolysis of $(\eta^5-C_9H_7)_2Ti(CH_3)_2$ [38]. This method therefore represents a more direct and convenient route to XI than the carbonylation of black titanocene described above.

The photolysis of I in the presence of diphenylacetylene was found to produce two organotitanium compounds and a variety of organic products. One of the compounds, 1,1-di-η^5-cyclopentadienyl-2,3,4,5-tetraphenyltitanole (XIII), is apparently derived by demethylation of I to produce monomeric $(\eta^5-C_5H_5)_2Ti$ (or possibly an acetylenic analog thereof) as a reactive intermediate. The yields of XIII vary from ca. 10—50% depending to some extent on the concentrations
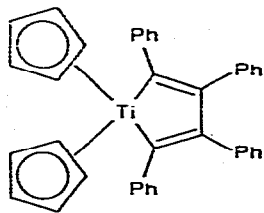
(XIII)
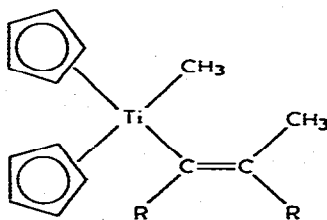
(XIV) R = C_6H_5
(XVII) R = C_6F_5

of I and diphenylacetylene in solution during the photolysis. An X-ray crystallo-

TABLE 2

ORGANIC PRODUCTS OBTAINED FROM THE PHOTOLYSIS OF $(\eta^5\text{-}C_5H_5)_2Ti(CH_3)_2$ AND DIPHENYL-ACETYLENE

| Product	Retention time (min) [a]	Product (mg)	Yield (%) [b]
cis-Stilbene	3.4	2.6	0.25
cis-1,2-Diphenyl-propene	4.0	134	12
Diphenylacetylene	6.0	320	32
trans-1,2-Diphenyl-propene	7.5	62	5.7
1,2,3,4-Tetraphenyl-1,3-pentadiene	22.6	2.1	0.18
2,3,4,5-Tetraphenyl-2,4-hexadiene	23.3	2.6	0.25

[a] GLC conditions: OV-101 column: temperature, 175—300°C at 12°/min: flow rate, 60 ml/min: chart speed, 0.5 cm/min. [b] Based on diphenylacetylene.

graphic study has uniquivocally confirmed that XIII has a metallocyclic struc-ture, in which the π-electron system is largely localized within the metallocyclo-pentadiene ring [39].

A second organotitanium product obtained in 17% yield from this reaction has very limited thermal and oxidative stability. The product is formulated as di-η^5-cyclopentadienylmethyl(1,2-diphenyl-1-propenyl)titanium (XIV) on the basis of its mass spectrum and its diagnostic proton NMR spectrum (see Experi-mental) [40]. Only one isomer appears to be produced in this photolysis, since the proton NMR spectrum shows only one resonance each for the cyclopenta-dienyl protons, the allylic methyl group protons, and the protons on the methyl group σ-bonded to the titanium atom. Acid hydrolysis of XIV yielded a 3/1 mixture of cis- and trans-1,2-dimethylpropene in addition to methane. It is likely that this mixture of isomers arises from isomerization of the starting material XIV during the hydrolysis step. A similar suggestion has been made for the hydrolysis reaction of the organorhodium product derived from $(Ph_3P)_3RhCH_3$ and diphenylacetylene [41]. Formulation of XIV as the cis-isomer must be regarded as tentative, however.

The two principal organic products obtained from the photolysis of I and di-phenylacetylene are cis- and trans-1,2-diphenylpropene (see Table 2). These products may be derived from homolysis of the Ti—CH$_3$ bond to produce inci-pient methyl radicals which then attack diphenylacetylene, followed by hydro-genation of the resulting methylstilbenyl radicals, or they could be formed by direct hydrogenation of intermediates such as XIV. The detection of very small amounts of 2,3,4,5-tetraphenyl-2,4-hexadiene (XV) and 1,2,3,4-tetraphenyl-
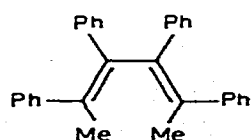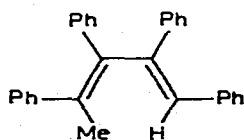
1,3-pentadiene (XVI) in this reaction can also be explained by the dimerization of methylstilbenyl radicals or by the further reaction of such radicals with additional diphenylacetylene followed by hydrogenation.

The photolysis of I in the presence of the highly fluorinated acetylene $C_6F_5C\equiv CC_6F_5$ did not result in formation of a titanacycle analogous to XIII but a product formulated as di-η^5-cyclopentadienylmethyl(1,2-bis(pentafluoro-phenyl)-1-propenyl)titanium (XVII) was produced in 21% yield together with both 1,2-bis(pentafluorophenyl)propene isomers (9.6% combined yield). The organotitanium product XVII was characterized by its mass spectral, proton NMR and IR spectra, and since it is appreciably more stable thermally and oxi-datively than is XIV, reliable elemental analyses were also obtained.

The isolation and characterization of XIV and XVII has additional signifi-cance, since it has long been postulated that Ziegler–Natta catalysis involves initial coordination of an olefin to a titanium atom followed by insertion of the coordinated olefin into a titanium—alkyl σ-bond [42—44]. Our results, which present the first definitive examples of insertion of an unsaturated hydrocarbon into a carbon—titanium σ-bond, thus provide confirmation for one of the im-portant steps in this mechanism.

The photolysis of I in the presence of anthracene was undertaken to deter-mine if the reaction was of a radical nature [45,46]. In addition to the aniticipated photodimer of anthracene, 9-methylanthracene was also isolated in 7.6% yield. This experiment implies the formation of methyl radicals during the photolysis of I, but it is also possible that the presence of anthracene changes the course of this photochemical reaction. In any event, it is doubtful that these reactions results in the formation of true free radicals, and that they more probably occur via caged radicals or other radical-like organometallic species [47,48].

Conclusions

It seems likely that the highly reactive black form of titanocene produced in these photolyses of I is oligomeric in nature, and contains both $(\eta^5\text{-}C_5H_5)_2$Ti as well as $(\eta^1 : \eta^5\text{-}C_5H_4)Ti_2$ bridging units, possibly connected by extended metal—metal bonds. Evidence for the presence of both structural units may be derived from deuterium labelling studies, from chemical reactions of black titanocene and by spectroscopic investigations. Some evidence has been obtained for formation of radical-like species during cleavage of the methyl—titanium bonds. Photolysis of I in the presence of reactive substrates such as CO and acetylenes substantially alters the course of the reaction, and products derived from the monomeric $(\eta^5\text{-}C_5H_5)_2$Ti unit as well as from overall insertion into carbon—tita-nium σ-bonds can result.

Experimental section

All operations were carried out under argon using Schlenk tube techniques. The argon was dried with H_2SO_4 and P_2O_5, and trace oxygen was removed using BTS catalyst. Hydrocarbon solvents were dried over calcium hydride and freshly distilled under argon. Ethyl ether and THF were predried over sodium and subsequently distilled under argon from sodium/benzophenone. Column

chromatography was carried out under argon using Alfa—Ventron neutral-grade alumina. The alumina was heated with mixing under vacuum for 2 h, then deactivated with 5% argon-saturated distilled water, and stored under argon.

Photolyses were conducted by means of a 450 W Hanovia photochemical lamp located in a quartz, water-cooled immersion well. This unit was placed ca. 1—2 cm from a Pyrex Schlenk tube containing the solution to be photolyzed. Both lamp and Schlenk tube were mounted in a large polyethylene tank which was cooled with water.

Gas chromatographic analyses were performed on a Varian Series 2400 gas chromatograph equipped with a flame ionization detector. Most analyses were made on a 5-ft 15% OV-101 column and a 12-ft 10% QF-1 column. The organic compounds were separated on both columns and the individual peaks compared with known samples whereever possible. Gas samples were separated on a 6-ft Porapak Q column and spiked with known materials. The 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, 3% SE 30 column or a 6-ft Porapak Q 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 obtained on a Beckman IR-10 or a Perkin—Elmer 237B infrared spectrophorometer using KBr pellets, Nujol mulls or hexane solutions and were calibrated versus polystyrene. IR spectra of very air-sensitive compounds were obtained by preparing Nujol mulls in either a desiccator or a plastic bag filled with argon and under a strong argon flow. The mulls were applied to sodium chloride plates in the desiccator and with the mulls between the plates, the spectra were obtained in the usual manner.

$(\eta^5-C_5H_5)_2Ti(CH_3)_2$ [28] was prepared by a modification of the literature procedure. The product was crystallized from pentane and stored under argon at —78°C in the dark. $(\eta^5-C_5D_5)_2Ti(CH_3)_2$ was prepared in an analogous manner, employing 350 mg (1.4 mmol) of $(\eta^5-C_5D_5)_2TiCl_2$ [49,50] and 1.5 ml (3.0 mmol) of CH_3Li in ethyl ether solution to yield 180 mg (61%) of product. An NMR spectrum of the material was integrated and showed that the cyclopentadienyl rings were 88% deuterated. Bis(pentafluorophenyl)acetylene was prepared by a modification of the method of Gilman et al. [51,52]. 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 minutes.

$(\eta^5-C_5H_5)_2Ti(CD_3)_2$

CD_3Br (99.5%, 5.0 g, 50 mmol) was cooled to —40°C and slowly added to small pieces of excess lithium metal in 200 ml of ethyl ether at this same temperature. The reaction started immediately and the temperature increased. The mixture was refluxed for 30 min, filtered through a frit, and cooled to —78°C. $(\eta^5-C_5H_5)_2TiCl_2$ (6.22 g, 25 mmol) was then added with stirring, the addition and subsequent operations being conducted in the dark. The mixture was allowed to warm to 0°C and the ether removed under reduced pressure. The yellow residue was extracted three times with ca. 50 ml portions of pentane, the pentane extracts were concentrated to ca. 50 ml and kept in dry ice over-

night. Long orange crystals of $(\eta^5\text{-}C_5H_5)_2Ti(CD_3)_2$ were formed; they were isolated by decanting the mother liquor and drying the product under high vacuum (yield 4.28 g (80%)).

Photolysis of $(\eta^5\text{-}C_5H_5)_2Ti(CH_3)_2$ in hexane

In a typical run, 2.08 g (10.0 mmol) of I was dissolved in 300 ml of hexane. The orange solution was irradiated in a Schlenk tube equipped with a magnetic stirrer and a mercury overpressure valve. The gas formed during the reaction was collected over water in an inverted graduated cylinder. During the initial period of irradiation, the mixture darkened slightly and gas evolution occurred only very slowly. After an induction period of 2—8 h, a vigorous reaction occurred. The solution darkened rapidly, and at the same time rapid gas evolution began, and continued for several min. After this time slow evolution occurred for a short period (10—20 min); a total of 152 ml (6.8 mmol) of volatile products was evolved. Gas chromatographic analysis (6-ft Porapak Q column at room temperature) showed that the gas was comprised of methane (ca. 99%), ethane (0.5%) and ethylene (0.05%). Following photolysis, about 80% of the solvent was removed under reduced pressure. The precipitate was collected on a frit under argon, washed several times with small amounts of hexane, and dried under high vacuum to yield 1.60 g (90%) of titanocene as a black pyrophoric solid. (Found: C, 67.87; H, 5.29; Ti, 26.73. $C_{10}H_{10}Ti$ calcd.: C, 67.44; H, 5.66; Ti, 26.90%. $C_{10}H_9Ti$ calcd.: C, 67.81; H, 5.13; Ti, 27.06%). Molecular weight measurements on titanocene were made in benzene using cryoscopic techniques under argon. Measurement of standard samples using this method indicated an accuracy of ca. 10%.

The photolyses of I in other hydrocarbon solvents were conducted analogously. Thus, photolysis of 2.04 g (9.8 mmol) of I in 330 ml of benzene proceeded in a similar manner, except that no precipitate was formed and 225 ml (10.0 mmol) of gas (>99% methane) was evolved. In order to isolate the titanocene, the solvent had to be removed.

Photolysis studies of $(\eta^5\text{-}C_5H_5)_2Ti(CH_3)_2$ and deuterated analogs in benzene and benzene-d_6

Approximately 80 mg (0.38 mmol) of the appropriate dimethyltitanocene was dissolved in 10 ml of benzene in a 30 ml Schlenk tube. The solution was frozen by placing the tube in dry ice, and the tube was then evacuated and subsequently closed off under reduced pressure. The solution was allowed to warm to room temperature and was then irradiated for 20—22 h with periodic swirling. After irradiation, the internal pressure was brought to atmospheric pressure by adding benzene under argon via a conical funnel attached to the sidearm of the Schlenk tube via a short piece of Tygon tubing. The methane samples collected in this manner were analyzed by mass spectrometry using a silicone plug on the liquid inlet of the mass spectrometer. The ionizing voltage employed was 15.5 eV which minimized fragmentation [18]. In this manner, the data in Table 1 were obtained.

Reaction of photochemically-generated titanocene with carbon monoxide

A solution of 356 mg (2.0 mmol) of titanocene in 50 ml of benzene was

prepared in a Schlenk tube, and a weak stream of CO was bubbled through the solution at room temperature. After ca. 10 min, the dark olive-black solution was allowed to stand for an additional 2 h under a CO atmosphere. The solution was then filtered through a frit which had been packed with 10 cm of silica gel. The solvent was subsequently removed at the water aspirator and finally under high vacuum. The residue was dissolved in pentane, filtered through a frit, and crystallized at −78°C to produce 281 mg (60%) of dark red-brown crystals, identified as $(\eta^5\text{-}C_5H_5)_2Ti(CO)_2$ by IR, proton NMR and mass spectral comparisons with an authentic sample [34].

In order to quantitatively determine the extent of this reaction, 110 mg (0.618 mmol) of titanocene in 200 ml of benzene was stirred under CO in a closed system connected to a gas burette. CO uptake occurred rapidly during the first few minutes, and after 2 h, 25 ml of CO had reacted (91%, based on up-take of 2 mol CO/mol of titanocene).

Reaction of photochemically-generated titanocene with hydrogen chloride

In a typical run, a solution of 178 mg (1.0 mmol) of titanocene in 100 ml of toluene was prepared in a 300 ml Schlenk tube. The contents were frozen in liquid nitrogen, the tube evacuated, and gaseous hydrogen chloride was then introduced to bring the system to atmospheric pressure. A dark purple colour immediately appeared on the surface of the frozen solution. The mixture was allowed to warm to room temperature, during which the colour changed to violet and then to red, and a dark precipitate formed. After 10 h at room temperature the solvent was removed under reduced pressure and the residue was sublimed under high vacuum. At 120°C, a small amount (33 mg, 15%) of a yellow precipitate sublimed, which was identified as $(\eta^5\text{-}C_5H_5)TiCl_3$ by mass spectral and proton NMR comparisons with an authentic sample [53]. Continued sublimation at 160°C produced 150 mg (60%) of $(\eta^5\text{-}C_5H_5)_2TiCl_2$, also identified by mass spectral and proton NMR comparisons with an authentic sample [26]. At temperatures over 200°C, a small amount of an unidentified black sublimate was also obtained. The yields of these products appear to depend on the ratio of titanocene and HCl, as well as on the temperature and the solvent used.

Reaction of photochemically-generated titanocene with bromine

In a typical run, 178 mg (1.0 mmol) of titanocene was dissolved in 100 ml of benzene and 0.4 ml (15 mmol) of bromine was added at room temperature. The original black-coloured solution turned dark green at first, and subsequently red-brown, accompanied by the formation of a dark precipitate. After standing for 15 h, the solvent was removed and the residue was sublimed under high vacuum. At 120°C, a yellow-brown product was obtained (141 mg, 40%) whose mass spectrum and proton NMR spectrum indicated it to be $(\eta^5\text{-}C_5H_5)TiBr_3$ [54]. Continued sublimation at 200°C produced 111 mg (30%) of a dark red product whose mass spectrum and proton NMR spectrum indicated it to be $(\eta^5\text{-}C_5H_5)_2$-$TiBr_2$ [26]. At temperatures over 250°C, a small amount of a dark brown sublimate could also be obtained. The mass spectrum of this product contained two peaks in the high mass region at m/e 478 and 414 which can be assigned to the ions $[(C_5H_5)(C_5H_4Br)_2TiBr]^+$ and $[(C_5H_5)(C_5H_4Br)TiBr_2]^+$, respectively.

The isotope pattern is consistent with the presence of three bromine atoms in each ion. The yields of the above products are dependent on the ratio of titanocene and bromine reacted, and to some extent on the solvent.

Photolysis of (η^5-C_5H_5)$_2$Ti(CH_3)$_2$ in the presence of carbon monoxide

(η^5-C_5H_5)$_2$Ti(CH_3)$_2$ (1.0 g, 5 mmol) was dissolved in 100 ml of pentane in a Schlenk tube. The solution was irradiated while a weak stream of CO was bubbled through. The orange solution turned red-brown after 10 min. The photolysis was continued in the presence of CO for 25 min and the pentane was removed at the water pump. The dark red-brown oily residue was dissolved in 10 ml of benzene and was filtered through a frit packed with 10 cm of silica gel. Elution with benzene gave a red-brown fraction. The solvent was then removed at the water pump and finally via high vacuum. Recrystallization of the residue from pentane at −78°C gave 0.67 g (60%) of dark red-brown crystals, identified as (η^5-C_5H_5)$_2$Ti(CO)$_2$ by IR, proton NMR and mass spectral comparisons with an authentic sample. Purification of (η^5-C_5H_5)$_2$Ti(CO)$_2$ can alternatively be accomplished by sublimation at 110°C/10^{-3} mmHg.

Photolysis of (η^5-C_5H_5)$_2$Ti(CH_3)$_2$ in the presence of anthracene

A solution of I (0.41 g, 1.97 mmol) and anthracene (1.5 g, 8.43 mmol) in 200 ml of benzene was irradiated in a Schlenk tube with stirring for 4 h. A white precipitate was collected, filtered and sublimed at 185°C/10^{-3} mmHg to yield 1.20 g (80%) of the photodimer of anthracene, m.p. 268—270°C (lit. [55] m.p. 272—274°C); mass spectrum, M^+ m/e 356. The solution was then reduced to 20 ml on the water pump at room temperature and 2 g of alumina was added. The remainder of the solvent was removed under high vacuum with continuous shaking and the residue was added to a dry-packed alumina column (4 × 25 cm). The column was eluted with hexane and subsequently with benzene to yield a colourless band (199 mg). The composition of this band was determined by gas chromatographic comparisons with authentic samples (5 ft, 15% OV-101 column) and by GLC—mass spectrometry to contain 141 mg (9.4%) anthracene and 58 mg (7.6%) 9-methylanthracene.

Photolysis of (η^5-C_5H_5)$_2$Ti(CH_3)$_2$ in the presence of diphenylacetylene

Diphenylacetylene (1.00 g, 5.62 mmol), I (0.59 g, 2.79 mmol) and 270 ml of hexane were added to a Schlenk tube (4 × 40 cm) and irradiated for 5 h with magnetic stirring. The resulting reddish-brown solution was concentrated to ca. 20 ml under reduced pressure and 2 g of alumina was added. The remainder of the solvent was removed under vacuum (10^{-3} mmHg) with continuous vigorous agitation and then added to an argon-filled chromatography column (2 × 50 cm) packed with dry alumina. The column was initially eluted with hexane and subsequently with 10/1 hexane/benzene yielding a colourless band containing 0.516 g of solid. The composition of this material was determined by gas chromatographic comparisons with authentic samples and by GC—mass spectrometry. The results are summarized in Table 2.

Further elution of the column with 10/1 hexane/benzene yielded a gold-coloured solid, di-η^5-cyclopentadienylmethyl(1,2-diphenyl-1-propenyl)titanium (188 mg, 17.4%). The proton NMR spectrum in C_6D_6 consisted of the follow-

ing resonances: τ (ppm) 10.38 (3H, s, Ti—CH$_3$); 8.49 (3H, s, $C=C(CH_3)$) 4.06 (10H, s, C$_5$H$_5$), and 2.7—3.3 (10H, m, C$_6$H$_5$). The mass spectrum contained the following major peaks: m/e 386 (1, M^+), 371 (4, $M - CH_3^+$), 194 (97, (C$_5$H$_5$)$_2$-TiHCH$_3^+$ and/or C$_6$H$_5$(CH$_3$)C=CHC$_6$H$_5^+$), 193 (28, (C$_5$H$_5$)$_2$TiCH$_3^+$), and/or C$_6$H$_5$(CH$_3$)C=CC$_6$H$_5^+$), 179 (100, (C$_5$H$_5$)$_2$TiH$^+$ and/or C$_6$H$_5$CH=CC$_6$H$_5^+$), 178 (68, (C$_5$H$_5$)$_2$Ti$^+$ and/or C$_6$H$_5$C$_2$C$_6$H$_5^+$), 115 (36, C$_5$H$_5$TiH$_2^+$), 105 (79, C$_6$H$_5$C$_2$H$_4^+$).

Continued elution of the column with 3/1 hexane/benzene yielded 160 mg (10.7%) of 1,1-di-η^5-cyclopentadienyl-2,3,4,5-tetraphenyltitanole, m.p. 157—159°C (dec.) [lit. [56] m.p. 150°C (dec.)] as dark green crystals (Found: C, 85.52; H, 5.65; Ti, 8.98. C$_{38}$H$_{30}$Ti calcd.: C, 85.38; H, 5.66; Ti, 8.96%). The proton NMR spectrum in C$_6$D$_6$ consisted of the following resonances: τ 4.00 (10H, s, C$_5$H$_5$), 2.75—3.55 ppm (20H, m, C$_6$H$_5$). The mass spectrum showed a weak molecular ion at m/e 536.

Photolysis of (η^5-C$_5$H$_5$)$_2$Ti(CH$_3$)$_2$ in the presence of bis(pentafluorophenyl)-acetylene

A solution of I (0.30 g, 1.4 mmol) and bis(pentafluorophenyl)acetylene (1.00 g, 2.8 mmol) in 250 ml of hexane was irradiated in a Schlenk tube with stirring for 4 h. The solution was concentrated to 100 ml under reduced pressure at room temperature and added to a dry alumina column (2 × 35 cm). The column was eluted with hexane and subsequently with 2/1 hexane/benzene to yield a colorless band containing 0.51 g of solid. The composition of this material was shown by GC—mass spectrometry to consist of a mixture of *cis*- and *trans*-1,2-bis(pentafluorophenyl)propene (9.6% combined yield) and bis-(pentafluorophenyl)acetylene (38% recovery).

Further elution of the column with 2/1 hexane/benzene yielded 170 mg (21%) of di-η^5-cyclopentadienylmethyl(1,2-bispentafluorophenyl-1-propenyl)titanium. The proton NMR spectrum in CDCl$_3$ consisted of the following resonances: τ (ppm) 10.23 (3H, s, Ti—CH$_3$); 8.53 (3H, s, $C=C(CH_3)$); 3.64 (10H, s, C$_5$H$_5$). The IR spectrum (KBr) exhibited the following major bands: 2960w, 1525s, 1435m, 1250w, 1105m, 1065m, 1005s, 965s, 920m, 875m, 810s cm^{-1}. The mass spectrum exhibited the following major peaks: m/e 566 (1, M^+), 551 (38, $M - CH_3^+$), 374 (20, C$_6$F$_5$CH=C(CH$_3$)C$_6$F$_5^+$), 358 (4, C$_6$F$_5$C$_2$C$_6$F$_5^+$), 193 (48, (C$_5$H$_5$)$_2$TiCH$_3^+$), 179 (54, (C$_5$H$_5$)$_2$TiH$^+$), 178 (100, (C$_5$H$_5$)$_2$Ti$^+$), 113 (46, C$_5$H$_5$Ti$^+$).

Acknowledgements

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