

196. Photochemical Ring Slippage of Bis(pentafluorophenyl)titanocene: Reaction Kinetics and Matrix Isolation of the Primary Photoproduct

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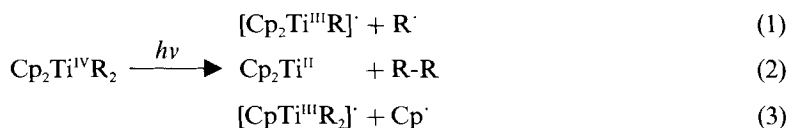
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Laser flash photolysis and matrix-isolation techniques were applied to elucidate the photochemistry of the orange complex bis(pentafluorophenyl)titanocene (= bis(η^5 -cyclopentadienyl)bis(pentafluorophenyl)titanium(IV), $\text{Cp}_2\text{Ti}^{\text{IV}}\{\text{C}_6\text{F}_5\}_2$, $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$, **1**) which is used as a polymerization photo-initiator. The primary photo-reaction of **1** is the formation of a highly reactive blue isomer **X** with unit quantum yield. In carefully dried and degassed benzene solution, the photoisomer **X** rearranges to starting material **1** with a first-order reaction, $k = 5 \cdot 10^3 \text{ s}^{-1}$ at room temperature. **X** is highly reactive towards H_2O , MeOH , acetone, MeCN , MeNO_2 , butane-1,4-diyl diacrylate, 2,2,6,6-tetramethylpiperidine *N*-oxide, CO , O_2 , and N_2 ; absolute bimolecular rate constants range from 10^6 to $10^9 \text{ M}^{-1} \cdot \text{s}^{-1}$. The primary photoisomerization $\mathbf{1} \rightarrow \mathbf{X}$ is tentatively ascribed to a cyclopentadienyl ring slippage from η^5 to a lower hapticity, a process that opens up coordinative unsaturation.

Introduction. – Low-valent organotitanium complexes are capable of nitrogen fixation [1] and are well-known as polymerization catalysts [2]. The photoreactions of Ti complexes have been studied rather extensively, and this work has been reviewed [3] but, surprisingly, flash photolysis has so far not been applied to a direct kinetic and spectrographic observation of the relevant reactive intermediates. We have investigated the primary photoprocesses of bis(pentafluorophenyl)titanocene (= bis(η^5 -cyclopentadienyl)bis(pentafluorophenyl)titanium(IV), $\text{Cp}_2\text{Ti}^{\text{IV}}\{\text{C}_6\text{F}_5\}_2$, $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$, **1**) by flash photolysis and matrix-isolation techniques in order to elucidate the mechanism by which **1** acts as a photo-initiator used for integrated circuit fabrication [4–8].



Three different primary processes have been proposed to account for the photo-reactions of various titanocene derivatives ($\text{Cp}_2\text{Ti}^{\text{IV}}\text{R}_2$, $\text{R} = \text{alkyl, aryl, Cl, Br}$): 1) homolysis of a σ -bond [9–11], 2) reductive elimination of two ligands R yielding divalent ‘titanocene’ ($\text{Cp}_2\text{Ti}^{\text{II}}$) [10] [11], and 3) homolysis of a $\text{Ti-Cp } \eta^5$ -bond [12] [13]. None of the primary organotitanium products has been positively identified. Labeling and CIDNP studies have indicated that in some cases the radical pair formed in process (1) dispropor-

tionates prior to escape from the solvent cage [3] [14] [15]. All attempts to isolate or fully characterize monomeric ‘titanocene’, the primary product of process (2), have failed [16]. The dissociation to a free cyclopentadienyl radical, process (3), was originally put forward by *Harrigan et al.* [12] for dimethyl and dihalide titanocene derivatives. This proposition was first questioned by *Brubaker* and coworkers who suggested hapticity reduction as a possible alternative for process (3) [17]. However, the same group has subsequently obtained evidence in favour of process (3) and, thus, did not maintain the earlier proposal [13].

The photochemistry of diphenyltitanocene (= bis(η^5 -cyclopentadienyl)diphenyltitanium(IV), $\text{Cp}_2\text{Ti}^{\text{IV}}\{\text{C}_6\text{H}_5\}_2$, **2**) has been attributed to a combination of paths (1) and (2) [10], and phenyl radicals were thought to act as polymerization initiators. Product studies and trapping experiments with 2,2,6,6-tetramethylpiperidine *N*-oxide (TMPO) have, however, indicated that titanocenes with perfluorinated Ph groups behave quite differently [4]. Since no organic radicals could be trapped, the question arose by which mechanism the fluorinated diphenyltitanocenes initiated polymerization. The present work establishes that the predominant primary photochemical reaction of electronically excited bis(pentafluorophenyl)titanocene (**1**) is neither of the dissociative processes (1) to (3), but yields a reactive isomer. We have determined rate constants for the rearrangement of the photoisomer back to **1** and for its reaction with a variety of reagents.

Experimental. – *Instrumentation.* Flash photolysis was done with the second harmonic of a Nd glass laser (530 nm, 300 mJ, 25 ns width at half height). The monitoring system for kinetic and spectrographic detection of the transient intermediates has been described in [18]. Matrix isolation of **1** was achieved by heating (*ca.* 150°) a small quartz recipient in front of the cooled (20 K) CsI window within the vacuum shroud of an *Air Products* closed-cycle *Displex* cooling system during the deposition of Ar, N₂, or CO gas, respectively. IR spectra were recorded on a *Perkin-Elmer 1800 FTIR* instrument operated with a resolution of 0.5 cm⁻¹.

Actinometry. Samples were irradiated with the 436-nm line filtered from the light of a stabilized medium-pressure Hg arc *Hanau St. 41*. The light flux passing the sample cell was determined by actinometry with azobenzene in MeOH soln. using a value of $Q(436) = 820 \text{ m}^{-1} \cdot \text{cm}^{-1}$ for the pseudo quantum yield [19]. The azobenzene solns. were preirradiated at 313 nm in order to produce larger absorbance changes upon irradiation at 436 nm. Relative rates of the photoreaction in various solvents and with different trapping reagents were determined with light from a stabilized Xe arc that was passed through an interference filter with maximal transmission at 463 nm and a band width at half intensity of *ca.* 20 nm.

Materials. Bis(pentafluorophenyl)titanocene (= bis(η^5 -cyclopentadienyl)bis(pentafluorophenyl)titanium(IV), **1**) and diphenyltitanocene (= bis(η^5 -cyclopentadienyl)diphenyltitanium(IV), **2**) were prepared according to the procedure in [20]. The ¹H-NMR spectrum of **1** in benzene consisted of a single sharp *singlet* at 5.72 ppm. Spectroscopy-grade solvents (acetone, MeCN, benzene, CCl₄, MeOH) were used as received. The H₂O content of benzene (declared as < 0.03% by the manufacturer) was found to be 0.015% by *Karl-Fischer* titration. Benzene, claimed to be ‘dry’ in this work, was kept over large quantities of molecular sieve, transferred under Ar, evacuated (air pressure < 1 Pa) after sample preparation and sealed together with molecular sieve in quartz/glass/*Teflon* vessels used for optical spectroscopy. High-purity N₂ (> 99.9999%) was used for the determination of the quenching rate by N₂.

Results. – *Kinetic and Spectrographic Flash Photolysis of 1.* A transient intermediate X with a broad absorption band in the long-wavelength part of the VIS region ($\lambda_{\text{max}} = 580$ nm) was formed within 25 ns upon flash photolysis of 10⁻³ M solutions of **1** in benzene with a 530-nm pulse from a Nd glass laser. *Fig. 1* displays the absorbance changes $\Delta A(\lambda)$ induced by laser flash photolysis of **1** in dry benzene; the first spectrum was taken prior to, the second with a delay of 80 ns after the laser pulse. The absorbance decrease in the range of 400 to 500 nm arises from photolytic bleaching of the absorbance due to **1**.

The decay of the intermediate X always adhered to a first-order rate law; the lifetime of X and the spectral changes associated with the decay of X strongly depended on the

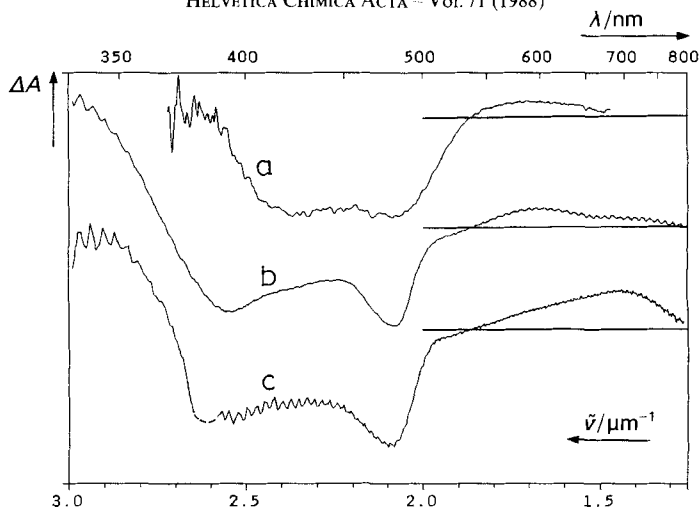


Fig. 1. Comparison of the transient absorbance changes induced by laser flash photolysis of **1** in dry benzene at ambient temperature (80-ns delay, curve a) and the persistent changes observed upon 436-nm photolysis of **1** isolated in an N_2 matrix (curve b) and in an Ar matrix (curve c) at ca. 12 K

H_2O content of the solution. Minor contributions to the transient absorbance during the first few μs were due to a second species (*vide infra*). In carefully dried, degassed solutions, the lifetime of X approached a maximum value of ca. 200 μs and the absorption spectrum of the solution was restored to original after the decay of the transient intermediate. No change of the limiting lifetime of X was observed when the concentration of **1** was varied in the range of $5 \cdot 10^{-3}$ to $5 \cdot 10^{-4}$ M. The decay rate of X rapidly increased, when traces of H_2O were admitted to the benzene solutions, and the reaction of X with H_2O gave a long-lived end absorption from 500 to > 700 nm. This blue coloration was persistent in degassed solutions.

Very similar observations were made upon flash photolysis of **1** in CCl_4 solutions; in particular, the difference spectrum obtained by flash photolysis was practically the same as in benzene solution (Fig. 1), and the lifetime of the transient absorption was equally sensitive to moisture.

Attempts to identify the blue product formed by irradiation of **1** in moist, degassed solutions have met with limited success. Gradual changes in the shape of the absorption spectrum occurred over a period of hours and indicated that slow dark reactions were proceeding after the irradiation. After this initial 'tempering', the blue solutions were stable for days, and the colorant could even be evaporated to dryness and redissolved without change. The blue color disappeared within a matter of seconds, when O_2 or CO were admitted during or immediately after irradiation; the 'tempered' solutions ($\lambda_{max} = 580$ nm) were less sensitive to these gases, but, upon admission of air, the color was also discharged within a few hours. Strong ESR signals of a radical ($g = 1.9783$) with no resolved hyperfine structure but weak satellite lines due to ^{47}Ti and ^{48}Ti ($a_{Ti} = 0.86 \pm 0.01$ mT) were observed when a moist, degassed solution of **1** was briefly irradiated at ambient temperature. Broad features in the 1H -NMR spectrum of the blue residue redissolved in (D_6)benzene also indicated the presence of paramagnetic species; in addition, the spectrum contained a single sharp *singlet* at 6.04 ppm (the *singlet* due to the Cp protons in **1**

appears at 5.72 ppm in (D_6)benzene and some much weaker complex signals in the range of 5 to 6.5 ppm.

Trapping Kinetics. Reaction rates for the trapping of the intermediate X were in most cases determined by adding the trapping reagents to aerated solutions of **1** in spectroscopy-grade benzene or CCl_4 which had not been especially dried. This usually caused an increase in the decay rate of X and, concomitantly, a reduction of the end absorption due to the blue product formed by the reaction of X with H_2O . To ensure a constant H_2O content, the solvent was taken from the same stock for all measurements within a series. The first-order rate constants observed for the decay of X were, then, linearly related to the concentration of added quencher [Q],

$$k_{obs} = k_o + k_w[H_2O] + k_Q[Q], \quad (4)$$

as required by the mechanism of *Scheme 1*. Second-order rate constants k_Q for various quenchers are given in the *Table*.

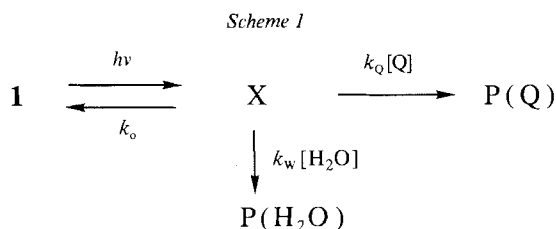


Table. Second-Order Rate Constants Determined from the Concentration Dependence of Observed First-Order Decay Rates

Reagent Q ^{a)}	Solvent	Conc. range [Q]/M	$k_Q/(10^7 \text{M}^{-1} \cdot \text{s}^{-1})^b$
TMPO	benzene	0.002–0.1	3.4 ± 0.1 (10)
TMPO	CCl_4	0.002–0.2	4.9 ± 0.4 (5)
MeCN	CCl_4	0.001–0.07	70 ± 1 (15)
Me_2CO	benzene	0.01–0.13	14.1 ± 0.6 (16)
Me_2CO	CCl_4	0.02–0.11	22 ± 2 (11)
MeOH	benzene	0.008–0.05	16.0 ± 0.5 (10)
$MeNO_2$	benzene	0.01–0.06	12.0 ± 0.5 (11)
BDDA	benzene	0.001–0.06	1.8 ± 0.1 (9)
H_2O	benzene	0.0073	27 ^{c)}
O_2	benzene	0.0091 ^{d)}	0.15 ^{c)}
CO	benzene	0.0075 ^{d)}	0.75 ^{c)}
N_2	benzene	0.0050 ^{d)}	0.18 ^{c)}

^{a)} Abbreviations: TMPO = 2,2,6,6-tetramethylpiperidine *N*-oxide, BDDA = butane-1,4-diyl diacrylate.

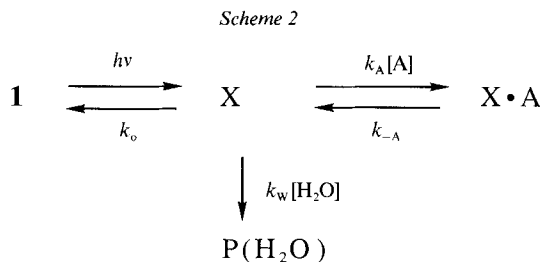
^{b)} Error limits are standard errors; the number of data points used in each linear regression (*Eqn. 4*) to determine the slope k_Q is given in brackets.

^{c)} Determined from the decay rate observed with a single reagent concentration [Q] in dry benzene (*Eqn. 6*).

^{d)} Gas solubility at 1 atm pressure, 25°: E. Wilhelm, R. Battino, *Chem. Rev.* **1973**, *73*, 1.

The quenching of X by acetone (A) required a special analysis, because the kinetic traces obeyed a dual exponential rate law. The faster process gave rise to a relatively minor absorbance increase which was best observed at 560 nm. The rate of this reaction increased linearly with [A], and this dependence was used to determine the second-order

rate constant for the reaction of X with A given in the *Table*. The rate of the slower process, observed as a decay of the absorbance at 560 nm, also increased with the concentration of various trapping reagents in the solution, *e.g.* MeCN or adventitious H₂O, but, for a given H₂O content, it *decreased* with increasing [A]. These findings are consistent with the reaction *Scheme 2* in which the reaction of X with acetone to yield the complex X · A is assumed to be a reversible reaction with an equilibrium constant $K = [X \cdot A] [X]^{-1} [A]^{-1} = k_A/k_{-A}$.



The acetone concentration [A] was chosen sufficiently high such that the rate of complexation with acetone was much faster than the reactions of X in the absence of acetone (re-isomerization to **1** and irreversible reaction with a quencher Q, *e.g.* H₂O), $k_A [A] \gg k_o + k_Q [Q]$. Then, following a brief 'induction period' immediately after the generation of X by the laser flash, the equilibrium between X and its acetone complex X · A may be considered to be maintained throughout the decay. Under these conditions, the reaction depicted in *Scheme 2* leads to a linear relation,

$$\tau_{\text{obs}} = \tau^0 (1 + K[A]), \quad \tau^0 = (k_o + k_Q [Q])^{-1}, \quad (5)$$

between the observed lifetime of the acetone complex, τ_{obs} , and [A], as was found experimentally. The slopes of these plots gave values of $(1.6 \pm 0.2) \cdot 10^2 \text{ M}^{-1}$ and $(0.41 \pm 0.04) \cdot 10^2 \text{ M}^{-1}$ for the equilibrium constants *K* in benzene and CCl₄, respectively.

The rate constants for the reaction of X with the gaseous reactants N₂, O₂, and CO given in the *Table* were determined by measuring the decay rate of X, first in a highly dry, degassed benzene solution ($k_{\text{obs}} = k_o$), then after equilibration with 1 atm of the respective gas ($k_{\text{obs}} = k_o + k_Q [Q]$), and finally after the solution was degassed once again ($k_{\text{obs}} = k_o$). In this way, it was ascertained that any lifetime reduction in the presence of the gas did not arise from an inadvertent introduction of humidity together with that gas, because the latter would not have been removed by the final degassing step. The trapping rate constants were then calculated as

$$k_Q = (k_{\text{obs}} - k_o)/[Q], \quad \text{with } k_o = 5.0 \cdot 10^3 \text{ s}^{-1}. \quad (6)$$

It was mentioned above that in addition to X a much weaker transient with a lifetime of *ca.* $\tau \approx 1 \mu\text{s}$ was observed in the wavelength range of 550 to 650 nm. Although the absorption by this second transient strongly overlapped with that of X, the kinetic data clearly showed that a different species was involved; in contrast to X, this transient was not sensitive to H₂O, but was quenched to a lifetime of < 50 ns when the solution was saturated with 1 atm of O₂. O₂ quenching did not affect the yield of X and the lifetime of X was much less sensitive to O₂ quenching. We tentatively identify the short-lived tran-

sient as the lowest excited triplet state of **1**, but have not investigated this minor side effect any further.

Photochemical Quantum Yields. The decomposition of **1** was monitored by the bleaching of the VIS absorption band ($\lambda_{\text{obs}} = 463 \text{ nm}$); the intensity of the photolysis light ($\lambda_{\text{irr}} = 436 \text{ nm}$) was measured by actinometry with azobenzene. The reactions proceeded uniformly as judged by optical spectroscopy (an isosbestic point was usually observed at *ca.* 390 nm), except in wet, degassed solutions where the blue photoproduct gave rise to complex secondary reactions. The quantum yield of decomposition of **1** did not depend on the solvent or on the presence of added reagents, unless the solvent was carefully dried. A constant value of $\phi_{\text{dec}} = 0.95 \pm 0.10$ was determined using the solvents CCl_4 , benzene, acetone, MeCN, and CCl_4 with 10% MeNO_2 .

When spectroscopic-grade benzene was degassed and further dried over molecular sieve, the photodecomposition rate of **1** gradually slowed down. The last traces of H_2O were best removed by photolysis of **1** and trap distillation of the solvent, until the compound was practically stable to irradiation, $\phi_{\text{dec}} < 2 \cdot 10^{-3}$. The addition of various reagents (TMPO, MeCN, etc.), then, resulted in an increase of ϕ_{dec} with increasing concentration of the additive Q up to the maximum value observed in moist solvents. The quantum yield of decomposition of **1** in dry solutions saturated with 1 atm of CO , N_2 , or O_2 gas, was determined as $\phi_{\text{dec}} = 0.74 \pm 0.10$, 0.57 ± 0.08 , and 0.61 ± 0.08 , respectively.

Extinction Coefficient of X. An upper limit for the molecular absorption coefficient of the intermediate X at 610 nm can be derived from the bleaching of **1** apparent between 400 and 500 nm in the absorbance difference spectrum (*Fig. 1*). The transient absorbance generated at 610 nm is about half as large as the bleaching at 420 nm due to the depletion of **1**. Assuming $\epsilon(\text{X}, 420 \text{ nm}) = 0$, we obtain an upper limit for $\epsilon(\text{X}, 610 \text{ nm}) \leq \epsilon(\text{1}, 420 \text{ nm})/2$. Since the bleaching curve follows the absorption of **1** in the range of 400 to 500 nm rather closely, it is in fact likely that $\epsilon(\text{X}, 420 \text{ nm}) \ll \epsilon(\text{1}, 420 \text{ nm})$ and thus the upper limit of $\epsilon(\text{X}, 610 \text{ nm}) \cong 500 \text{ M}^{-1} \cdot \text{s}^{-1}$ is probably a reasonable estimate of the true value. This approximation is commonly known as the 'Method of singlet depletion' [22] and is used predominantly to estimate molar absorption coefficients of triplet intermediates.

Product Analyses. 2-(Pentafluorophenyl)cyclopentadiene is isolated as the major organic photolysis product of **1** [4]. In contrast, the photolysis of diphenyltitanocene (**2**) yields biphenyl and, presumably, 'titanocene' $\text{Cp}_2\text{Ti}^{\text{II}}$ (process 2). Products attributed to trapping of titanocene with CO or diphenylacetylene were reported by Rausch *et al.* [10]. For a direct comparison, we have reproduced some of those trapping experiments; the formation of the green metallocycle 1,1-bis(η^5 -cyclopentadienyl)-2,3,4,5-tetraphenyltitanole (**3**) upon photolysis of **2** in a degassed benzene solution of $2 \cdot 10^{-2} \text{ M}$ diphenylacetylene [10] was readily monitored by the grow-in of the electronic absorption of **3** ($\lambda_{\text{max}} = 624 \text{ nm}$ [21]). Irradiation of **1** under similar conditions did not give rise to the formation of **3**. Photolysis of **2** in degassed, dry benzene gave a dark blue solution that turned red-brown upon saturation with CO [10]. The resulting dicarbonyl titanocene (**4**) was readily identified by two characteristic C=O absorption bands of about equal intensity at 1960 and 1880 cm^{-1} . Formation of **4** could not be detected after similar treatment of **1** in either dry or moist benzene.

Photoreaction of Matrix-Isolated 1. Matrices of Ar, CO, or N_2 were deposited on a CsI window held at *ca.* 20 K, while the complex **1** was sublimed at *ca.* 140° from a small quartz vessel, situated within the vacuum shroud. IR spectra were recorded at 12 K; bandwidths

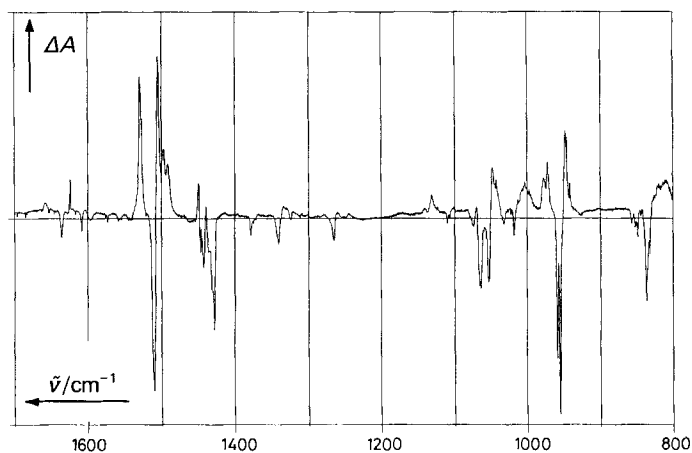


Fig. 2. IR absorbance difference spectrum obtained upon 436-nm photolysis of **1** isolated in an Ar matrix at 12 K. Upward peaks are due to absorption by the photolysis product(s), downward peaks to the photodecomposition of **1**.

of a few wavenumbers or less indicated satisfactory matrix isolation of **1**. The high photoreactivity of **1** was found to be undiminished in these matrices; after a few minutes of irradiation with the 436-nm line of a high-pressure Hg arc, the IR spectrum of **1** was replaced by a new spectrum which did not change much upon further irradiation. A difference spectrum displaying the changes induced in the region of 800 to 1700 cm^{-1} by irradiation of an Ar matrix containing **1** is shown in Fig. 2. Ignoring minor shifts of one or two wavenumbers, the difference spectra obtained upon irradiation of **1** in CO or N_2 matrices were nearly identical; salient differences were found only in the range of 2000 to 2500 cm^{-1} . In the CO matrix a strong, broad band with some fine structure appeared at 2036 cm^{-1} which was absent in the Ar matrix and which indicated that the photoproduct was able to bind CO from the matrix. In the N_2 matrix, a new, weak band appeared at 2288 and 2282 cm^{-1} , characteristic of metal-bound N_2 . Optical absorption difference spectra of the same matrices showed strong bleaching between 400 and 500 nm and a very broad absorption increase above 500 nm (λ_{max} 680 nm), similar to the absorbance difference spectra obtained by flash photolysis at ambient temperature (Fig. 1).

Discussion. – The fluorinated complex **1** is much more stable towards air oxidation and thermal decomposition than parent diphenyltitanocene **2**, and it was claimed to be useful as a polymerization initiator offering several advantages over conventional UV polymerization photoinitiators: high photospeed, sensitivity to VIS light (enabling its use with UV-opaque formulations), and photobleaching (allowing for the production of images of up to 70 μm thickness) [4–8].

A transient intermediate X is formed within 25 ns upon flash photolysis of a solution of **1** in both benzene and CCl_4 . The spectrum of the intermediate and its reactivity towards various additives are essentially the same in both solvents. We conclude that these solvents may be considered as inert media and that the same species is observed in both cases. The lifetime of this reactive intermediate X is strongly dependent on the H_2O

content of the medium. In degassed benzene, a maximum lifetime of *ca.* 200 μs is reached when moisture is carefully excluded.

The simple reaction depicted in *Scheme 1* accounts for the kinetic behavior of the transient intermediate X observed by flash photolysis (*Table*); as a special case the trapping by acetone requires inclusion of a reversible decay path for the acetone complex $\text{X} \cdot \text{A}$ (*Scheme 2*). In both *Schemes* the photochemical formation of X is considered to be a reversible process and that requires compound **1** to be photostable, when H_2O is rigorously excluded and other trapping agents are absent. This is indeed observed: in carefully dried solutions (H_2O content < 50 ppb) the quantum yield of decomposition upon photolysis at 436 nm drops to a very low value, $\phi_{\text{dec}} < 2 \cdot 10^{-3}$. In the presence of traces of moisture or deliberately added reagents, the lifetime of X decreases and the quantum yield of photodecomposition approaches a constant limiting value of $\phi_{\text{dec}} = 0.95 \pm 0.1$. The relationship between ϕ_{dec} and the concentrations of trapping agents Q and H_2O required by the reaction in *Scheme 1* is given by *Eqn. 7*.

$$(\phi_{\text{dec}})^{-1} = (\phi_{\text{X}})^{-1} \{1 + k_{\text{o}}/(k_{\text{Q}}[\text{Q}] + k_{\text{w}}[\text{H}_2\text{O}])\} \quad (7)$$

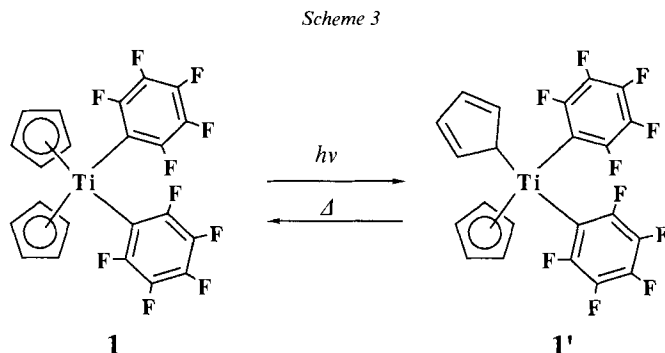
where ϕ_{X} is the quantum yield for the formation of the transient intermediate X in the primary photochemical process. When high concentrations of trapping agents are present, the formation of X is practically irreversible, $k_{\text{o}} \ll k_{\text{Q}}[\text{Q}] + k_{\text{w}}[\text{H}_2\text{O}]$, and $\phi_{\text{X}} \approx \phi_{\text{dec}} = 0.95 \pm 0.1$. Hence, the transient X is formed with unit efficiency in the primary photoreaction. In dry solutions under 1 atm of CO, N_2 , and O_2 , ϕ_{dec} was determined as 0.74 ± 0.10 , 0.57 ± 0.08 , and 0.61 ± 0.08 , respectively. These values are in satisfactory agreement with the estimates of 0.92, 0.64, and 0.70, respectively, calculated independently from *Eqn. 7* using the rate constants k_{Q} given in the *Table*.

Absorbance difference spectra (*Fig. 1*) indicate that the same photoproduct X is formed as a persistent species when **1** is irradiated in an Ar matrix at 12 K. The IR spectrum of the photoproduct in the Ar matrix (*Fig. 2*) differs from the corresponding spectra in CO and N_2 matrices in one important respect: additional bands appear at 2036 cm^{-1} (CO) and at 2282 and 2288 cm^{-1} (N_2). This observation provides strong evidence that X is capable to bind CO and N_2 when generated in matrices of these diatomic gases.

This work has confirmed and substantiated an assertion made previously (on the basis of trapping experiments with TMPO), namely that the photoreaction of **1** follows an entirely different course than that of **2** [4]. Flash photolysis of titanocene dichloride and of **2** gave only very weak signals under conditions where **1** had given quite intense transient absorption due to X. Furthermore, organotitanium intermediates have been trapped by photolysis of **2** in the presence of CO and diphenylacetylene [10]. No such products were detected, when **1** was irradiated under similar conditions.

What is the nature of the transient intermediate X? We can safely exclude an electronically excited state of **1**, because the rate of quenching of X by O_2 in solution is four orders of magnitude below the diffusion controlled limit, rather slower in fact than the reaction of X with N_2 , and because X is stable indefinitely in low-temperature matrices. CIDNP experiments have indicated that the primary photoproduct of dimethyl-titanocene is a radical pair (*Eqn. 1*) partitioning between in-cage recombination and radical trapping reactions [15]. It is, however, quite inconceivable that such a radical pair in the solvent cage could survive for 200 μs , the lifetime observed for X in dry benzene. *The observation that, in the absence of trapping reagents, the formation of X is entirely*

reversible by a first-order reaction then requires that *X* is an isomer of **1**. We tentatively identify *X* as the isomer **1'** formed by η^5 -to- η^1 cyclopentadienyl ring slippage, but do not wish to exclude a η^3 -isomer from consideration; such reactions have precedent in the (photo)chemistry of other metallocenes [23] [24] (Scheme 3). Hapticity reduction would reduce the number of electrons in valence shell of Ti from 16 to 14 (η^3) or 12 (η^1) and, thereby, open up new coordination sites on the transition metal. This would explain the



high reactivity of *X* towards many reagents with rate constants k_Q ranging from 10^6 to $10^9 \text{ M}^{-1} \cdot \text{s}^{-1}$ (Table). The decay of the intermediate *X* in the absence of trapping agents would, then, correspond to the reverse reaction $\mathbf{1}' \rightarrow \mathbf{1}$. Although the absolute rate of such a simple ring-slippage reaction has not to our knowledge been determined previously, the rate constant of $k_0 = 5 \cdot 10^3 \text{ s}^{-1}$ obtained in this work seems reasonable in view of the facile interchange of η^1 - and η^5 -cyclopentadienyl ligands observed for $(\eta^1\text{-Cp})_2(\eta^5\text{-Cp})_2\text{Ti}$ by Cotton and coworkers [25].

Conclusion. – The complex photoreactions of **1** have been traced back to a single primary photoprocess which yields a highly reactive isomer *X* with unit quantum yield. The reversible reaction $\mathbf{1} \rightarrow \mathbf{X}$ is attributed to a cyclopentadienyl ring slippage reaction $\mathbf{1} \rightarrow \mathbf{1}'$; the hapticity reduction opens up new coordination sites by reducing the number of electrons in the valence shell of the Ti-atom and, thus, offers a reasonable explanation for the remarkably high electrophilic reactivity of the isomer **1'**. The high reactivity of *X* towards H_2O suggests that the efficiency of **1** as a photoinitiator will be sensitive to the presence of moisture.

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