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PHOTOCHEMISTRY OF TITANOCENE(IV) DERIVATIVES

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Summary

Irradiation of cyclopentadienyl (Cp) derivatives of titanium(IV) in solvents containing halogen atoms leads to photolysis and abstraction of halogen The dihalides Cp_2TiCl_2, Cp_2TiBr_2, and $(CpMe_5)_2TiCl_2$ all undergo photolysis to give the corresponding cyclopentadienyltrihalotitanium(IV) compounds in chloroform or carbon tetrachloride. Cp_2TiCl_2 gives $CpTiCl_2$ when irradiated in pure benzene and $CpTiCl_3$ in benzene saturated with hydrogen chloride.

Introduction

Although there has been a recent surge of interest in the photochemistry of inorganic and organometallic compounds and ions containing various ligands bound to atoms of the transition elements, there are also many parts of the general field which have received little attention. For example, the photochemistry of metallocenes has been sparingly investigated with the sole exception of ferrocene [1a,1b,2] and there has been relatively little work done with any of the compounds of titanium. An exception is the observation of photoreduction of titanium(IV) alkoxides by Hunt and Winter [3] and McFarlane and Tindall [4] Consequently, we have initiated a study of various titanocene derivatives with interesting results. Notably, we find that in the titanocene dihalides photolytic cleavage occurs to give cyclopentadienyl radicals. The only previous reports of such cleavage comes from a flash photolytic study of ferrocene in the vapor phase [5].

Experimental

Materials. Dicyclopentadienyldichlorotitanium(IV) was purchased from

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Alpha Chemical Company and recrystallized from toluene Dicyclopentadienyldibromotitanium(IV) was purchased from Alpha Chemical Company and purified by vacuum sublimation at 110°. Dicyclopentadienyldifluorotitanium(IV) was prepared by the reaction of hydrogen fluoride with Cp_2TiCl_2 [6]. Dicyclopentadienyldimethyltitanium(IV), bis(pentamethylcyclopentadienyl)dichlorotitanium(IV), and bis(pentamethylcyclopentadienyl)dimethyltitanium(IV) were supplied by Dr. John E. Bercaw. Chloroform, spectroquality, was purchased from Matheson, Coleman and Bell. Material from a freshly opened bottle gave results identical with those obtained using chloroform purified by distillation from molecular sieves so the former was used in most experiments. Chloroform-*d* was purchased from Merck, Sharp, and Dome and used as received.

Irradiations All samples were degassed by repeated freeze-pump-thaw cycles with evacuation to 10^{-6} mm Hg. Sample tubes were then sealed under vacuum. Samples were normally prepared either in NMR tubes or in one cm optical cuvettes, depending upon the chosen analytical method. All irradiations were carried out at room temperature (except for Cp_2TiMe_2, which was irradiated at —60°). The course of reaction was followed using either a Varian T-60 NMR spectrometer or a Cary 17 spectrophotometer. Most photoproducts were identified by comparison of their NMR spectra with those of known samples Both dilute (10^{-5} *M*) and saturated solutions (for NMR studies) were employed. No significant concentration effects were found. All irradiations were carried out using filters designed to provide excitation in the first absorption bands of the starting materials and to minimize competitive absorption by primary photoproducts (see Table 1). Absorption overlap was so extensive with Cp_2TiMe_2 and $(CpMe_5)_2TiMe_2$ that photolysis of the monomethyl derivatives could not be avoided.

Results

The absorption spectra of the compounds studied are shown in Fig 1. Due to the thermal instability of Cp_2TiMe_2 we were not able to obtain a clean absorption spectrum of this compound

TABLE 1

FILTERS USED IN PHOTOLYSIS

Compound	Spectral range of irradiation (nm)	Filter system
Cp_2TiCl_2	> 480	7 cm $K_2Cr_2O_7$ (0 3 g/l) + Corning 3 71 glass filter
Cp_2TiBr_2	> 580	7 cm Fe(*o*-phen)$_3$SO$_4$^{a}
Cp_2TiMe_2	> 300	Pyrex glass
$(CpMe_5)_2TiCl_2$	> 545	7 cm $K_2Cr_2O_7$ (30 g/l) + Corning 3-67 glass filter
$(CpMe_5)_2TiMe_2$	390–465	$CuSO_4$ $5H_2O$ + 5*M* NH_4OH^{b}
Quantum yields^c	485-605	Corning 3-70 + 4-96 glass filters

^{a}Concentration was adjusted until absorbance at 580 nm was 2 0. ^{b}$CuSO_4$ $5H_2O$ was added until absorbance at 390 nm equaled 2 0 ^{c}Quantum yields of Cp_2TiCl_2, Cp_2TiBr_2, and $(CpMe_5)_2TiCl_2$ were investigated.

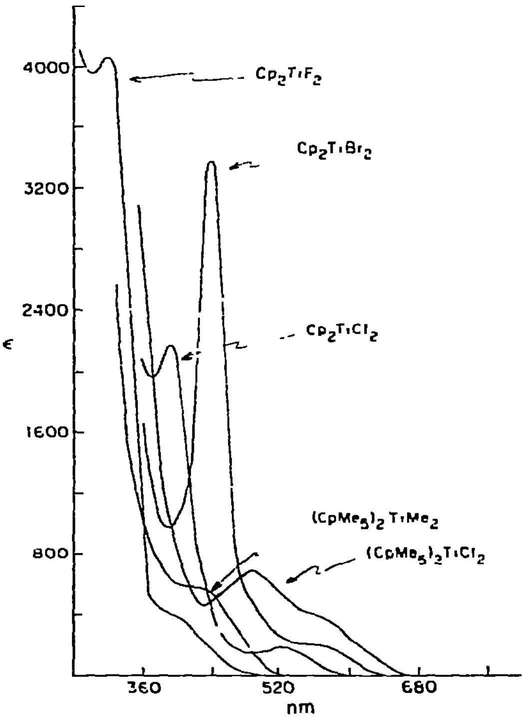

Fig. 1 Electronic absorption spectra of various dicyclopentadienyltitanium(IV) derivatives in $CHCl_3$ solution (1 cm cell)

Generally, irradiation of the dihalide complexes in chlorocarbon solvents leads to ring–metal bond scission followed by rapid formation of the trihalide complex. For example, irradiation of $(CpMe_5)_2TiCl_2$ in chloroform gives clean conversion to $(CpMe_5)TiCl_3$, as indicated by the maintenance of an isosbestic point throughout the photolysis (Fig. 2). The photolysis of Cp_2TiCl_2 in chloroform similarly yields clean conversion to $CpTiCl_3$.

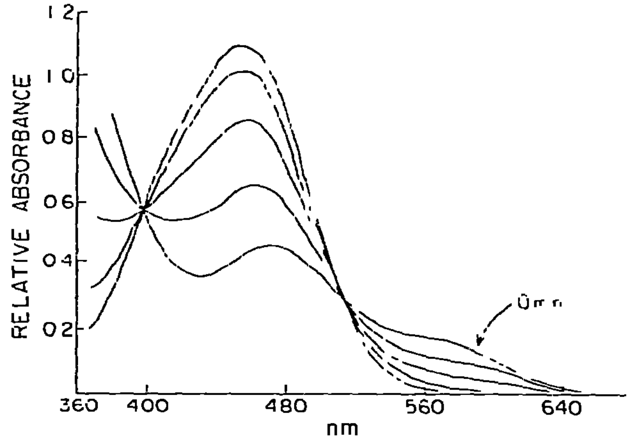

Fig. 2 Absorption spectral changes during irradiation of 6 4 × 10^{-4} M bis(pentamethylcyclopentadienyl)titanium(IV) dichloride in chloroform with light of wavelength greater than 545 nm

Cp_2TiBr_2 was irradiated in chloroform to check the possibility that breaking of Ti—Cl bonds occurs in the dihalide complexes but is obscured because the primary Ti^{III} photoproduct, L_2TiCl, regenerates the original material by abstracting chlorine from the solvent. No evidence for formation of $Cp_2Ti(Br)Cl$ or Cp_2TiCl_2 was observed. Instead, a new product was produced and is believed to be $CpTi(Cl)Br_2$, because of the similarity of its NMR spectrum to that of $CpTiCl_3$.

Reasonably rapid reaction was obtained only when the medium contained some source of halogen atoms. The same changes were observed in carbon tetrachloride as occurred in chloroform and in benzene saturated with hydrogen chloride. In the absence of a halide source, such as neat degassed benzene, prolonged irradiation (3 weeks in a room with shuttered windows and lighted by fluorescent lamps 24 h per day) of Cp_2TiCl_2 did lead to a small amount of a very air-sensitive mauve solid. The color of this solid is identical to that of $CpTiCl_2$, which was prepared following the method of Coutts et al. [7]. Further, other properties of this compound, such as its insolubility in benzene, and its rapid air oxidation to a yellow material, are all consistent with the formulation of $CpTiCl_2$ [8] For comparison, we note that Cp_2TiCl is green (sometimes reported [9] as green-brown) and soluble in benzene. Although the amount of solid was too small to allow collection and analysis, its physical properties convinced us that it is indeed $CpTiCl_2$ Additionally, irradiation of Cp_2TiCl_2 in neat, degassed benzene leads to broadening of the NMR signal of the ten equivalent hydrogens in Cp_2TiCl_2, indicating the generation of a paramagnetic species.

The photochemical behavior of the L_2TiMe_2 compounds in $CHCl_3$ was found to differ from that of L_2TiCl_2. The NMR spectra used to follow the course of the photochemical reaction showed that irradiation of Cp_2TiMe_2 and $(CpMe_5)_2TiMe_2$ produces some secondary products. Due to the fact that the visible absorption bands of the products are red-shifted with respect to the starting dimethide complexes, initial photoproducts are in turn photolyzed, yielding mixtures of L_2TiMe_2, $L_2Ti(R)Me$, L_2TiCl_2, and $LTiCl_3$. However, the primary product of the photolysis of L_2TiMe_2 in $CHCl_3$ appears to be $L_2Ti(R)Me$ Thus, in Cp_2TiMe_2 the methyl resonance at $\tau 10.2$ decreases and a new peak appears at $\tau 9.4$ ppm. This new peak is assumed to be the methyl resonance of $Cp_2Ti(R)Me$. Peak integration agrees with this assignment. Additionally, the methyl resonance of $(CpMe_5)_2TiMe_2$ at $\tau 11.0$ decreases upon irradiation and a new peak appears at $\tau 9.8$ ppm, attributable to the methyl resonance of $(CpMe_5)_2Ti(R)Me$. Examination of the NMR spectra obtained during the complete $(CpMe_5)_2TiMe_2$ photolysis revealed, however, a number of side products not attributable to $(CpMe_5)_2TiCl_2$ nor $(CpMe_5)TiCl_3$ formation. This observation suggests that competitive ring—metal bond scission occurs, giving mixed products. Formation of L_2TiCl_2 during these photolyses suggests that R = Cl, but the photointermediates were not positively identified.

Attempts were made to measure quantum yields of the dihalides using Reinecke's salt as an actinometer [10] Precision was poor because the quantum yields are quite low (approximately 2×10^{-2} or lower). It was, however, ascertained that the relative quantum yields for Cp_2TiCl_2 are approximately the same in carbon tetrachloride and in chloroform and about equal to the quantum yields with Cp_2TiBr_2. Significantly, the quantum yield for $(CpMe_5)_2TiCl_2$ in chloroform is about fifteen times greater

Discussion

It is felt that the above results are consistent with reductive dissociation associated with excitation to a charge-transfer (CT) state predominantly ring → metal in nature. The four spectra in Fig. 1 show common features In each there is a band of relatively low intensity at long wavelength which is relatively poorly resolved and sometimes appears only as a shoulder on a more intense band having a maximum extinction coefficient ranging from 750 in $(CpMe_5)_2TiCl_2$ to 4050 in Cp_2TiF_2. Despite the fact that the intensities are somewhat lower than might be expected, we assign these bands to Cp → Ti charge-transfer (LMCT) transitions. The progressive red shift of the bands as the halide is changed from fluoride to chloride to bromide probably reflects the order of reduced π-bonding of the halide p-electrons with the d orbitals of the metal. Decrease in this competitive interaction would move the Cp → Ti transitions to lower energies. The shift to lower energy resulting from the addition of electron-donating methyl groups to the cyclopentadienide unit is also expected On the other hand, replacement of the relatively electronegative halide ions by methide should increase the electron density at the central metal atom by a large increment, accounting for the shift of absorption to much shorter wavelengths in Cp_2TiMe_2 and $(CpMe_5)_2TiMe_2$

The chemical mechanism of the reactions seems clear. Some excited states must decay by dissociation to a free radical, cyclopentadienyl or pentamethylcyclopentadienyl, plus a titanium(III) compound The latter then abstracts a halogen atom from a solvent molecule. The following sequence is illustrative·

$$Cp_2TiCl_2 \overset{h\nu}{\rightleftharpoons} CpTiCl_2 \xrightarrow{CHCl_3} CpTiCl_3 + \cdot CHCl_2$$

Formation of $CpTiCl_2$ as a distinct intermediate prior to reaction with solvent is supported by the negligible effect of solvent on the quantum yield and the order of magnitude increase in quantum yield upon permethylation of the cyclopentadienide ring This latter effect is seen as a decreased probability of ring—metal bond reformation due to greatly increased steric hindrance Additionally, formation of $CpTiCl_2$ in neat benzene in very low quantum yield indicates that reductive dissociation is an open reaction pathway and that recombination of the cyclopentadienyl radical with $CpTiCl_2$ is, as expected, quite efficient. We feel that photocleavage probably occurs relatively efficiently and that recombination is the process which limits efficiency of photoreaction.

Verification of the proposed reaction of $CpTiCl_2$ with halogenated solvents shows that this reaction can indeed occur $CpTiCl_2$ prepared by reduction of $CpTiCl_3$ following Coutts et al. [7] was found to react with $CHCl_3$ to give $CpTiCl_3$. The analogy is not perfect, as our mechanism postulates monomer reaction with $CHCl_3$ and solid $CpTiCl_2$ exists almost certainly as a chloride-bridged dimer. However, we would expect the monomer to be even more reactive in the halide abstraction reaction.

The loss of cyclopentadienyl, or pentamethylcyclopentadienyl, radicals on photolysis of the dihalides is the kind of photoreductive step which has been associated with LMCT states in titanium(IV) complexes [4]. However, this correlation obviously does not have powerful predictive value in our case for two reasons. First, quantum yields are low, showing that nonradiative decay pathways leading back to the original state are the most important excited state processes Second, the dimethyl compounds cleave to break the Ti—Me bonds, even though we believe that excitation still has a primary labilizing effect on the ring-to-metal bonding These two phenomena may be related, as metal—halogen bond stretching might well be involved in the nonchemical radiationless decay which is predominant in the L_2TiX_2 compounds.

Given the observed photolability of the ring—metal bond in the titanocene derivatives, it is interesting to speculate on the reason for the extreme photostability of ferrocene Sohn et al [11] have studied the absorption spectra of a series of metallocenes in detail and have assigned the two low-intensity visible bands (22 700 and 30 800 cm^{-1}) in ferrocene to *d—d* transitions. The electronic nature of the lowest excited state is such that the ring—metal bonds are not weakened substantially [11], which would suggest [12,13] a low probability of photocleavage from this state. Another important factor is that the cyclopentadienide ring may be viewed as a rigid, multidentate ligand, and it is most unlikely that several axes of ligation could be simultaneously labilized in the lowest *d—d* excited state.

There has been only one report of metal—bond cleavage yielding Cp radicals as a primary photoprocess in ferrocene [5] The experiment in question involved flash photolysis in the vapor phase. From the general experimental description, one can infer that unfiltered flash irradiation was employed. Such irradiation could well excite the LMCT states in ferrocene [11], producing cyclopentadienyl radicals. Although this may seem to stand in counterdistinction to the photostability of condensed phase ferrocene systems, it may simply reflect enhanced non-radiative deactivation of upper excited states in the condensed phase over the vapor phase.

Other reports of metal—ring bond labilization in selected ferrocene derivatives have appeared [14,15]. Ali et al [14] have argued that although metal—ring cleavage subsequently occurs upon photolysis of ferrocenyl ketones, the primary photochemical reaction is in fact solvation without cleavage of the ring—metal bond. Cleavage follows a thermal, secondary reaction pathway. We might suggest that metal—ring labilization may occur to some extent due to shifting of the CT states providing some CT character to the low energy absorption bands. Spectra of some substituted ferrocenes show dramatic shifts and intensity changes in the CT region of the spectrum [16]. However, without the aid of a rigorous spectroscopic investigation, assignment of such spectral alterations strictly to charge transfer phenomena is very speculative [11]. There has been no systematic study of the reported metal—ring bond scission observed in other substituted ferrocene systems [1a] and such scission might well not be the primary process.

Another system of relevant interest is the monocation, dibenzenechromium(I) This compound exhibits photochemistry upon irradiation in the region of the strong absorption bands in the near ultraviolet and visible [17], which are almost certainly charge-transfer in nature The wavelength dependence of the quantum yields suggests that metal—ring bond cleavage occurs only when the CT states are populated and not when the lowest lying (~ 1160 nm) ligand field band is irradiated While this might at first appear to be clear evidence of the labilization effect of CT excitation, one must be cautious. In analogy with the isoelectronic ferricenium ion [18], it might be suspected that the low-lying absorption band in dibenzenechromium(I) involves a CT transition between essentially nonbonding π-type orbitals One would not expect this type of transition to lead to a very photoactive state However, in further analogy with the ferricenium ion, one might expect excitation of the type $d \to d\sigma^*$ to fall in the same region as the lowest CT absorption. This might cause rupture of the metal—ring bond in dibenzenechromium(I), especially since the ligand, benzene, is a neutral species and is less strongly held than a cyclopentadienyl group in Fe^{III} or Fe^{II} Such ideas would be in agreement with the experimental observations of Traverso et al [17], which show that no redox processes occur in the initial photochemical reaction. Also, theoretical considerations would indeed be consistent with no photoactivity in the ligand field state at ~1160 nm [11] Clearly, a rigorous spectroscopic study of dibenzenechromium(I) is needed before the photochemistry of this ion can be understood

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