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Photoreactivity of (HBpyrazolyl$_3$) TiCl$_3$ and (C$_5$H$_5$)TiCl$_3$ initiated by ligand-to-metal charge transfer excitation

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Abstract

The isoelectronic complexes LTi^{iv} Cl$_3$ with $L^- = C_5H_5^-$ and HBPz$_3^-$ (hydrotrispyrazolylborate) show long-wavelength LMCT absorptions $\lambda_{max} = 382$ and 314 nm, respectively. LMCT excitation is assumed to generate L radicals and TiCl$_3$ in the primary photochemical step. In CHCl$_3$ solution TiCl$_3$ is reoxidized by the solvent to TiCl$_4$ which is formed with $\phi = 0.003$ at $\lambda_{irr} = 405$ nm ($L^- = C_5H_5^-$) and $\phi = 0.002$ at $\lambda_{irr} = 366$ nm ($L^- = HBPz_3^-$). © 1998 Elsevier Science S.A. All rights reserved.

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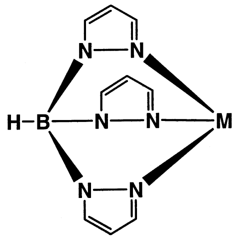
1. Introduction

Hydrotris(1-pyrazolyl)borate HBPz$_3^-$ and its derivatives are versatile tridentate anionic ligands which coordinate to many main group and transition metals in high as well as low oxidation states [1–5].



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Such complexes have attracted much attention owing to their importance for diverse applications including catalysis and bioinorganic chemistry. While HBPz$_3^-$ complexes have been characterized by many different methods very little is known on their electronic spectra and photochemistry. A few spectral assignments [6–8] and photochemical observations [9,10] have been reported. However, HBPz$_3^-$ seems to act as a spectator ligand in these cases. Electronic transitions and photoreactions with direct participations of coordinated HBPz$_3^-$ are apparently unknown [11]. We explored this possibility and selected (HBPz$_3$)Ti^{IV}Cl$_3$ as a suitable transition metal complex for the present study. This choice was based on the following considerations.

With the exception of intraligand (IL) transitions [11] only charge transfer excitations are associated with a direct participation of a particular ligand. HBPz$_3^-$ may thus serve as acceptor for metal-to-ligand charge transfer (MLCT) or donor for ligand-to-metal charge transfer (LMCT). However, there are indications that MLCT transitions occur only at very high energies owing to the instability of the π^* orbitals of the pyrazolyl substituents. The spectrum of Re(I) carbonyl complexes are diagnostic for the identification of low-energy MLCT transitions [12–14]. In the case of (HBPz$_3$)Re^I(CO)$_3$, MLCT states are apparently located well above ligand field (LF) excited states as indicated by the facile photosubstitution of a carbonyl ligand [10] in analogy to the behavior of CpRe(CO)$_3$ [13,15] ($Cp^- = C_5H_5^-$).

As an alternative, HBPz$_3^-$ may function as a donor ligand for LMCT transitions. This expectation is based on the general properties of BR$_4^-$ anions. For example, BH$_4^-$ is a strong reductant and BPh$_4^-$ has been shown to act as a donor for outer sphere CT transitions [16,17]. Moreover, a certain similarity between HBPz$_3^-$ and Cp$^-$ has been frequently emphasized [1–5]. Both anionic ligands are tridentate and able to stabilize transition metals in low and high oxidation states. While coordinated Cp$^-$ is not involved in low-energy MLCT transitions cyclopentadienyl complexes with oxidizing metals are characterized by long-wavelength LMCT absorptions [13,18,19]. In particular, d^0 centers such as Ti(IV) are appropriate metals because any interference

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with low-energy LF states is then avoided. For the purpose of comparison in addition to (HBPz$_3$) the complex CpTiCl$_3$ is included in the present study. Previous work on related titanocene complexes [13] such as Cp$_2$TiCl$_2$ [20,21], Cp$_2$TiS$_5$ [22] and Cp$_2$Ti[NCRu(CN)$_5$]$_2^{6-}$ [23] are expected to facilitate the investigation of the spectroscopy and photochemistry of (HBPz$_3$)TiCl$_3$ and CpTiCl$_3$. Finally, the photochemistry of CpTiCl$_3$ and the isoelectronic complex CpRe^{VII}O$_3$ [24] may reveal some common features which can be rationalized on the same basis.

2. Experimental

2.1. Materials/instrumentation

All solvents and chemicals were used as purchased without further purification. (C$_5$H$_5$)TiCl$_3$ and (HBPz$_3$)TiCl$_3$ were obtained from Strem. Absorption spectra were measured in carefully dried and argon saturated spectrograde CHCl$_3$ with a Hewlett Packard 8452A diode array spectrometer.

2.2. Photolyses

The light source was an Osram HBO 100W/2 or a Hanovia Xe/Hg 977 B-1 (1 kW) lamp. Monochromatic light was obtained using a Schoeffel GM 250/1 high-intensity mono-chromator (band width 20 nm). The photolyses were carried out in solutions of CHCl$_3$ in 1 cm spectrophotometer cells at room temperature. Progress of the photolyses was monitored by UV-visible spectrophotometry. For quantum yield determinations the complex concentrations were such as to have essentially complete light absorption. The total amount of photolysis was limited to less than 5% to avoid light absorption by the photoproduct. Absorbed light intensities were determined by a Polytec pyroelectric radiometer which was calibrated by actinometry and equipped with a RkP-345 detector.

3. Results

The electronic spectrum of CpTiCl$_3$ in CHCl$_3$ (Fig. 1) shows absorptions at $\lambda_{max} = 382$ ($\varepsilon = 2100$ dm^3 M^{-1} cm^{-1}) and 326 (4100) nm. (HBPz$_3$)TiCl$_3$ in CHCl$_3$ displays a band at $\lambda_{max} = 314$ nm (14800) (Fig. 2). For comparison the spectrum of TiCl$_4$ was measured, too. The longest-wavelength absorption which occurs as maximum at 287 nm [25] in cyclohexane, appears only as inflection in CHCl$_3$ because this solvent cuts of at $\lambda < 240$ nm.

Solutions of CpTiCl$_3$ in CHCl$_3$ are light sensitive. The photolysis is accompanied by spectral changes (Fig. 1) which indicate the formation of TiCl$_4$. The final spectrum is very close to that of TiCl$_4$ in CHCl$_3$. Other photolysis products, in particular organic compounds, absorb apparently only at shorter wavelength. The appearance of two isosbestic points at $\lambda = 300$ and 253 nm (Fig. 1) is an indication of a clean photoreaction. The progress of the photolysis is followed by measuring the decrease of the optical density at 326 nm taking into account the residual absorption of TiCl$_4$ at this wavelength ($\varepsilon = 1600$). The quantum yield for the formation of TiCl$_4$ was $\phi = 0.003$ at $\lambda_{irr} = 405$ nm.

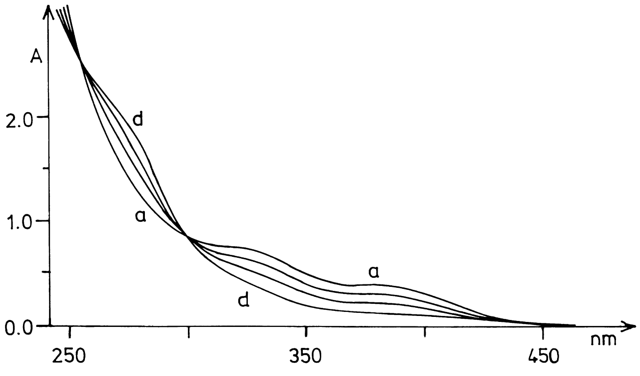

Fig. 1. Spectral changes during the photolysis of 1.83×10^{-4} M CpTiCl$_3$ in CHCl$_3$ under argon at R.T after 0 (a), 10, 30 and 60 (d) min irradiation time with $\lambda_{irr} > 320$ nm (Osram HBO 100W/2 lamp), 1 cm cell.

Solutions of (HBPz$_3$)TiCl$_3$ in CHCl$_3$ are also photosensitive. The photolysis leads to results which are very similar to those obtained for CpTiCl$_3$. However, the spectral variations (Fig. 2) include a rather diffuse isosbestic 'point' which indicates the occurance of secondary and/or side reactions. Nevertheless, TiCl$_4$ is also formed as final photoproduct. The formation of TiCl$_4$ ($\phi = 0.002$ at $\lambda_{irr} = 366$ nm) was determined by the decline of the absorbance at 314 nm.

4. Discussion

TiCl$_4$ is a tetrahedral d^0 complex which shows only LMCT absorptions [25]. The longest-wavelength LMCT

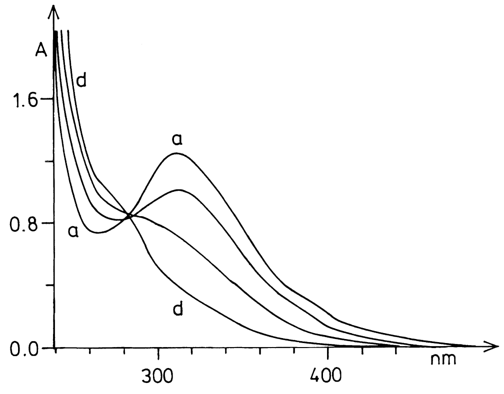

Fig. 2. Spectral changes during the photolysis of 8.78×10^{-5} M (HBPz$_3$)TiCl$_3$ in CHCl$_3$ under argon at R.T after 0 (a), 5, 10 and 30 (d) min irradiation time with $\lambda_{irr} = 366$ nm (Xe/Hg 977 B-1 lamp), 1 cm cell.

band at $\lambda_{max} = 287$ nm is assigned to the HOMO (t_1) → LUMO (e) transition from chloride π antibonding with respect to the Ti–Cl interaction.

$CpTiCl_3$ and $(HBPz_3)TiCl_3$ are obtained from $TiCl_4$ by replacing a chloride by a Cp^- and $HBPz_3{}^-$ ligand, respectively. In a simplified picture both complexes can be viewed as pseudotetrahedral molecules although a description as pseudo-octahedral complexes is also appropriate since Cp^- (half sandwich) and $HBPz_3{}^-$ occupy three coordination sites at Ti.

Since Cp^- is a stronger donor than Cl^- the lowest-energy transitions of Cp_2TiCl_2 [20,21,26] and certainly also of $CpTiCl_3$ are of the $Cp^- \rightarrow Ti^{IV}$ LMCT type. They are shifted to lower energies in comparison to $TiCl_4$ [25]. For $CpTiCl_3$ this relatively intense $Cp^- \rightarrow Ti^{IV}$ LMCT band appear at $\lambda_{max} = 382$ nm (Fig. 1) in close proximity to the corresponding LMCT band of Cp_2TiCl_2 (in THF, $\lambda_{max} = 385$ nm, $\varepsilon = 2730$) [21].

The longest-wavelength $\pi\pi^*$ absorption of free and coordinated $HBPz_3{}^-$ appear at $\lambda_{max} = 215$ nm [11]. It follows that the 314 nm band of $(HBPz_3)TiCl_3$ can be only assigned to a $HBPz_3{}^- \rightarrow Ti^{IV}$ LMCT transition. The occurance of a such LMCT transition at rather low energies is expected in view of the well-known donor properties of anions such as $BPh_4{}^-$ [16,17]. However, the comparison of the LMCT transitions of $CpTiCl_3$ and $(HBPz_3)$ $TiCl_3$ shows that $HBPz_3{}^-$ is a somewhat weaker donor than Cp^-.

A variety of titanocene derivatives undergo a photochemical reduction of Ti(IV) and ligand oxidation in the primary photochemical step upon LMCT excitation [13,20–23]. If the lowest-energy LMCT transition is of the $Cp^- \rightarrow Ti^{IV}$ type, Cp radicals are apparently generated initially [13,20,21]. While in the absence of suitable scavengers an efficient recombination can take place, chlorinated alkanes such as $CHCl_3$ are able to intercept and oxidize Ti(III) [13,20–23]. In analogy to these titanocene derivatives the photolysis of $CpTiCl_3$ in $CHCl_3$ should proceed according to a very simple scheme:

$$CpTiCl_3 - - - hv \rightarrow Cp^{\cdot} + TiCl_3$$

$$TiCl_3 + CHCl_3 \rightarrow TiCl_4 + {}^{\cdot}CHCl_2$$

The fate of the $Cp^{\cdot}$ radicals is unknown. However, an investigation of $CpReO_3$ which is isoelectronic to $CpTiCl_3$ has shown that the Cp^- radicals which are produced in the primary photochemical step undergo various secondary processes including radical coupling reactions such as dimerization [24].

The photolysis of $(HBPz_3)TiCl_3$ in $CHCl_3$ induced by LMCT excitation takes place apparently in analogy to $CpTiCl_3$:

$$(HBPz_3)TiCl_3 - -hv \rightarrow (HBPz_3)^{\cdot} + TiCl_3$$

$$TiCl_3 + CHCl_3 \rightarrow TiCl_4 + {}^{\cdot}CHCl_2$$

Although no attempt was made to reveal the fate of the $(HBPz_3)^{\cdot}$ radical a reasonable assumption is based related observations. The outer sphere CT oxidation of $BPh_4{}^-$ [16,17] or $B(benzyl)Ph_3{}^-$ [27] leads initially to the formation of $BPh_4^{\cdot}$ or B(benzyl) $Ph_3^{\cdot}$ radicals which undergo a fragmentation to $BPh_3 + Ph^{\cdot}$ or $BPh_3 + benzyl^{\cdot}$, respectively. Accordingly, the $(HBPz_3)^{\cdot}$ radical may yield $HBPz_2$ and $Pz^{\cdot}$ or BPz_3 and H atom in a subsequent fragmentation process, which is followed by further reactions of these reactive intermediates.

5. Conclusion

Hydrotris (1-pyrazolyl) borate ($HBPz_3{}^-$) is a donor ligand for optical CT. In combination with oxidizing metals low-energy LMCT transitions are expected to occur. In the case of $(HBPz_3)Ti^{IV}Cl_3$ this LMCT absorption appears at $\lambda_{max} = 314$ nm. LMCT excitation is assumed to lead to the generation of a $HBPz_3$ in the primary photochemical step. $TiCl_3$ is reoxidized by $CHCl_3$ to yield $TiCl_4$ as final product.

Acknowledgements

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