Photochemistry of tris(pyrazolyl)borate titanium(IV) complexes

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Abstract

The electronic features and photochemistry of TpTiCl$_3$ (**1**) (Tp = hydrotris(pyrazol-1-yl)borate) and Tp*TiCl$_3$ (**2**) (Tp* = hydrotris(3,5-dimethylpyrazol-1-yl)borate) were studied in THF. Reactive decay of the excited states produced either HBpz$_3$$^•$ (or HBpz$_3$$^{•*}$) and metal center Ti(III) radicals via homolytic cleavage of the Tp → Ti (Tp* → Ti) bond. Cleavage of the Tp → Ti and the Tp* → Ti bond as a primary photoprocess is shown to be consistent with LMCT Tp → Ti and Tp* → Ti excitation. TpTiCl$_2$(THF) (**3**) and Tp*TiCl$_2$(THF) (**4**) were also prepared by stoichiometric reduction of **1** and **2** with Li$_3$N. The THF ligand in **3** and **4** was replaced by the stable nitroxyl radical TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) to provide the new complexes TpTiCl$_2$-(TEMPO) (**5**) and Tp*TiCl$_2$(TEMPO) (**6**) in which the TEMPO ligand is η^1 coordinated to Ti(IV). Photolysis of **5** and **6** generate Ti(III) and the TEMPO radical in the primary photochemical step.
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1. Introduction

Poly(pyrazolyl)borates anions are well established, versatile ligands in the field of transition-metal chemistry [1]. The transition-metal complexes of poly (pyrazolyl)borate anions, have several attractive properties. Some of them have been masterfully brought into focus by a review from Trofimenko on Recent Advances in Poly(pyrazolyl)borate (Scorpionate) Chemistry [2].

In particular, the hydrotris(pyrazolyl)borate ligands are able to tune the electronic and steric environment of the central metal atoms by introducing various sub- stituents to the pyrazolyl ring [3]. In addition to this feature, by virtue of their steric properties, the hydrotris(pyrazolyl)borate anions stabilize unusual coordination geometries and high degrees of coordinative unsaturation. The chemistry of hydrotris(pirazolyl)borates is, to some degree, reminiscent of that of the cyclopentadienyl ligand (Cp = C$_5$H$_5$$^-$) [1]. Given this background, we began an investigation of the photochemistry of hydrotris(pyrazolyl)borate (HB(pyrazolyl)$_3^-$ (Tp), HB(3,5-Me$_2$-pyrazolyl)$_3^-$ (Tp*)) complexes of Ti(IV) with the aim to gain full understanding of the intrinsic relationship between electronic structure and spectroscopic properties. Comparison of the photochemical properties of the pyrazolyl titanium (IV) complexes with those of their Cp congeners would provide us with insight into the role of ancillary ligands in various catalytic and spectroscopic functions applicable to organic transformations.

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2. Experimental section

2.1. Reagent and general techniques

Most chemicals were of commercial origin unless otherwise indicated. Tetrahydrofuran, THF, was distilled over sodium and benzophenone under an atmosphere of dry nitrogen. Argon (99.99% purity) was passed through a column 4 Å molecular sieves prior to use. Potassium hydrotris(pyrazo-1-yl)borate hydrate KTp and potassium hydrotris(3,5-dimethylpyrazol-1-yl)borate KTp* were purchased from Stream Chemical and used as received. High purity titanium (IV) chloride $TiCl_4$, high purity lithium nitride Li_3N and 3-nitrosodurene were purchased from Aldrich and used as received. The nitroxide radical (2,2,6,6-tetramethyl-1-piperidinyloxy) TEMPO was purchased from Aldrich and sublimed prior to use. $TpTiCl_3$ and $Tp*TiCl_3$ were prepared by reaction of KTp or KTp* with $TiCl_4$ using modified literature procedures [4,5].

All manipulations were carried out under an atmosphere of dry nitrogen or argon using standard Schlenk and drybox techniques. All glassware was oven-dried prior to use. Solvents were freshly distilled under argon from Na or K prior to use.

^1H and ^{13}C NMR spectra were recorded on a Bruker AMX 200 and AMX 400. ^1H and ^{13}C NMR chemical shifts were referenced to residual ^1H and ^{13}C signals of the deuterated solvents.

Infrared spectra were recorded on an FT-IR Bruker mod. IFS88.

Elemental analyses were performed by the microanalytical laboratory at the University of Ferrara.

Electronic spectra of solutions of complexes under study were recorded at room temperature with a Perkin Elmer Lambda 40 spectrometer.

Irradiations were conducted at 315 nm using a Oriel 500 W Hg lamp equipped with corning glass 315 filter cut off and 400 band pass. The complex to be studied was dissolved in THF and the solution placed in an evacuable quartz UV cell which was subsequently degassed by three freeze-pump cycles. The solution was then irradiated with the appropriate lamp, and the electronic spectra were periodically recorded.

ESR experiments were performed at room temperature (295 K). An H-shaped mixing chamber attached to a fused quartz flat cell was used. An ESR 200tt Bruker Spectrometer operating at X-band was used for the ESR experiments with DPPH serving as the standard for determination of the g values. Field calibration was carried out by measuring the hyperfine splitting of di-*tert*-butyl nitroxide in benzene ($a_N = 1.536$ mT). All coupling constants were determined by at least three independent measurements. The experimental error was ±0.004 mT for the coupling constant and ±0.0005 mT for the g values. The photolysis was carried out directly in the ESR cavity in order to gain insight into the formation of short lived intermediates during the photoinduced primary process. The nitrosodurene (ND) was used as spin trap. The light beam of a Hg lamp was focused onto the window of the cavity after passage through an appropriate filter.

2.2. Synthesis of $TpTiCl_3$ (1)

A slurry of KTp (1.50 g, 5.9 mmol) in THF (20 mL) was cooled to -10 °C, and then $TiCl_4$ (0.66 mL, 5.9 mmol) was added dropwise. The resulting yellow suspension was stirred and refluxed for 12 h. The yellow solid was collected by filtration, dried in vacuo, and sublimed yielding an yellow-orange solid $TpTiCl_3$.

Yield: 1.90 g (87% based on KTp). ^1H NMR (200 MHz, C_6D_6) δ: 8.08 ppm (d, 3H, pz-H_3); 6.85 ppm (d, 3H, pz-H_5); 5.48 ppm (t, 3H, pz-H_4). FT-IR (Nujol): $v_{C-H} = 3133$ cm^{-1}, $v_{H-B} = 2519$ cm^{-1}.

2.3. Synthesis of $Tp*TiCl_3$ (2)

A slurry of KTp* (1.06 g, 3.2 mmol) in THF (20 mL) was cooled to -10 °C, and then $TiCl_4$ (0.36 mL, 3.2 mmol) was added dropwise. The resulting orange suspension was stirred and refluxed for 12 h. The orange solid was collected by filtration, dried in vacuo, and sublimed yielding an yellow-orange solid $Tp*TiCl_3$.

Yield: 1.12 g (79% based on KTp*). ^1H NMR (200 MHz, CD_2Cl_2) δ: 5.85 ppm (s, 3H, pz-H_4); 2.78 ppm (s, 9H, Me); 2.45 ppm (s, 9H, Me). FT-IR (Nujol): $v_{C-H} = 3119$ cm^{-1}, $v_{H-B} = 2555$ cm^{-1}.

2.4. Synthesis of $TpTiCl_2(THF)$ (3)

A solution of $TpTiCl_3$ (228 mg, 0.620 mmol) in THF (10 mL) was added at 0 °C, drop by drop, to a suspension of Li_3N (8 mg, 0.230 mmol) in THF (6 mL) to generate a yellow solution. A rapid reaction occurred accompanied by the evolution of a gas (N_2) and the solution gradually became blue. After 2 h stirring at room temperature, the reaction was considered complete. The solution was filtered and removal of the reaction solvent in vacuo yielded a green solid identified as $TpTiCl_2(THF)$ [4]. Yield: 201 mg (80% based on $TpTiCl_3$). FT-IR (Nujol): $v_{C-H} = 3120$ cm^{-1}, $v_{B-H} = 2512$ cm^{-1}. UV–Vis spectrum in THF: $\lambda_{max} = 561$ nm. ESR spectrum in THF: $g = 1.988$. Anal. Calc. for $C_{13}H_{18}BCl_2N_6OTi$: C, 38.66; H, 4.49; N, 20.81. Found: C, 38.42; H, 4.35; N, 20.64%.

2.5. Synthesis of $Tp*TiCl_2(THF)$ (4)

A solution of $Tp*TiCl_3$ (150 mg, 0.332 mmol) in THF (10 mL) was added at 0 °C, drop by drop, to a suspension of Li_3N (4 mg, 0.115 mmol) and THF (4 mL) to

generate a yellow solution. A rapid reaction occurred accompanied by the evolution of a gas (N_2) and the solution gradually turned blue. After 2 h stirring at room temperature, the reaction was considered complete. The solution was filtered and in vacuo removal of the reaction solvent yielded a blue solid identified as Tp*TiCl$_2$(THF). Yield: 126 mg (78% based on Tp*TiCl$_3$). FT-IR (Nujol): $v_{C-H} = 3118$ cm^{-1}, $v_{B-H} = 2510$ cm^{-1}. UV–Vis spectrum in THF: $\lambda_{max} = 570$ nm. ESR spectrum in THF: $g = 1.988$. Anal. Calc. for $C_{19}H_{30}BCl_2N_6OTi$: C, 46.72; H, 6.19; N, 17.22. Found: C, 46.61; H, 6.04; N, 17.15%.

TpTiCl$_2$(TEMPO) (**5**) and Tp*TiCl$_2$(TEMPO) (**6**) were prepared by two procedures. Method A involves the formation of THF complex which may be isolated and purified and then subjected to further reactions by displacement of the THF by TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy). Method B comprises the production in situ of TpTiCl$_2$(THF) which then reacted with the present TEMPO.

2.6. Synthesis of TpTiCl$_2$(TEMPO) (5)

2.6.1. Method A

A solution of TpTiCl$_3$ (312 mg, 0.848 mmol) in THF (10 mL) was added at 0 °C, drop by drop, to a suspension of Li$_3$N (10 mg, 0.287 mmol) in THF (6 mL) to generate a yellow solution. A rapid reaction occurred accompanied by the evolution of a gas (N_2) and the solution gradually turned blue. After 2 h at −65 °C, this solution was quickly added to a solution of TEMPO (132 mg, 0.848 mmol) in THF (5 mL) to generate a red-orange solution. After 2 h stirring at room temperature, in vacuo removal the solvent yielded a red-orange solid. The solid produced was washed with 25 mL of toluene and dried in vacuo to give red orange TpTiCl$_2$(TEMPO).

Yield: 248 mg (60% based on TpTiCl$_3$). FT-IR (Nujol): $v_{C-H} = 3127$ cm^{-1}, $v_{B-H} = 2514$ cm^{-1}. ^{1}H NMR (200 MHz, CD$_2$Cl$_2$) δ: 10.04 ppm (d, 1H, pz-H$_3$); 7.49 ppm (d, 2 × 1H, pz-H$_3$); 7.83 ppm (d, 1H, pz-H$_5$); 6.57 ppm (d, 2 × 1H, pz-H$_5$); 6.42 ppm (t, 1H, pz-H$_4$); 5.65 ppm (t, 2 × 1H, pz-H$_4$); 1.70 ppm (m, 6H, TEMPO) 1.60 ppm, 1.37 ppm (2s, 4 × 3H, CH$_3$, TEMPO). ^{13}C NMR (200 M Hz, CD$_2$Cl$_2$), δ: 144.2, 142.2 ppm (CH–C$_3$, pz); 134.6, 133.4 ppm (CH–C$_5$, pz); 104.2, 104.1 ppm (CH–C$_4$, pz); 68.6 ppm (TEMPO); 36.7 ppm (TEMPO); 28.3, 20.3 ppm (CH$_3$ TEMPO); 16.2 ppm (TEMPO). Anal. Calc. for $C_{18}H_{28}BCl_2N_7OTi$: C, 44.29; H, 5.78; N, 20.09. Found: C, 43.96; H, 5.56; N, 19.88%.

2.6.2. Method B

A solution of TpTiCl$_3$ (275 mg, 0.749 mmol) in THF (10 mL) was added at −65 °C, drop by drop, to a solution of TEMPO (117 mg, 0.749 mmol) in THF (5 mL) and to a suspension of Li$_3$N (9 mg, 0.258 mmol) in THF (6 mL) to generate a red-orange solution. After 2 h stirring at room temperature, in vacuo removal the solvent yielded a red-orange solid. The solid produced was washed with 25 mL of toluene and dried in vacuo to give red-orange TpTiCl$_2$(TEMPO).

Yield: 172 mg (47% based on TpTiCl$_3$).

2.7. Synthesis of Tp*TiCl$_2$(TEMPO) (6)

2.7.1. Method A

A solution of Tp*TiCl$_3$ (137 mg, 0.303 mmol) in THF (10 mL) was added at room temperature, drop by drop, to a slurry of Mn powder (42 mg, 0.764 mmol) in THF (6 mL). After 2 h, the dark green reaction was filtered to yield a dark green solution which was added at −65 °C, drop by drop, to a solution of TEMPO (47 mg, 0.303 mmol) in THF (10 mL) to generate a red-orange solution. After 2 h stirring at room temperature, in vacuo removal the solvent yielded a red-orange solid. The solid produced was washed with 25 mL of toluene and dried in vacuo to give red orange Tp*TiCl$_2$(TEMPO). Yield: 80 mg (46% based on Tp*TiCl$_3$). For the presence of traces of radical TEMPO the ^{1}H resonances of Tp*TiCl$_2$(TEMPO) are broadened to such an extent that assignment became difficult. The presence of $v_{C-H} = 3116$ cm^{-1}, $v_{B-H} = 2535$ cm^{-1} and the analytical data however confirm the formulation of **6** as the complex Tp*TiCl$_2$(TEMPO). Anal. Calc. for $C_{24}H_{40}BCl_2N_7OTi$: C, 50.38; H, 7.05; N, 17.13. Found: C, 49.88; H, 6.98; N, 17.07%.

2.7.2. Method B

A solution of Tp*TiCl$_3$ (228 mg, 0.620 mmol) in THF (10 mL) was added at −65 °C, drop by drop, to a to a solution of TEMPO (96 mg, 0.620 mmol) in THF (5 mL) and to a suspension of Li$_3$N (7 mg, 0.207 mmol) in THF (6 mL) to generate a red-orange solution. After 2 h stirring at room temperature, in vacuo removal the solvent yielded a red-orange solid. The solid produced was washed with 25 mL of toluene and dried in vacuo to give red orange Tp*TiCl$_2$(TEMPO).

Yield: 115 mg (38% based on Tp*TiCl$_3$).

3. Results and discussion

3.1. Spectroscopic characterization

The complexes TpTiCl$_3$ (**1**) and Tp*TiCl$_3$ (**2**) are soluble in chloroform and in tetrahydrofuran. The resulting solutions are very light sensitive. Figs. 1(a) and (b) present the absorption spectra of complexes **1** and **2** in the UV–Vis region as dilute solutions in THF.

Fig. 1. (a) Absorption spectrum of 5.11×10^{-5} M TpTiCl$_3$ in THF. (b) Absorption spectrum of 5.23×10^{-5} M Tp*TiCl$_3$ in THF.

Each spectrum shows a low-energy band at $\lambda_{\max} = 315$ nm ($\varepsilon = 14{,}000$ M cm^{-1}) for complex **1** and at 328 nm (11,800 M cm^{-1}) for complex **2**. These are followed by intense transitions at higher energies ascribed primarily to ligand localized π–π^*. Since **1** and **2** are formally complexes of the d^0 Ti(IV), the observed bands must represent charge transfer transitions. The longest wavelength π–π^* absorption of free and coordinate Tp$^-$ and Tp*$^-$ ligands appears in the 210–230 nm region [6–8]. As the Tp was changed to Tp*, the band showed a red shift, reflecting the increased π donation of the Tp* to the metal d orbitals. This observation and the fact that Cl $\rightarrow$ Ti transitions occur at higher energy [9–11], indicate that the band at 315 nm for **1** and at 328 nm for **2** can reasonably be assigned, respectively, to Tp $\rightarrow$ Ti and Tp* $\rightarrow$ Ti transitions. The photochemistry of TpTiCl$_3$ and Tp*TiCl$_3$ complexes strongly support this interpretation as the lowest excited state.

Complexes **3** and **4** were prepared by stoichiometric reduction of TpTiCl$_3$ and Tp*TiCl$_3$ with Li$_3$N in THF. Anaytical and spectroscopic data are consistent with the formulation TpTi(III)Cl$_2$(THF) (**3**) and Tp*Ti(III)Cl$_2$(THF) (**4**). The blue complexes **3** and **4** did not give crystals suitable for X-ray analysis. In the electronic spectra of **3** and **4**, absorptions are present

at 561 and at 570 nm, respectively, very close to the values reported in the literature for Ti(III) complexes of known structure [12]. Solutions of **3** and **4** exhibit ESR signals at room temperature with the expected ^{47}Ti ($I = 7/2$) and ^{49}Ti ($I = 5/2$) satellites. The study of the ESR and electronic absorption spectra of a complex make it possible to assign a value to the spin–orbit coupling constant of the complex [13]. Therefore, calculation of the values of these constants for the complexes TpTi(III)Cl$_2$(THF) (**3**) and Tp*Ti(III)Cl$_2$(THF) (**4**) makes it possible to evaluate the effect a steric environment has on the electronic spectra of Ti(III) as it goes from Tp to Tp*. The theory for g value predicts $g\|= 2$ and $g\perp = 2(1 - 3\zeta/\Delta)$, where ζ is the spin–orbit coupling parameter and Δ is the energy difference between t$_{2g}$ ground state and e$_g$ excited state [14,15]. With the experimental data obtained from ESR experiments and the electronic spectra of **3** and **4**, we can calculate the value of ζ (Table 1). Complexes **3** and **4** both have an ESR spectra constituted by a singlet with $g = 1.988$. The values of the energy difference Δ for complexes **3** and **4** are calculated from the LF transition at 17,825 and 17,544 cm^{-1}, respectively.

In an O$_h$ field, the metal d orbitals should split into two sets d$_{xz}$, d$_{yz}$, d$_{xy}$ and d_{z^2}, $d_{x^2-y^2}$. The unpaired elec-

Table 1
ESR and electronic data for the complexes **3** and **4**

Complex	$g\perp$	Δ (cm^{-1})	ζ (cm^{-1})
TpTiCl$_2$(THF)	1.988	17,825	35.65
Tp*TiCl$_2$(THF)	1.988	17,544	35.09

tron on titanium should hence lie in the lowest lying degenerated dπ orbitals and the band at 561 nm for **3** and at 570 nm for **4** can be assigned as the e$_g$ ← t$_{2g}$ transitions. Accepting these considerations, and on the basis of the experimental values of Δ and ζ, we can only postulate a pseudo-octahedral structure in solution for the TpTi(III)Cl$_2$(THF) and Tp*Ti(III)Cl$_2$ (THF) complexes. The observed transitions and the calculated values of ζ are in good agreement with those reported for related compounds of know structure [16].

Although an exact MO scheme for complexes **3** and **4** is unknown, one should expect that, because of the electron-donating methyl groups, both the HOMO and the LUMO of ligand Tp* are higher in energy than those for unsubstituited Tp. The decrease in the separation Δ (281 cm^{-1}) of the two lowest sets of orbitals found upon going from Tp to Tp* as coligands may be rationalized in terms of π-bonding effects, the Tp* ligand being a much better π donor than Tp.

By virtue of the lability of the THF ligand, complexes **3** and **4** provide a convenient, useful entry point into the coordination chemistry of {TpTiCl$_2$} and Tp*TiCl$_2$ fragments. Thus the THF ligand in **3** and **4** is readily replaced by the TEMPO ligand to provide complexes TpTiCl$_2$(TEMPO) (**5**) and Tp*TiCl$_2$ (TEMPO) (**6**) (Eq. (1)).

3: L = Tp
4: L = Tp*

5: L = Tp; 6: L = Tp*

(1)

The identity of **5** and **6** was established by spectroscopic (^{1}H NMR, ^{13}C NMR, FT-IR, ESR) and analytical data. ESR study of solutions of **5** and **6** indicate that these complexes are ESR silents. These results are consistent with the assignment of **5** and **6** as Ti(IV) complexes containing a reduced η^1 TEMPO ligand similar to what was reported by Waymouth for the complex CpTiCl$_2$TEMPO [17]. Due to the high oxophylicity of the Ti center, and on the basis of the methyl group resonances, we felt that the reduced TEMPO as oxyaminato ligand, is η^1 bonded to Ti(IV) forming a Ti–O bond [18]. These considerations are supported by analysis of the electronic absorption spectra of **5** and **6** which show the absence of any absorption due to Ti(III) in the region 500–700 nm.

The spectra of **5** and **6** are virtually featureless below 350 nm, whereas TpTiCl$_2$ (THF) and Tp*TiCl$_2$ (THF) show a distinct absorption at 561 and at 570 nm, respectively. For complexes **5** and **6**, the prominent spectral feature is a sharp, intense band in the 250–320 nm region which most likely results from the superimposition of the LMCT TEMPO-Ti (IV) (associated with the Ti–O bond) with the absorptions Tp → Ti and the Tp* → Ti LMCT. Since the Ti–O bond is normally very strong [17,19], the associated LMCT absorption is predicted to occur at high energy.

3.2. Photochemistry

Photochemical experiments were carried out in order to identify the following:

(1) The primary products of the excited state electron transfer between Tp or Tp* to Ti(IV);
(2) The formation of the Tp$^\bullet$ (HBpz$_3$)$^\bullet$ or Tp$^{\bullet*}$ (HBpz$_3$)$^{\bullet*}$ and Ti(III) centerd radicals since the LMCT state would lead to formal reduction of the metal and oxidation of the ring system.

Figs. 2(a) and (b) and 3(a) and (b) illustrate the electronic spectral changes during λ = 315 nm photolysis of TpTiCl$_3$ and λ = 328 nm photolysis of Tp*TiCl$_3$ in degassed THF solution.

Inspection of these spectral changes shows bleaching of the LMCT absorption at 315 nm for **1** and at 328 nm for **2**. A new feature appears with maximum absorbance at 570 nm; this feature is assigned to d^1 complex TiCl$_3^\bullet$THF.

3.3. ESR studies

Unlike an unirradiated solution, a solution of TpTiCl$_3$ (or Tp*TiCl$_3$), when photolyzed in the ESR cavity, displayed a singlet with g = 1.9776 with the expected ^{47}Ti (I = 7/2) and ^{49}Ti (I = 5/2) satellites. These findings make it possible to unambiguously attribute the signal to the electron d^1 at Ti(III).

The possible generation of Tp$^\bullet$ and Tp$^{\bullet*}$ radicals in addition to the Ti metal centred radical from the irradiation of TpTiCl$_3$ (**1**) and Tp*TiCl$_3$ (**2**) was put on a more qualitative basis by studying the photolysis of the complexes by ESR using nitrosodurene as appropriate spin-trapping agent.

Photolysis of **1** and **2** in THF containing nitrosodurene led to spin adducts with ^{14}N hyperfine splitting constants $a_N \approx 1.07–1.35$ mT. These nitroxides may be assigned to the spin adducts of Ti(III), pz$^\bullet$ and pz$^{\bullet*}$ (Table 2).

The, UV–Vis and ESR data are consistent with the immediate generation of trivalent d^1 metal compound TiCl$_3$ and (HBpz$_3^\bullet$) radical via LMCT excitation

Fig. 2. (a) Spectral changes during the photolysis of 5.11×10^{-5} M TpTiCl$_3$ in THF after 0 (a), 15, 30, 60, 90 (e) s irradiation time with $\lambda = 315$ nm. (b) Spectral changes during the photolysis of 5.45×10^{-4} M TpTiCl$_3$ in THF with $\lambda = 315$ nm.

Fig. 3. (a) Spectral changes during the photolysis of 5.23×10^{-5} M Tp*TiCl$_3$ in THF after 0 (a), 10, 20, 30, 45, 60, 90, 120 (h) s irradiation time with $\lambda = 328$ nm. (b) Spectral changes during the photolysis of 3.54×10^{-3} M Tp*TiCl$_3$ in THF with $\lambda = 328$ nm.

$$TpTiCl_3 \xrightarrow[\text{THF}]{h\nu} (HBpz_3^{\bullet}) + TiCl_3(THF) \qquad (2)$$

The primary photoproduct TiCl$_3$ has it vacant coordination site saturated with THF solvent molecule. However, the appearance of the ESR signals of ArNO · pz adduct indicated that the primary photoproduct (HBpz$_3^{\bullet}$) undergo rapid B–N fragmentation forming HBpz$_2$ and pz$^{\bullet}$ intermediates

Table 2
Spin adducts of the radicals to nitrosodurene(ArNO)

Complex	g	a_N (mT)	Radical
TpTiCl$_3$	2.012	1.35	$^{\bullet}$Ti(III)
	2.012	1.07	pz$^{\bullet}$
Tp*TiCl$_3$	2.012	1.34	$^{\bullet}$Ti(III)
	2.012	1.08	pz$^{\bullet *}$

$$(HBpz_3^{\bullet}) \xrightarrow{\Delta} HBpz_2 + pz^{\bullet} \qquad (3)$$
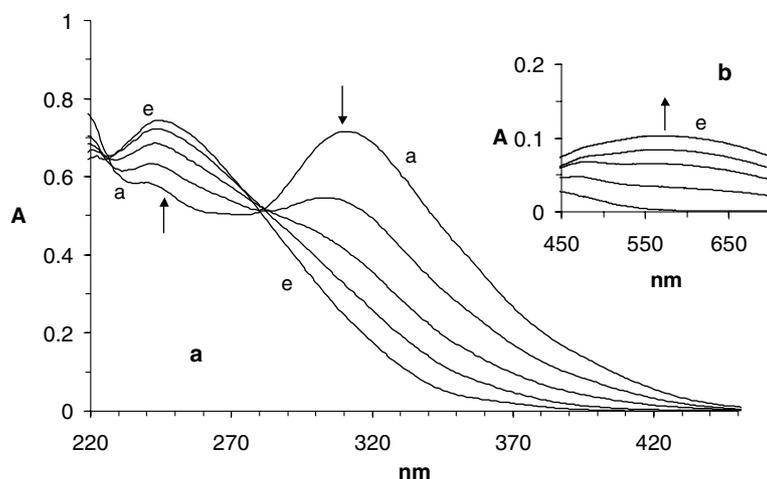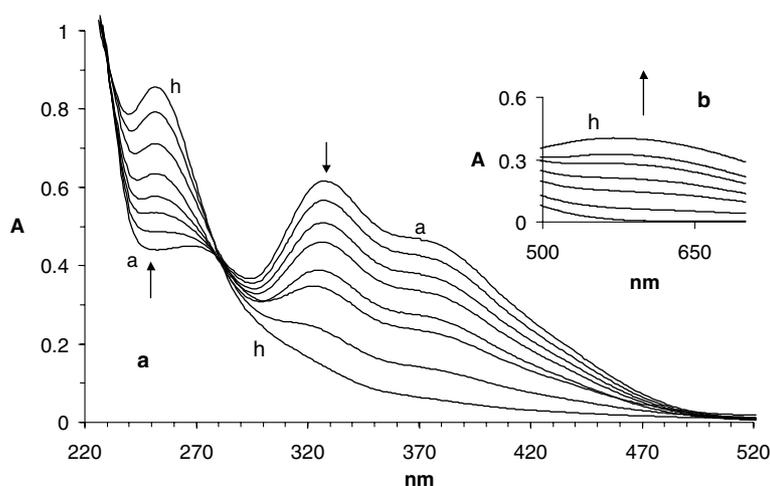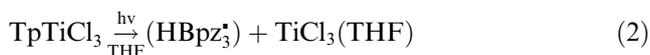
Apart from the changes due to the presence of 3,5 dimethyl groups, the behaviour of Tp*TiCl$_3$ is as for TpTiCl$_3$. These findings are consistent with related observations that alkyltriphenylborates $(R - BPh_3^-)$ undergo fragmentation to BPh$_3$ and benzyl [20]. We believed that fragmentation process occurs thermally. The possibility that this process occurs as secondary photolysis can be ruled out, since the longest wavelength π–π^* absorption of free Tp or Tp* appears in the 210–230 nm region.

From a practical standpoint, the primary photoproducts (HBpz$_3$)$^{\bullet}$ (HBpz$_3$)$^{\bullet *}$ and TiCl$_3$ are attractive initiating species for the polymerization of monomers such as the acrylates [10].

In order to design an effective system for photochemical polymerization, the study of a donor-acceptor

complex that could undergo a rapid chemical process triggered by photolysis could prove interesting. Our studies in this direction were guided by Waymouth's [17] recent work which indicates that CpTi(III) species can be trapped by nitroxyl radical TEMPO (2,2,6,6-tetramethylpiperidine-*N*-oxyl) to form the complex CpTiCl$_2$(TEMPO). Thus, in this study we have focused attention on systems {TpTiCl$_2$·TEMPO} (**5**) and {Tp*TiCl$_2$·TEMPO} (**6**) which pair the metal acceptor {TpTiCl$_2$} and {Tp*TiCl$_2$} fragments with the donor Lewis base TEMPO. These systems are of interest for their photochemical behaviour. In fact irradiation of **5** by 280 nm light leads to immediate consumption of the complex as made evident by the bleaching of the absorption band in the 250–320 nm region. Simultaneously a new absorption feature at 570 nm, typical of Ti(III) species, appears. Related experiments conducted in the ESR cavity show the immediate formation of the stable TEMPO radical. The behaviour of **6** is analogous to that observed for **5**.

The above experiments show that the primary photoproducts in the photolysis of **5** and **6** are Ti(III) species and TEMPO radical. The active excited state leading to the homolysis of Ti–O bond must come from the η^1 TEMPO-Ti LMCT transition. However the ill-defined spectra of the photoactive complexes preclude positive assignment of the absorption. The observed photocleavage sequences of Ti–O bond in **5** and **6** complexes may be used in meaningful chemical processes such as the initiation of polymerisation [10].

4. Concluding remarks

We have reported here the synthesis and the photochemistry of some Ti(IV) complexes with tris(pyrazolyl)borate ligands. Analysis of the electronic spectra of these complexes shows the presence of LMCT (tris(pyrazolyl)borate → Ti) transitions. The radical species involved in the photoinduced cleavage of the ligand–metal bond have been identified by ESR spectroscopy. Studies aimed at exploring the potential of TpTiCl$_3$, Tp*TiCl$_3$, TpTiCl$_2$(TEMPO) and Tp*TiCl$_2$-(TEMPO) complexes as photoinitiators for the polymerization of acrylates are currently in progress.

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