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**Preliminary communication**

# SPECTROSCOPY AND PHOTOCHEMISTRY OF TETRAKIS-(1-NORBORNYL)TITANIUM(IV)

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## Summary

Dominant electronic spectral features in the complex tetrakis(1-norbornyl)-titanium(IV) are due to ligand-to-metal charge transfer (LMCT) transitions. Near-ultraviolet irradiation of this complex in non-polar solvents yields homolytic cleavage of the titanium—norbornyl bond as a consequence of this LMCT excitation. Quantum yields were measured using a liquid chromatographic method.

Even though the photochemistry of complexes having alkyl ligands is currently of some interest [1], in those systems where metal—alkyl cleavage is a primary photoprocess little is known in detail about the reasons for that cleavage. In order to eliminate interfering absorptions and photochemistry associated with other ligands [2], we are investigating the spectroscopy and photochemistry of homoleptic tetraalkyl transition metal complexes [3]. Our study of the photochemistry of tetranorbornyl chromium, $Cr(NOR)_4$, has led us to assign the photoinduced metal—alkyl cleavage observed in that system as arising from ligand-to-metal charge transfer (LMCT) excited states [4]. In order to study the photochemistry associated with LMCT transitions in the absence of competing ligand field absorptions, we are investigating the electronic spectroscopy and photochemistry of the title complex; preliminary results are reported here.

The yellow tetranorbornyltitanium (I) can be prepared by literature procedures [5] from 1-norbornyllithium and $TiCl_4(THF)_2$. The complex, after recrystallization from hexane, gives a satisfactory elemental analysis (C, H, Ti) and has zero magnetic moment (Evans method [6]) indicating no unpaired electrons; Proton NMR and mass spectra are also consistent with a symmetrical tetraalkyltitanium(IV) complex. Contrary to published data [5a], $Ti(NOR)_4$ displays a

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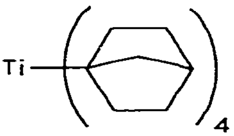

$Ti(NOR)_4$

(I)

slight sensitivity to oxygen in our hands, so samples were stored under $N_2$ or vacuum to avoid decomposition.

The electronic absorption spectrum of $Ti(NOR)_4$ in solution (see Fig. 1) is dominated by an intense band in the ultraviolet ($\lambda_{max}$ 245 nm, $\epsilon$ 29200 l $mol^{-1}$ $cm^{-1}$, in hexane) that we assign to the fully allowed LMCT transition ${}^1A_1(a_1^2t_2^6) \rightarrow {}^1T_2(a_1^2t_2^5e^1)$, see Scheme 1. A less intense band ($\lambda_{max}$ 367 nm, $\epsilon$ 253 l $mol^{-1}$ $cm^{-1}$ in hexane) and shoulders (312,412 nm) can be assigned to other LMCT transitions which are spin- or orbitally-forbidden*. Visible absorptions seen in $Cr(NOR)_4$ [4] and attributable to ligand field excitations are totally lacking, as expected for a $d^0$ complex.

Near-ultraviolet irradiation of rigorously degassed samples of $Ti(NOR)_4$ in hexane produces norbornane and 1,1′-binorbornyl. Irradiation in the presence of

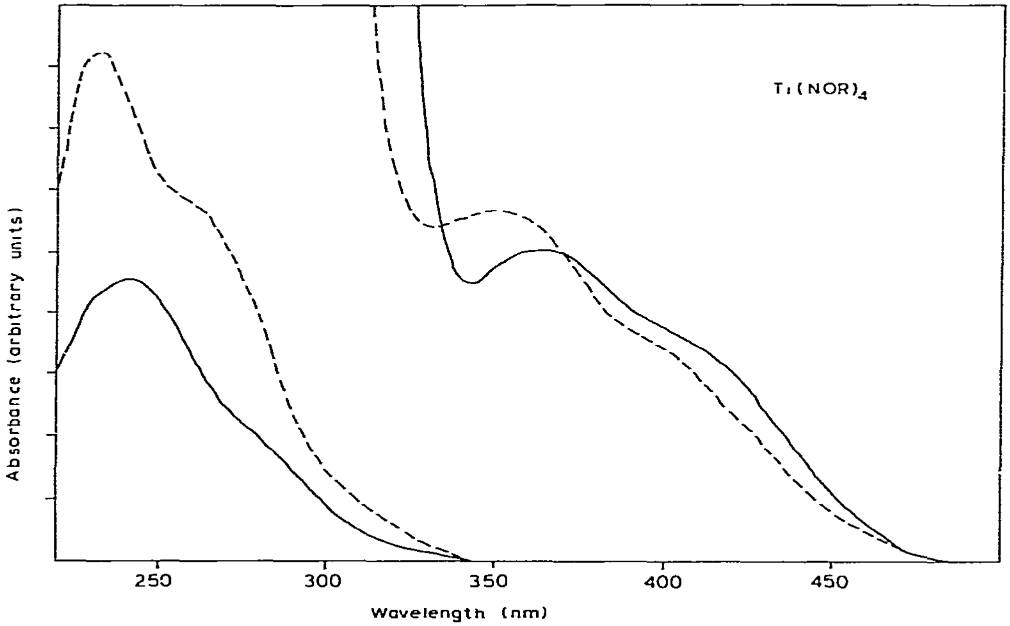

Fig. 1. Electronic absorption spectrum of $Ti(NOR)_4$ in EPA (5/5/2 diethyl ether/2-methylbutane/ethanol) solution at 298 K (——) and 77 K (- - - -), not corrected for solvent contraction. The portion to the right shows the spectrum of a more concentrated solution.

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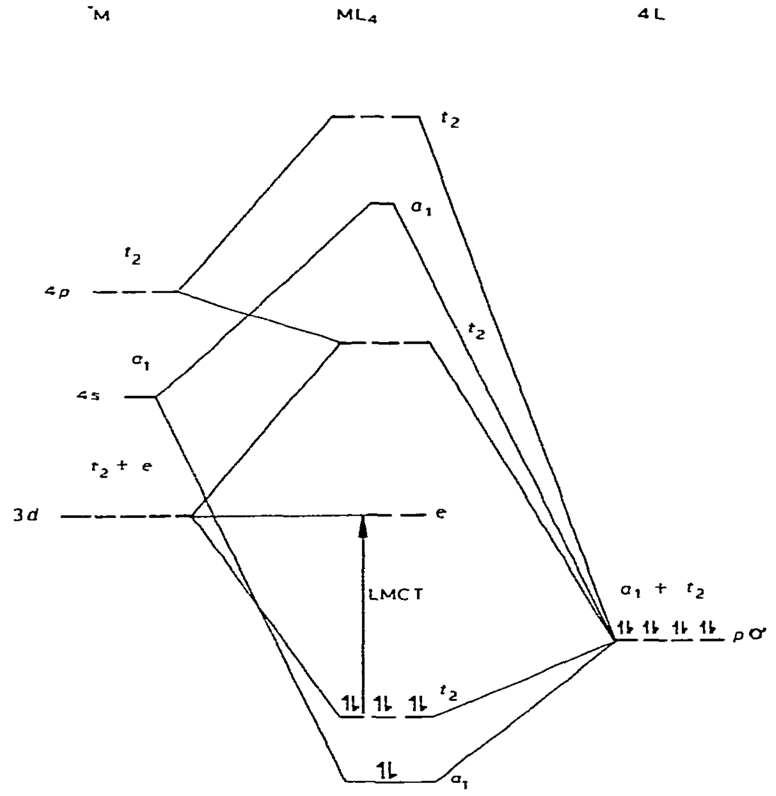
*Possible transitions include: orbitally forbidden, spin allowed ${}^1A_1 \rightarrow {}^1T_1(a_1^2t_2^5e^1)$ and ${}^1A_1 \rightarrow {}^1E(a_1^1t_2^6e^1)$: orbitally allowed, spin forbidden - ${}^1A_1 \rightarrow {}^3T_2(a_1^2t_2^5e^1)$. See Scheme 1. These assignments are rigorous only in the case of strict $T_d$ symmetry. Reduction of symmetry to, e.g., $D_{2d}$, would result in the ${}^1A_1 \rightarrow {}^1E$ component of formerly forbidden ${}^1A_1 \rightarrow {}^1T_1$ becoming allowed and thus perhaps contributing to the intense UV band.



SCHEME 1. One-electron molecular orbital diagram for a tetrahedral complex considering only σ bonding. Electron occupancies are shown for M = Ti(IV), L = NOR$^-$. Ordering of filled bonding levels is arbitrary.

carbon tetrachloride leads to 1-chloronorbornane and hexachloroethane as the major organic products but still accompanied by norbornane and binorbornyl. (Organic products were identified by gas chromatography and GC/MS and compared with authentic samples.) These products are consistent with homolytic cleavage of a titanium—norbornyl bond as the primary photoprocess, thereby producing norbornyl radicals (eq. 1), which is the kind of chemistry expected to

$$\mathrm{Ti(NOR)_4} \xrightarrow{h\nu} \mathrm{Ti(NOR)_4^{\star}} \rightarrow \mathrm{Ti(NOR)_3} + \mathrm{NOR}\cdot \qquad (1)$$

arise from LMCT excited states. Longer term irradiation, especially in hydrocarbon solvents (e.g., hexane, toluene) leads to changes in the original yellow color, to green, and finally black, with the eventual precipitation of a dark solid. The compounds responsible for these changes are air-sensitive and thermally unstable, and we have not yet been able to isolate or fully characterize them. However, measurement of their magnetic susceptibility in toluene solution [6] shows the presence of no unpaired electrons, implying that the expected $\mathrm{Ti^{III}}$ primary photoproduct has dimerized or disproportionated to yield a spin-paired system.

Optical quantitation of $\mathrm{Ti(NOR)_4}$ to determine disappearance quantum yields was rendered impossible by the absorbance of these uncharacterized product species over the whole ultraviolet region. Consequently, we have developed a liquid chromatographic method to separate photoproducts from and to quantitate unreacted $Ti(NOR)_4$ [7]. The system consists of a pump (40—50 ml/h, 50—100 psi), small volume loop injector, pellicular alumina column, and fixed-wavelength UV detector, with 0.02% methanol in hexane as the eluting solvent. Using an aromatic ketone dissolved in hexane as an external standard, we can measure the concentration of $Ti(NOR)_4$ remaining after irradiation. Disappearance quantum yields determined using this method are listed in Table 1; they are marginally higher than those for $Cr(NOR)_4$ under similar conditions [4]. (As a check on the accuracy of the method, quantum yields for $Cr(NOR)_4$ disappearance were also measured by this method [7] and found to be the same as those derived from optical quantitation [4].)

As might have been anticipated, the spectroscopy and photochemistry of $Ti(NOR)_4$ parallel those of $Cr(NOR)_4$ in the ultraviolet region. Since no ligand field (*d—d*) absorptions or photochemistry are possible in the titanium complex, this provides conclusive evidence that our earlier assessment that LMCT excited states are responsible for metal—alkyl homolytic cleavage in $Cr(NOR)_4$ is correct and can be extended to other homoleptic metal-alkyl complexes. Indeed, it is likely that similar LMCT excitations are responsible for the photoinduced metal—alkyl homolysis observed in other early transition metal complexes containing alkyl ligands.

TABLE 1

DISAPPEARANCE QUANTUM YIELDS FOR $Ti(NOR)_4$ [a]

| Wavelength (nm) | $[Ti(NOR)_4]$ (m*M*) | $\Phi$ ± 20% |
|---|---|---|
| 366 | 0.5 | 0.055 |
| 366 | 0.9 | 0.047 |
| 366 | 2.8 | 0.062 |
| 366 | 3.6 | 0.041 |
| 366 | 4.6 | 0.044 |
| 313 | 1.3 | 0.041 |
| 254 [b] | 0.8 | 0.065 |

[a] 4.0 ml of a hexane solution of complex degassed by 4 freeze/thaw cycles hermetically sealed in 15 mm od. Pyrex ampules and irradiated with Hg emission lines isolated from a Hanovia 450 W medium pressure-mercury lamp. Complex concentration measured by quantitative liquid chromatography [7] and light intensity determined by ferrioxalate actionmetry [8]. [b] Low pressure mercury lamp light source.

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