

Preliminary communication

SPECTROSCOPY AND PHOTOCHEMISTRY OF TETRAKIS(1-NORBORNYL)CHROMIUM(IV)

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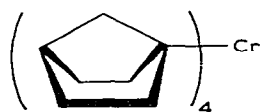
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Summary

Near-ultraviolet irradiation of tetrakis(1-norbornyl)chromium(IV) yields homolytic cleavage of the metal–alkyl bond as the result of a ligand-to-metal charge transfer (LMCT) transition. Ligand field excited states appear not to be photoactive.

Photochemical reactions of transition metal–carbon σ bonds are currently generating considerable interest [1], likely due to the importance of metal alkyls as models and precursors for catalytic intermediates. In order to isolate transitions associated with metal–alkyl bonding from possible interferences associated with the presence of other ligands [2], we have undertaken the study of the electronic structure and photochemical reactivity of homoleptic*** transition metal-alkyl complexes, encouraged by a previous report of their photosensitivity [3].



(I)

The title compound, I, was prepared from 1-lithionorbornane and $\text{CrCl}_3(\text{THF})_3$ following literature procedures [3–5]. Two major band systems are present in the electronic absorption spectrum of $\text{Cr}(\text{NOR})_4$ (Fig. 1). The intense ultraviolet absorption (λ_{max} 265 nm, ϵ 29700 l mol⁻¹ cm⁻¹) can

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*** Homoleptic alkyls are complexes of the form MR_n which contain only identical groups as ligands (also referred to as "binary alkyls").

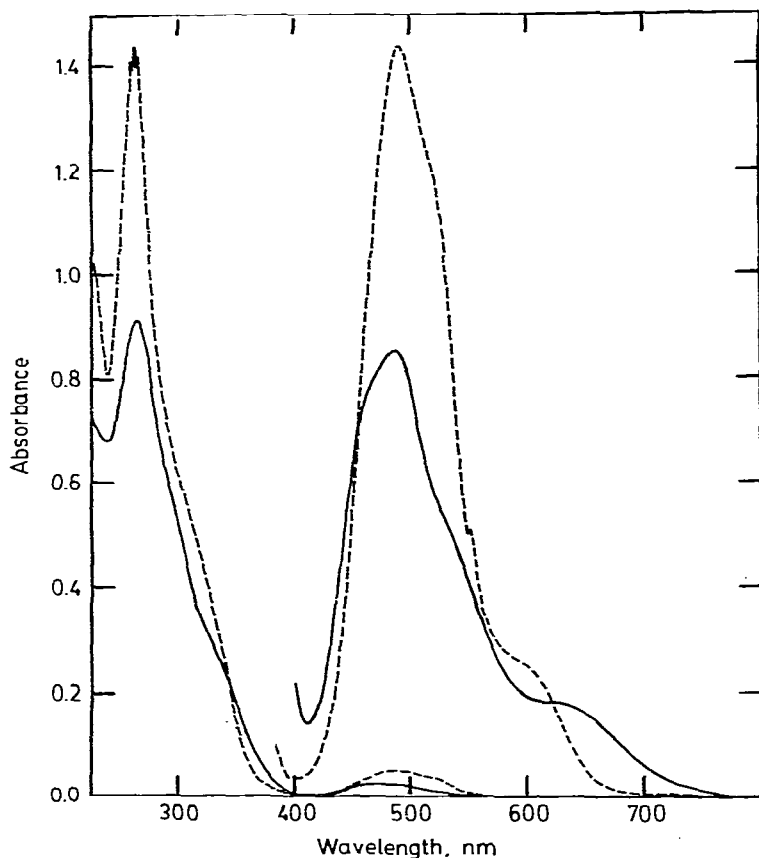
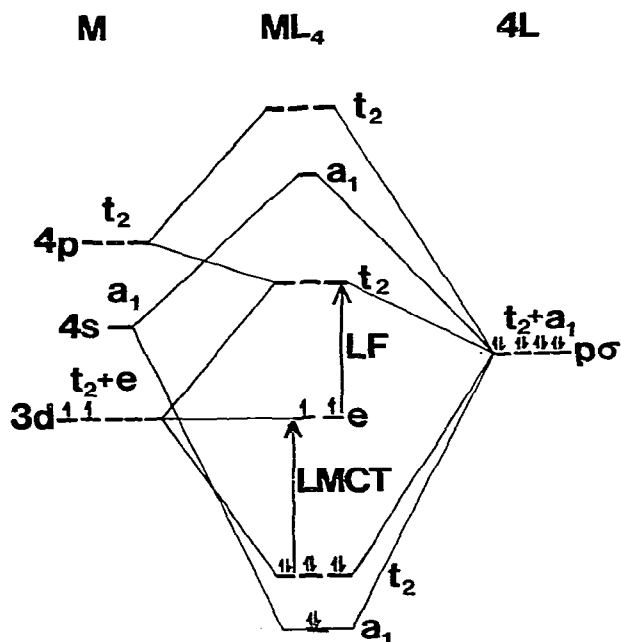


Fig. 1. Electronic absorption spectrum of $\text{Cr}(\text{NOR})_4$ in EPA (5/5/2 diethyl ether/2-methylbutane/ethanol) solution at 298 K (—) and 77 K (---). The portion to the right shows the spectrum of a more concentrated solution.

be assigned to a ligand-to-metal charge transfer (LMCT) transition (Scheme 1) on the basis of intensity and temperature dependence as well as the fact that a similar band is present in spectra of $\text{Ti}(\text{NOR})_4$ [6], a complex lacking d electrons. The major component of the visible band (λ_{max} 486 nm, ϵ 1340 $\text{l mol}^{-1} \text{cm}^{-1}$) is likely due to a ligand field (LF) transition ($e^2 \rightarrow e^1 t^1$) (Scheme 1) based on its lack of shift upon cooling to liquid nitrogen temperature and its absence in spectra of d^0 $\text{Ti}(\text{NOR})_4$ [6]. Another LF absorption is expected [7] and may be one of the shoulders in the near-ultraviolet. The other features remain unassigned at this point, but may be due to spin-flip LF or spin-forbidden LMCT transitions.

Irradiation of rigorously deoxygenated hexane solutions of $\text{Cr}(\text{NOR})_4$ produces clean changes in the absorption spectrum of the complex (Fig. 2), with an isosbestic point at 479 nm. The quantum yield for disappearance of $\text{Cr}(\text{NOR})_4$ dissolved in hexane/ CCl_4 mixtures upon near-ultraviolet irradiation is constant independent of the mole fraction of CCl_4 present or the concentration of complex. Quantum yield is also relatively independent of irradiation wavelength in the ultraviolet, but visible light irradiation



Scheme 1. One-electron molecular orbital diagram for a tetrahedral complex considering only sigma bonding. Electron occupancies are shown for $M = \text{Cr}$.

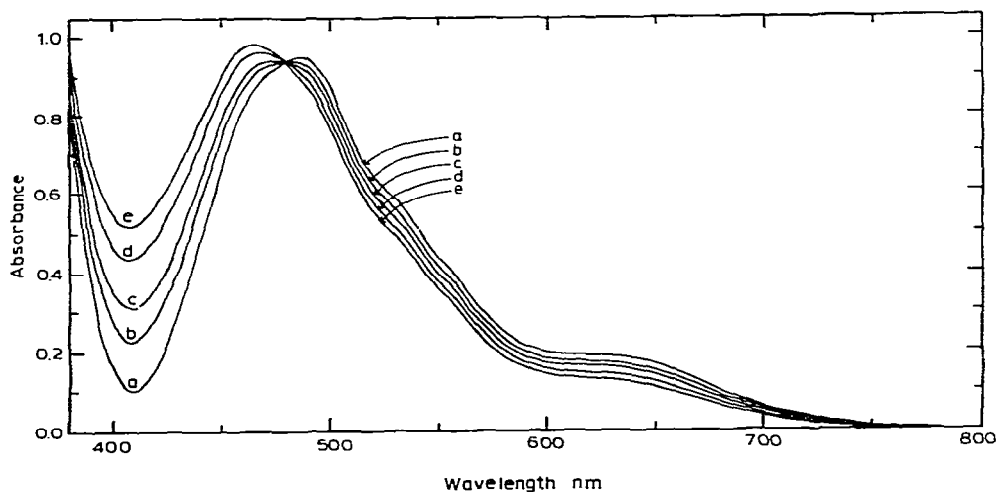


Fig. 2. Electronic absorption spectra of $\text{Cr}(\text{NOR})_4$ in hexane containing 1 M CCl_4 . Spectral changes were induced by irradiation at 366 nm for the following periods: (a) 0 min, (b) 12 min, (c) 20 min, (d) 34 min, (e) 44 min.

produces quantum yields lower by as much as two orders of magnitude. (Quantum yields and conditions are recorded in Table 1). Using qualitative gas chromatography/mass spectrometry, norbornane, 1-chloronorbornane, and hexachloroethane have been identified as organic products of photolyses in the presence of CCl_4 by comparison with authentic samples. The ratio of 1-chloronorbornane/norbornane increased with increasing CCl_4 content

TABLE 1

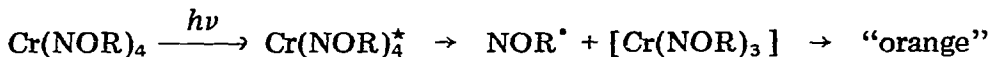
DISAPPEARANCE QUANTUM YIELDS FOR $\text{Cr}(\text{NOR})_4$ ^a

Wavelength (nm)	$[\text{CCl}_4]$ (M)	$[\text{Cr}(\text{NOR})_4]$ (mM)	$\Phi \pm 15\%$
254	10.3 ^b	1.0	0.059
313	10.2 ^c	7.0	0.032
313	10.3 ^b	1.4	0.036
313	0.0	1.4	0.038
366	1.0	7.4	0.037
366	1.0	1.2	0.035
366	1.0	0.7	0.036
366	0.1	7.6	0.038
366	0.0	1.0	0.033
436	0.0	3.6	0.0045
550	0.0	3.6	0.00023

^a 3.0 ml of deoxygenated solution of complex and CCl_4 irradiated at 25°C in a 1 cm quartz cuvette with Hg emission lines isolated from a Hanovia 450 W medium pressure mercury lamp. ^b Neat CCl_4 . ^c Neat CCl_4 containing 0.1 M decane.

of the solution. These observations are consistent with the production of 1-norbornyl radicals upon photolysis. An as yet uncharacterized air-sensitive orange chromium-containing material is also produced as a primary photo-product.

These results imply that the primary photoprocess is homolytic cleavage of a chromium—norbornyl bond:



likely resulting from a LMCT excitation. This assignment is reinforced by the observation that similar photochemistry obtains for $\text{Ti}(\text{NOR})_4$ [6], where only LMCT transitions are possible, and by the fact that exhaustive irradiation of the analogous $\text{Cr}(\text{neopentyl})_4$ in hydrocarbon solution produces low-valent metal complexes and polymerization of vinyl monomers [8].

The “chromium orange” produced in these photolyses has two unpaired electrons per chromium as measured by the Evans susceptibility technique [9] and is almost certainly not a monomeric CrR_3 complex, related examples of which are green with three unpaired electrons per chromium [3]. The strongest possibility is that this material is dimeric $\text{Cr}_2(\text{NOR})_6$ or a related material.

In any case, it is apparent that the excited state responsible for photo-induced homolytic cleavage of metal—alkyl bonds is, at least in the case of early transition metals, likely ligand-to-metal charge transfer in character. Further study of homoleptic alkyl complexes is in progress to extend our understanding of the reactivity of these LMCT excited states.

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References

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