Chemiluminescent Reactions of Bis(η^5-pentamethylcyclopentadienyl)ytterbium Derivatives

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The tetrahydrofuran adducts of two organoytterbium complexes, $Yb^{II}(C_5Me_5)_2$ (**1**) and $Yb^{III}(C_5Me_5)_2Cl$ (**2**), exhibit chemiluminescence characteristic of Yb^{III} species when reacted with O_2 and, in the case of (**1**), with O_2^-.

Although organolanthanide (OL) chemistry is developing rapidly,[1] little is yet known about the excited-state properties of these species. We are exploring these properties and have recently reported that adducts of $(C_5H_5)_3Yb^{III}$, Cp_3Yb, exhibit photoluminescence (PL) at 295 K;[2] a similar observation has been reported for Cp_3Tb and $(C_5H_4Me)_3Tb$.[3]

Chemiluminescence (CL) is another tool for investigating excited-state properties, but its application to lanthanides has largely been limited to energy-transfer studies involving β-diketonate complexes.[4] We report in this paper that tetrahydrofuran (THF) adducts of two organoytterbium complexes, $Yb^{II}(C_5Me_5)_2$[5] (**1**) and $Yb^{III}(C_5Me_5)_2Cl$[6] (**2**), exhibit CL characteristic of Yb^{III} species when reacted with O_2 and, in the case of (**1**), with O_2^-. To our knowledge, these are the first reported chemiluminescent reactions of OL complexes, and they demonstrate that CL can be observed in reactions which result in the net oxidation of ligand, metal, or ligand and metal.

$Yb^{II}(C_5Me_5)_2$ (**1**) $Yb^{III}(C_5Me_5)_2Cl$ (**2**)

Initial studies were conducted with *ca.* 5 mM THF solutions of (**1**) which is known to be a strong ground-state reductant.[5a,7] In this solvent, (**1**) exists predominantly as the bis-THF adduct, (**1**)·$(THF)_2$, and exhibits PL when excited in its visible absorption bands;[8] the PL spectrum, shown in Figure 1, is a broad band (full width at half maximum height *ca.* 100 nm) with an uncorrected $\lambda_{max.}$ at *ca.* 935 nm. The near i.r. spectral region also serves as a diagnostic for Yb^{III}; the f^{13} electronic configuration gives rise to sharp absorption and PL bands from *ca.* 950 to 1000 nm, corresponding to transitions between the $^2F_{7/2}$ ground state and $^2F_{5/2}$ excited state.[2,9] Given the low-lying Yb^{III} excited state at *ca.* 1.3 eV and the strong reducing properties of (**1**), we sought to populate the emissive Yb^{III} excited state by reacting (**1**) with strong oxidants.

Introduction of O_2 into the THF solutions of (**1**), either as the gas or dissolved in THF, yielded CL; the duration of CL was approximately the time of mixing. A CL spectrum, shown in Figure 1, was acquired from ratios of monochromatized to total emissive output.† The narrow spectral distribution with $\lambda_{max.}$ *ca.* 990 nm is characteristic of excited Yb^{III}. Conversion into Yb^{III} is also reflected in the PL spectrum of the reaction mixture which, as indicated in the figure, is similar to the CL spectrum.

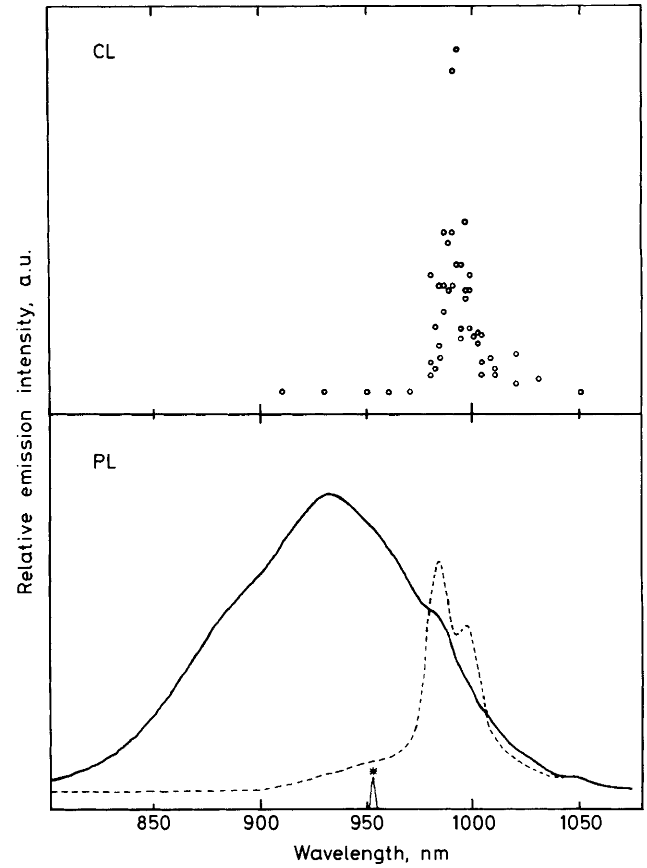

Figure 1. CL (top panel) and PL (bottom panel) accompanying the addition of a THF solution of O_2 to a THF solution of $Yb^{II}(C_5Me_5)_2$ (**1**). The CL spectrum displays the ratio of monochromatized to total emission intensity as a function of wavelength as the solution of (**1**) is titrated with O_2. PL spectra were obtained before addition of O_2 (solid curve) and after addition of 1 equivalent of O_2 (dashed curve) using 476.5 nm excitation. The peak labelled with an asterisk is a calibration line at 953.0 nm.

The CL-producing reaction turns the initially wine-red solution yellow. On standing, a flocculent yellow solid precipitates whose appearance is hastened by the addition of an excess of O_2; a PL spectrum of the solid indicates the presence of Yb^{III}. Characterization of the reaction mixture shows it to be complex. Hydrolysis with a small quantity of deoxygenated water followed by v.p.c. analysis reveals the presence of at least four components. The dominant species appears to be the hydroperoxide $Me_5C_5O_2H$.‡ Stable to v.p.c. conditions, this species accounts for a substantial quantity of

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† For obtaining CL spectra, 0.1 ml aliquots of 10—15 mM THF solutions of the OL complex were added by syringe to solutions saturated with oxidant. Mixing occurs in a volume of *ca.* 2 ml, and all manipulations of the OL complexes and O_2^- are carried out under an inert atmosphere. Monochromatic CL intensity was monitored using the emission spectrometer described in ref. 2. Total emitted light resulting from each aliquot of OL complex was simultaneously measured using an EG&G Model 550–2 multiprobe radiometer. A CL spectrum was generated wavelength-by-wavelength from the ratios of monochromatized to total emitted intensity.

‡ ^1H N.m.r. $(CDCl_3)$ δ 1.15 (s, 3H), 1.71 (s, 6H), 1.73 (s, 6H). High resolution mass spectroscopy, exact mass for $C_{10}H_{16}O_2$ calc. *m/z* 168.1146, found 168.1150. I.r. (film) ν(OH) 3320 cm^{-1} (s, br.). The compound gave a positive starch–iodide test for peroxide.

the added O_2; although the exact quantity of $Me_5C_5O_2H$ recovered appears to depend on the reaction stoicheiometry, a typical yield of the hydroperoxide is *ca.* 60—70% from an equimolar reaction of O_2 with (**1**).

The chemiluminescent reaction, which results in both metal *and* ligand oxidation, is clearly complex and prompted us to examine related systems for CL. We explored ligand oxidation by adding O_2 to THF solutions of $K^+Me_5C_5^-$ and also to solutions of (**2**). In the former case, no CL was found, but the product mixture resembled that observed in the reaction of (**1**) with O_2, with $Me_5C_5O_2H$ again the major component. The reaction of O_2 with (**2**) did lead to CL. However, in contrast to the experiment with (**1**), the Yb^{III} CL signal was *ca.* 5 times weaker and persisted for several seconds beyond the time of mixing; another difference is that although the CL and PL spectra are similar to one another, their maxima at *ca.* 980 nm are slightly blue-shifted relative to the bands of Figure 1. For this reaction of (**2**) with O_2, only net ligand oxidation obtains: product workup, as described above, yielded a similar organic mixture by v.p.c. to those found in the reactions of (**1**) or $K^+Me_5C_5^-$ with O_2, including a quantity of $Me_5C_5O_2H$ corresponding to *ca.* 50—60% of the 1 equivalent of O_2 added. A plausible mechanism for CL from (**2**) is energy transfer to Yb^{III} from a species derived from the reaction of O_2 with the $C_5Me_5^-$ ligand.

To probe whether metal-centred electron transfer could lead to CL, we reacted THF solutions of (**1**) with several one-electron oxidants. Although they produced metal oxidation, neither THF solutions of $AgPF_6$ nor of $Cp_2Fe^+FeCl_4^-$ effected CL. That oxophilicity may also play a key role in producing CL is suggested by experiments with O_2^-. A solution of O_2^- in MeCN, where the solubility of the K^+ salt was enhanced by complexation with 18-crown-6 ether, led to Yb^{III} CL when reacted with the THF solution of (**1**).§ The CL intensity, temporal properties, and spectral distribution (PL as well as CL) resembled those observed for the reaction of (**1**) with O_2. For the superoxide reaction, nearly quantitative ligand recovery occurs when O_2^- (*ca.* 1 equiv.) is added, as shown by v.p.c. analysis. The chemiluminescent reaction of (**1**) with O_2^- is thus accompanied by only net metal oxidation.¶ Addition of O_2^- to a THF solution of (**2**) causes decomposition of the complex but does not yield CL, indicating that, unlike the reaction with O_2, an efficient pathway for energy transfer to Yb^{III} does not exist for this system.

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§ In a control experiment, neither oxidation of (**1**) nor CL is observed when a THF solution of (**1**) is reacted with an MeCN solution of 18-crown-6 ether.

¶ Of course, quantitative ligand recovery does not preclude the possibility that ligand oxidation occurs at some stage of the reaction. For example, oxidation to $Me_5C_5{}^{\bullet}$ followed by abstraction of $H^{\bullet}$ from solvent would lead to ligand recovery.