Luminescence studies on substituted niobocene ketene complexes: evidence for thermally activated excited-state processes involving arene torsion

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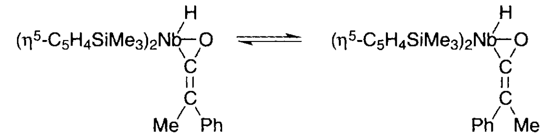
Photophysical studies on the η^2-C,O bound niobocene ketene complexes [Nb(η^5-$C_5H_4SiMe_3$)$_2$(H)(O=C=CRR′)] (R = R′ = Ph 1, R = Me, R′ = Ph 2) provide evidence for solution luminescence and temperature-dependent decay rates; the failure of 2 to exhibit photochemical *E–Z* isomerization is consistent with the operation of arene torsional modes in the thermal decay processes.

We have been studying niobocene complexes of disubstituted ketenes, [Nb(η^5-$C_5H_4SiMe_3$)$_2$(H)(η^2-*C,O*-OCCRR′)] (R = R′ = Ph **1**; R = Me, R′ = Ph **2**), in which the ketene ligand is bound in the η^2-C,O mode;[1] the ketene O–C–C and Nb–C–C angles are expected to be *ca.* 135 and 154°, respectively, and the C=CPh_2 portion of the ligand should therefore resemble a substituted diarylalkene. A variety of arylalkenes exhibit efficient fluorescence and thermally activated excited-state dynamical processes involving some combination of rotation about the alkene C–C bond and aryl–C torsional modes;[2–17] because *E–Z* isomerization is usually part of the photochemistry, it can be difficult to separate the contributions due to these two processes. We have previously shown that **2** may be isolated as the pure *E* isomer, and that it undergoes slow thermal equilibration to a 50 : 50 mixture of *E* and *Z* isomers [eqn. (1)].



(1)

E-**2** *Z*-**2**

Compounds **1** and **2** thus comprise arylalkene model systems in which one end of the alkene is anchored by the metal centre. We have thus undertaken a luminescence study of the complexes **1** and **2**. Herein we report that they exhibit ligand-based luminescence, do *not* undergo photochemical *E–Z* isomerization, and yet still show evidence for the operation of dynamical effects related to those seen in uncomplexed arylalkenes. The latter two characteristics may ultimately prove useful in apportioning the contributions due to the two possible torsional modes.

In toluene solution, **1** exhibits an intense absorption at *ca.* 288 nm (ε = 6600 ± 200 $dm^3\ mol^{-1}\ cm^{-1}$) and a much weaker shoulder centred at 490 nm ($\varepsilon \approx$ 70 $dm^3\ mol^{-1}\ cm^{-1}$). Inasmuch as **1** has a Nb^V, d^0 centre, we can eliminate ligand-field or MLCT transitions from consideration.[18] Irradiation in the vicinity of the low-energy absorption band gives rise to a luminescence spectrum (Fig. 1) with max 502 nm. If this emission is monitored at 502 nm, the excitation profile (Fig. 1) exhibits moderate structure and a maximum at 490 nm. The use of fluorescein actinometry[19] allows the determination of an emission quantum yield of 0.012 at 25 °C. Interestingly, however, the emission quantum yield shows clear evidence of a temperature dependence, rising smoothly to 0.092 at 173 K. This indicates the operation of a thermally activated process on the excited state potential surface, such that **1*** must overcome a barrier to reach a non-emissive conformation. Compound **2** exhibits similar behaviour (luminescence emission and excitation maxima at 503 and 490 nm), but the dependence on temperature is much less pronounced; the quantum yield for emission varies only from 0.008 to 0.018 over the same temperature range. This strongly suggests that the excited state is largely ligand centred, although we cannot dismiss the possibility of some LMCT character.[20]

The emission described above exhibits prompt decay in benzene solution. In an effort to probe for effects due to torsional motions, the emission of **1** was studied in benzene–Nujol mixtures in which the Nujol content ranged up to 75% by volume. The emission exhibited biexponential decay kinetics, and the intensity data from samples in pure benzene were fit with lifetimes of 0.68 ± 0.20 ns and 2.94 ± 0.40 ns. The first of these increases to 1.3 ± 0.2 ns, while the second increases to 5.75 ± 1.2 ns when the Nujol content is increased to 75% by volume. The key point is that **1** exhibits clear evidence of biexponential decay. We have determined the fraction of light arising from the two emissive states, and that of the long-lived state is plotted *vs.* Nujol content in Fig. 2. The fraction arising from the short-lived state (not shown) increases with increasing viscosity, while the fraction of emitted light arising from the long-lived state decreases with increasing solvent viscosity. This suggests that there are thermal barriers to conversion of the first state into the second *and* conversion of the second state into a dark state, consistent with the operation of a torsional process involving the phenyl groups.[13*b*,16,21,22]

Compound **1** exhibits photophysics similar to those of tetraphenylethylene (TPE), which has been studied in several laboratories.[2–8,16] The results suggest that TPE is excited to a vertical state (^{1}v*) which is probably diradicaloid in nature. This undergoes a conformational change to the relaxed state ^{1}r*, which is the minimum energy diradicaloid species. The third excited species (^{1}p*) exhibits zwitterionic character and orthogonal Ph_2C termini, and the conversion of ^{1}r* to ^{1}p* has a thermal barrier arising from an avoided crossing between the

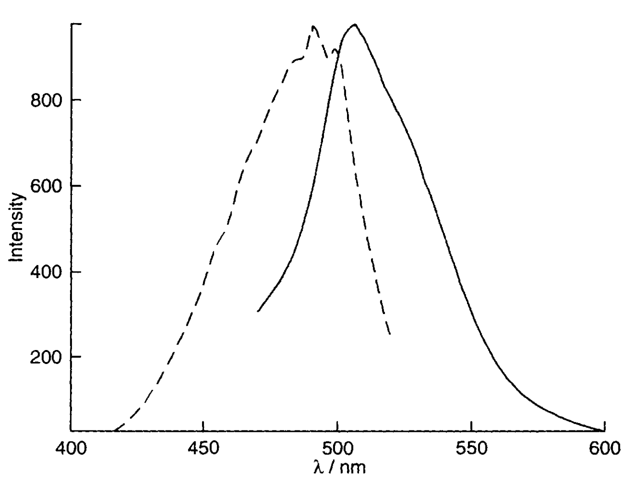


Fig. 1 Emission (solid line) and excitation (dashed line) spectra for **1** (0.28 mmol dm^{-3}) in toluene solution. Intensity units are arbitrary.

diradicaloid S_1 and zwitterion S_2 excited states. The overall sequence of states is depicted in eqn. (2); bear in mind that ${}^1v^*$

$$\mathrm{TPE} \xrightarrow{h\nu} {}^1v^* \xrightarrow{\Delta} {}^1r^* \rightleftarrows {}^1p^* \qquad (2)$$

is emissive, ${}^1p^*$ is dark, and ${}^1r^*$ exhibits prompt and delayed emission due to its equilibration with ${}^1p^*$. The actual geometry of ${}^1r^*$ or the conformational changes involved in the ${}^1v^*$ to ${}^1r^*$ conversion are not fully understood. Work by Schultz and Fox involves the study of tethered cyclophanylidenes, TPE models in which the *meta* positions of geminal phenyl groups are linked by hydrocarbon chains of variable length.[10] These studies show that the emission depends on the length of the linking chain, suggesting that phenyl torsion makes a significant contribution to the torsional modes interconverting the excited species.

As a means of studying the torsional modes involved in the ketene complexes, we utilized the potential for *E–Z* isomerization in **2**. As noted above, the thermal process is slow in benzene solution, so we generated the *E* isomer for photochemical studies, Indeed, we find that prolonged irradiation into the excitation band of *E*-**2** (using either a broad spectrum sun lamp or a 5 W argon laser with a line at 488 nm) gives *no* isomerization to the known *Z* isomer. This indicates that alkene twisting is not the cause of the excited-state thermal barriers noted above, and suggests that phenyl torsion is also an important contributor to the dynamics of the ketene complexes **1** and **2**.

The emission for **1** is reminiscent of that of TPE, and the small Stokes shift for **1** suggests that the emission occurs in part from an excited state that has undergone little structural change (relative to the ground state); this would involve one phenyl ring with small dihedral angle (relative to the C=C) and one nearly orthogonal to the equatorial plane containing the C=C bond.[23] By analogy with the cyclophanylidenes,[10] we propose that the excited state relaxes to a conformation in which this phenyl dihedral angle diminishes. Another torsional mode then intervenes, and this mode does not involve significant ketene C–C torsion or isomerization of the ketene ligand to the η^1-O binding mode; either would lead to isomerization to the *Z* isomer. We have provided voltammetric and EPR evidence for the intermediacy of a complex in which the Nb–O bond cleaves and the ketene moiety rotates about the Nb–C bond to give a transient with presumed diradical character.[24] This would retain the C=C geometry while providing another torsional mode for relaxation, and it is formally analogous to a torsional mode involving a second alkene substituent (the metal centre). More information is required to develop a detailed picture of the excited-state potential surface for the ketene complexes, but the present study shows that the bent ketene ligand exhibits electronic properties and photophysical behaviour consistent with the arylalkene bonding picture; it also indicates that thermal deactivation pathways need not involve alkene rotation, consistent with a mechanism involving aryl torsion.

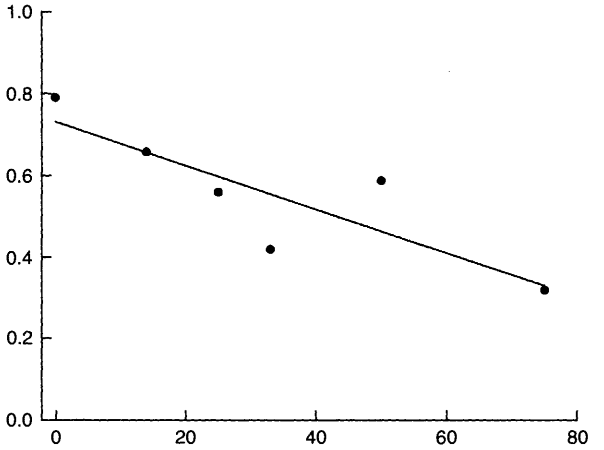


Fig. 2 Fractions of emitted light the long-lived state of **1** as a function of Nujol content in Nujol–benzene mixtures

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