Note Added in Proof. The "hydrate" of nitrone **7** has been shown to be 2-methyl-2-(hydroxyamine)propyl hexanoate.

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On the "Variation of Fluorescence Quantum Efficiency with Selective Population of Vibrational Levels" in Chemiluminescent Electron-Transfer Reactions

Sir:

A recent paper by Keszthelyi,[1] which deals with a supposed comparison between the fluorescence quantum yields of thianthrene when populated by optical excitation or cation-anion annihilation, contains serious errors which cast considerable doubt upon his conclusions.

Basically, the author is talking about what is normally referred to as a wavelength effect in which the photochemistry and/or photophysics of an excited molecule may depend on the initial level of excitation. This is certainly known and understandable when one is dealing with different electronic states but is not expected in the lower vibrational levels of the lowest excited singlet state. In general, vibrational relaxation in S_1 (ca. 10^{12} sec^{-1}) is fast compared to intersystem crossing for molecules which fluoresce and this is to be expected for a molecule such as thianthrene which has τ_F of ca. 30 nsec. A significant variation in Φ_F across the lowest energy absorption band would be unusual. On the other hand, wavelength effects can occur when the excited state lifetime is comparable to vibrational state lifetimes.[2]

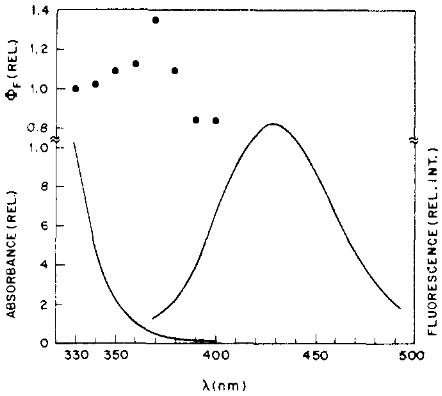

Figure 1. The absorption tail of thianthrene (ca. 10^{-3} *M*) in acetonitrile and the fluorescence spectrum (corrected) excited at 320 nm. The upper left part of the figure gives the relative quantum yields of fluorescence, measured at the maximum (428 nm), for solutions with optical density <0.1 (to avoid errors caused by differing absorption depths).

The author has not distinguished between the onset of absorption (the 0–0 band of the first transition) and the wavelength of maximum absorption intensity which frequently involves absorption to a higher lying state. This is the case for thianthrene where the strong band, peaking at 4.8 eV, has a long tail extending out nearly to the visible (see Figure 1). Thus the first transition is only weakly allowed, necessitating a long-lived excited state and accounting for the low fluorescence yield. This point has been discussed briefly by Bonnier and Jardon.[3] Their results (Φ_F = 3.6%, $\tau_F = 3 \times 10^{-8}$ sec) suggest a natural lifetime of about 1 μsec, indicating a very weak transition. The absorption band related to the fluorescence appears to be hidden under the tail of the intense band and thus there is really no large Stokes shift. Further, there is confusion regarding the 0–0 band of the fluorescence (or its onset) and λ_{max}; the former, not the latter, represents the energy of the excited state in question.

The question of a wavelength effect on the fluorescence of thianthrene can be decided by simply measuring the relative values of Φ_F as a function of excitation wavelength. We have done this experiment and found no evidence for any meaningful variation in Φ_F in the absorption tail. We believe that our experimental error is certainly less than 50% and this is sufficiently accurate for comparison with the enormous factors of 2, 10, 50, and 1000 reported by Keszthelyi. The absorption and fluorescence (corrected) spectra are shown in Figure 1 which also includes Φ_F. The errors are as large as they are because of the very weak absorbance of the solution in the region of the long tail into the visible. It is also quite possible that a trace impurity could be responsible for the observed deviation of the quantum yield.

The experimental results given by Keszthelyi do not support his conclusions in any substantive manner and the following points are noteworthy. (1) The luminescence intensity observed when DPA is present is enormously greater than that for thianthrene itself. The two fluorescence spectra overlap, and the measurement does not and, indeed, cannot distinguish which species is the emitter. Note that the fluorescence yield of DPA (~1) is more than 25 times that of TH. (2) The oxidation potential of DPA in CH_3CN (1.3 V vs. SCE) is so little above TH that it would not be possible to oxidize the latter without involving the former. Thus the reaction of DPA^- with DPA^+ can compete with the DPA^- TH^+ reaction. The same conclusion results from a consideration of data for DMF solutions given recently by Keszthelyi, Tachikawa, and Bard.[4] (3) The triplet level of TH (~480 nm, 2.6 eV)[4] is considerably above that of DPA (ca. 1.7–1.8 eV). Thus any triplets produced by the reaction would end up as $^3DPA^*$ which could undergo triplet–triplet annihilation, producing $^1DPA^*$. This cannot be the sole route, because of the absence of a significant magnetic field effect, but it could account for perhaps 35% of the intensity.

The results obtained with PPD and PPO are less clear as we do not know anything about the triplets in these systems but they may well lie below TH and (3) may apply. The reduction of phenanthrene is close to the solvent-electrolyte background level and the anion is not stable.

To sum up, the author has presented a hypothesis which is unsubstantiated by the data selected to support it. The basic phenomenon of a wavelength effect in fluorescence quantum yields is not discussed correctly in terms of existing knowledge and our experiment indicates that it is not a significant factor.

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A Definitive Example of Cis Chloropalladation. The Structure of Chloro(2,5-dithiahexane)-{1-(1,4-di-*tert*-butyl-4-chloro)butadienyl}palladium

Sir:

We report the preparation and structure of a complex derived from the $PdCl_2$ induced dimerization of *tert*-butylacetylene, which has several novel features and which also shows that a cis chloropalladation of the acetylene occurs in the first step.

The stereochemistry and mechanism of the addition of PdCl to mono- and diolefins and acetylenes are the subject of considerable controversy. For monoolefins Henry[1] has shown that the $Pd_2Cl_6^{2-}$ catalyzed exchange of chloride between vinylic chlorides and LiCl in acetic acid occurs nonstereospecifically and has suggested that cis chloropalladation is more important than trans chloropalladation in the initial step. *Both* stereospecific cis[2] and stereospecific trans[3] chloropalladation of diolefins in aprotic solvents have been reported, and Yukawa and Tsutsumi[4] have described the trans addition of Pd–Cl to the acetylenes $PhC{\equiv}CCH_2NMe_2$ and $HC{\equiv}CCMe_2NMe_2$ in methanol in the presence of LiCl.

It has been proposed that the oligomerization of acetylenes with $PdCl_2(PhCN)_2$ in aprotic solvents (typically benzene or dichloromethane) occurs in a stepwise manner, the first, rate determining, step of which is a cis chloropalladation of the coordinated acetylene.[5] In order to study the mechanism further, the reaction of the hindered *tert*-butylacetylene (**1**) was examined in detail. $PdCl_2(PhCN)_2$, in solvents such as C_6H_6, CH_2Cl_2, or $CHCl_3$ at 20°, has recently been shown to react with **1** to give the interconverting isomers **2a** and **2b**.[6] A kinetic study of the formation reaction by NMR at −20° in $CDCl_3$[7] showed complicated behavior owing to the existence of a preequilibrium involving a metal π-acetylene complex,[8] but a plot of log [**1**] vs. time gave a straight line up to the point where 3 equiv of **1** per Pd had been consumed; thereafter the rate slowed down by a factor of ca. 10 and the formation of **2** began to be detected.

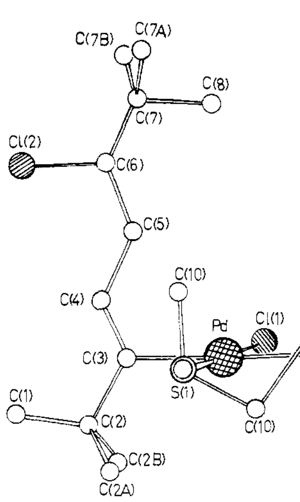
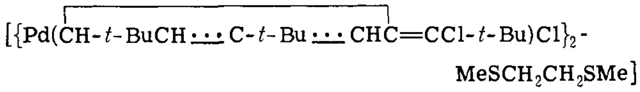


Figure 1. The structure of chloro(2,5-dithiahexane){1-(1,4-di-*tert*-butyl-4-chloro)butadienyl}palladium (**3**). Bond lengths (esd's in parentheses) are: Pd–Cl(1), 2.333 (7); Pd–S(1), 2.268 (7); Pd–S(2), 2.400 (7); Pd–C(3), 2.06 (2); C(3)–C(4), 1.31 (3); C(4)–C(5), 1.46 (3); C(5)–C(6), 1.36 (3) Å. Bond angles are: S(1)PdS(2), 88°; S(1)PdC(3), 90°; S(2)PdCl(1), 90°; Cl(1)PdC(3), 91°; PdC(3)C(4), 118°; C(3)C(4)C(5), 125°; C(4)C(5)C(6), 127°; C(2)C(3)Pd, 118°; C(2)C(3)C(4), 125°; C(5)C(6)Cl(2), 117°; Cl(2)C(6)C(7), 116°; C(5)C(6)C(7), 127°.

The reaction was repeated on a preparative scale in toluene at −10°. After 30 min, the solution was divided into two equal portions. The one was allowed to stand for 6 hr at 20°; after addition of 2,5-dithiahexane an 86% isolated yield of the dithiahexane adduct of **2b**



$$[\{\mathrm{Pd}(\mathrm{CH}\text{-}t\text{-}\mathrm{BuCH}\cdots\mathrm{C}\text{-}t\text{-}\mathrm{Bu}\cdots\mathrm{CHC}{=}\mathrm{CCl}\text{-}t\text{-}\mathrm{Bu})\mathrm{Cl}\}_2\text{-}\mathrm{MeSCH_2CH_2SMe}]$$

was obtained. The other portion was treated with 2,5-dithiahexane immediately and gave a 60% isolated yield of a complex (**3**) which was shown by analysis, molecular weight determination, and ^1H and ^{13}C NMR and ir spectroscopy to be $[Pd\{C\text{-}t\text{-}Bu{=}CHCH{=}CCl\text{-}t\text{-}Bu\}Cl\{MeSCH_2CH_2SMe\}]$. This was confirmed by an X-ray crystal structure determination: crystal data, $C_{16}H_{30}Cl_2PdS_2$; mol wt, 463.8; crystals are trigonal with $a = 25.62$, $c = 18.32$ Å (hexagonal setting); space group $R\bar{3}$; $Z = 18$. The structural analysis was based on Fourier and least-squares analysis of 1306 reflections which were observed using a Stoe STADI 2 diffractometer (Mo Kα radiation) having $F^2 \geq 3\sigma(F^2)$. R has converged to 0.070.

The significant features of the structure are shown (Figure 1). The Pd is square planar, two (cis) coordination sites are occupied by the two S's of the dithiahexane, one by a terminal Cl, and the remaining one by the σ-butadienyl ligand. It is clear that two acetylenes have been linked tail-to-tail and that both have reacted in a cis manner.

Although this is the first case where a dienylpalladium complex has been isolated, the intermediacy of such complexes had been predicted in previous discussions of the general mechanism of palladium(II) induced acetylene trimerization,[5] in which the first step was proposed to be a cis chloropalladation and the second a cis vinylpalladation of the coordinated acetylene. Scheme I shows the suggested mechanism for reaction of **1**. Since the kinetic data show that three molecules of **1** are consumed in the first stages, we presume that the intermediate (**4**) has the same σ-butadienyl ligand as **3** but that an additional acetylene is coordinated to the metal. Steric effects can be expected to slow