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Photosensitization of the Norbornadiene to Quadricyclene Rearrangement by an Electronically-Excited Copper(I) Compound

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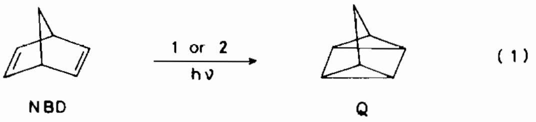
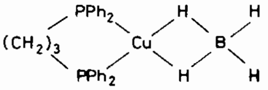
During a recent investigation of the spectral and photochemical properties of a series of copper(I)–phosphine compounds [1], we observed that $Cu(PPh_3)_2BH_4$ (*1*) and $Cu(PPh_2Me)_3BH_4$ (*2*) are effective photosensitizers for the energy-storing valence isomerization of norbornadiene (NBD) to quadricyclene (Q), reaction 1. Based upon several lines of indirect evidence, it was proposed that sensitization results from a bimolecular interaction (*e.g.* energy transfer) of the photoexcited copper(I) compound with a NBD molecule. Because this type of mechanism was unprecedented for copper(I)-sensitized photoreactions of olefins, we have extended our study of reaction 1 to include Cu(prophos)BH_4 (*3*, prophos is 1,3-bis(diphenylphosphino)propane). Although belonging to the same general class of compounds as *1* and *2*, *3* displays a substantially longer-lived emission in room-temperature fluid solution. Most importantly, we find that this emission can be quenched by NBD. Consequently, it has proven possible to monitor the excited-state kinetic behavior of *3* under conditions which result in the production of Q. Herein we report the first *direct* evidence that an electronic excited state of a copper(I) compound participates in the sensitized photoreaction of an olefin.





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Analytically pure *3* was prepared by a procedure similar to that reported for [1,2-bis(diphenylphosphino)ethane] tetrahydroboratecopper [2]. Absorption, emission, and lifetime measurements, photolyses, and product analyses were performed using equipment and techniques described previously [1]. Sample solutions were deaerated by bubbling with nitrogen prior to all spectral and photochemical runs.

The absorption spectrum of *3* in cyclohexane contains a maximum at 259 nm and a shoulder at ~300 nm. Excitation at 313 nm produces a broad, rather structureless emission with a maximum at 510 nm and a decay time, τ^0, of 4.2 μsec at 25 °C. Addition of NBD has no discernible effect upon the absorption spectrum, thereby discounting the formation of a ground state Cu(prophos)BH_4–NBD complex. The emissive excited state, on the other hand, is quenched by the diene. Quenching data obtained from lifetime and steady-state intensity measurements obey the usual Stern–Volmer relationship given by eqn. 2, where I^0 and τ^0 denote the emission

$$\frac{I^0}{I} = \frac{\tau^0}{\tau} = 1 + K_{sv}[NBD] \tag{2}$$

intensity and lifetime, respectively, of *3* in the absence of NBD, I and τ represent the corresponding quantities in the presence of the diene, and K_{sv} is the Stern–Volmer quenching constant. As shown in Fig. 1, plots of I^0/I and τ^0/τ *vs.* [NBD] are linear with a

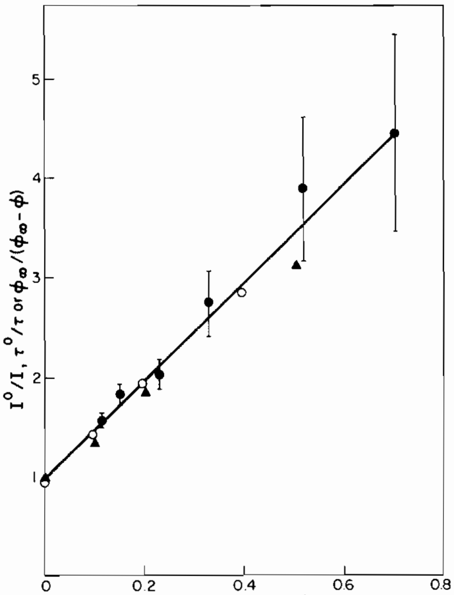

Fig. 1. Stern–Volmer plots for processes involving Cu(prophos)BH_4: emission intensity quenching (▲), emission lifetime quenching (○), sensitized production of Q (●). Error lines for the sensitization data represent standard deviations.

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common slope. Such behavior establishes that NBD quenches the emissive state via a dynamic, collisional process [3].

Benzene solutions containing *3* and NBD produce Q when irradiated at 313 nm. The quantum efficiency, ϕ, of this process obeys Stern–Volmer kinetics; thus a plot of ϕ^{-1} *vs.* $[\mathrm{NBD}]^{-1}$ is linear and yields a limiting efficiency, ϕ_∞, of 0.88 ± 0.06 at high diene concentrations. Replotting the data as $\phi_\infty/(\phi_\infty - \phi)$ *vs.* [NBD] allows a direct comparison of the sensitization, lifetime, and intensity results. As seen in the Figure, the three sets of measurements fall on a *single* straight line with a slope, K_{sv}, of 5.0 ± 0.2 L mol^{-1}.

The emission spectrum and lifetime are clearly properties of an electronic excited state of *3*. Hence the direct correlation between emission quenching by NBD and sensitized production of Q strongly indicates that the latter process also involves an excited state of the copper(I) compound. The simplest situation would be one in which emission and sensitization originate from the same excited state. Alternatively, the two processes could occur from different excited states that are kinetically coupled (*e.g.* exist in steady-state equilibrium) [4]. Additional studies are underway in an attempt to differentiate between these one- and two-state schemes.

Acknowledgements

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