4 appeared as an additional product when **2** was added to the buffer containing either intact or boiled coral acetone powder.[11] Thus, constituents of the coral mediate formation of cyclopropyl fatty acid **4** from allene oxide **2**.

Prostaglandin A_2 isolated from *P. homomalla* contains 3–15% of the unusual 5,6-trans double bond isomer **10**.[12,13] The origin of **10** is an intriguing biochemical problem in that 5,6-*trans*-arachidonic acid has not been found in the coral.[14] However, 5,6-*cis*-arachidonic acid could give rise to 5,6-*trans*-prostaglandin A_2 by isomerization at a later step. Solvolysis of allene oxide **2** involves heterolytic cleavage of the C8–oxygen bond to yield a carbocation (Scheme I), which if correctly constrained can delocalize over the 5,6-double bond and give trans orientation of substituents on the resulting cyclopropyl ring. Hydrolysis of the cyclopropylcarbinyl cation would give **4**. However, if the lifetime of the cation is sufficient, rotation about the 5,6-bond would occur, and a 5,6-trans double bond could arise by reopening of the cyclopropyl ring.[15] In effect, cyclopropyl fatty acid **4** may be solvolytic trapping evidence for the existence of a cyclopropylcarbinyl cation intermediate in the pathway to 5,6-*trans*-prostaglandins in the coral.

Acknowledgment. The cooperation of the Department of Development & Natural Resources of the Cayman Islands in collection of samples of *P. homomalla* is gratefully acknowledged. We thank Christiana D. Ingram for technical assistance. Research was supported by Grants DK-35275 and ES-07028 from the U.S. Public Health Service.

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(11) Taking the HPLC peak areas at 205 nm as an approximate quantitation of the allene oxide-derived products, the relative proportions were as follows: (a) in buffer only, γ-ketol **7** ~0.2, cyclopropyl fatty acid **4** not detected (<0.01), α-ketol **5** ~10, and cyclopentenone **6** ~1. (b) In the presence of coral, the relative proportions were ~0.4, ~1, ~10, ~1, respectively. Hydrolysis in the presence of coral gave a mixture of 11*Z* and 11*E* isomers of α-ketol.

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Dynamic Quenching of the Metal-to-Ligand Charge-Transfer Excited State of Cu_4I_4(pyridine)$_4$. Exciplex Formation and Self-Quenching

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Received March 6, 1989

Recently, it has been demonstrated that the lowest lying, triplet metal-to-ligand charge-transfer state (MLCT*) of the copper(I) complex $Cu(dmp)_2^+$ (dmp = 2,9-dimethyl-1,10-phenanthroline) is quenched by various Lewis bases in solution.[1,2] The mechanism proposed by McMillin[1a] involves association between the (formally) Cu(II) center of the MLCT* and the two-electron donor to form a shorter lived, nonemissive five-coordinate exciplex. Another Cu(I) complex shown to be luminescent in ambient temperature solution is the tetranuclear cluster $Cu_4I_4py_4$ (I, py = pyridine), which displays emissions from two remarkably uncoupled states, a MLCT* (λ_{max} = 490 nm, τ = 0.45 μs) and a lower energy metal cluster centered state (MCC*) (λ_{max} = 690 nm, τ = 10.7 μs).[3] Described herein is the demonstration that the MLCT*, *but not the MCC**, of I is subject to analogous dynamic quenching by Lewis bases. Also described is an unusual example of self-quenching of this cluster's MLCT emission which we attribute to bimolecular energy transfer from the higher energy MLCT* of one I to the MCC* of another I. These observations are further manifestations of the remarkably uncoupled nature of these two states.[3]

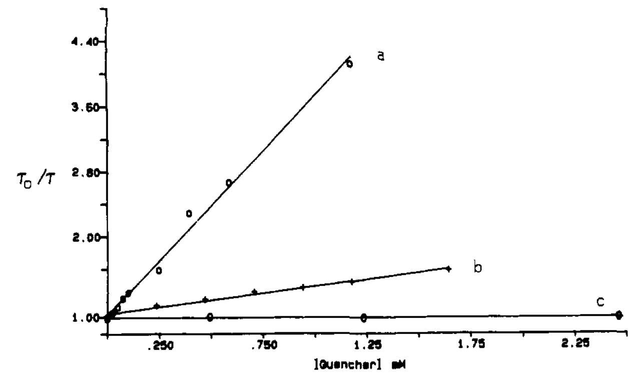

Figure 1. Stern–Volmer plots of the dependence of τ (MLCT) for $Cu_4I_4py_4$ on added quencher concentration in benzene solution (21 ± 1 °C). Quenchers are (a) pyridine, (b) 2,6-dimethylpyridine, and (c) 2,6-di-*tert*-butylpyridine.

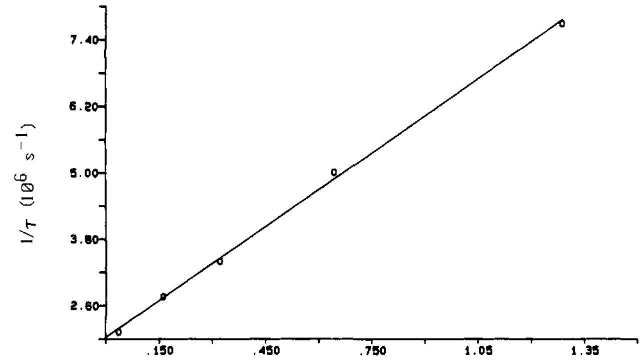

Figure 2. Plot of τ^{-1} (MLCT*) vs [$Cu_4I_4py_4$] in benzene solution (21 ± 1 °C).

Addition of pyridine to a $Cu_4I_4py_4$ solution in dry, deaerated benzene led to systematic decreases in the MLCT* emission lifetime,[4,5] but the MCC* lifetime remained invariant within experimental error. Figure 1a depicts the Stern–Volmer plot[6] of τ_0/τ vs [py] (where τ_0 is MLCT* lifetime, 0.45 μs, in the absence of added quencher). The plot is linear with an intercept of 1.0 ± 0.06 and a slope (K_{SV}) of 270 ± 10 M^{-1}. Given that $K_{SV} = k_q\tau_0$, the bimolecular quenching constant k_q equals 5.9 ± 0.5 × 10^9 M^{-1} s^{-1}. Energy transfer from the MLCT* to free pyridine

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(4) (a) Emission lifetimes at 21 ± 1 °C were measured by using an apparatus based on a Quanta-Ray DCR-1A Nd:YAG pulse laser with harmonic generator operating at 355 nm. The emission was monitored at right angles at 510 (MLCT) or 690 (MCC) nm with an RCA 8852 or EMI 9816A PMT through a Spex double monochromator. The PMT signal was processed by a Tektronix 7912AD transient digitizer and a Tektronix 4052 or Zenith ZF-158-24 microcomputer.[4b] (b) Weber, W.; DiBenedetto, J.; Offen, H.; van Eldik, R.; Ford, P. C. *Inorg. Chem.* **1984**, *23*, 2033–2038.

(5) Benzene (Burdick and Jackson high purity grade) was dried over CaH_2 and distilled under N_2 before use. Pyridine (Fisher), 2,6-dimethylpyridine (Aldrich), and 2,4-di-*tert*-butylpyridine (Aldrich) were dried over KOH pellets and distilled under N_2. All solutions and quenchers were deaerated by bubbling with dinitrogen.

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can be ruled out since the pyridine lowest lying triplet state (29 650 cm^{-1})[7] is energetically too high. Thus, exciplex formation as described above would appear to be an attractive alternative mechanism for MLCT* quenching. This proposal draws support from the effects of pyridine substituents in the sterically significant ortho position.[8] Plots of τ_0/τ vs [2,6-dimethylpyridine] and [2,6-di-*tert*-butylpyridine] (Figure 1 (parts b and c, respectively)) depict the marked decreases in quenching rates with increases in substituent steric bulk. The corresponding k_q values are $9.5 \pm 0.9 \times 10^8$ and $\leq 10^6$ M^{-1} s^{-1}.

During the quenching studies, the MLCT emission lifetime also proved to be sensitive to the concentration of I, but the MCC emission lifetime was invariant over the same range of conditions. Figure 2 demonstrates the linear dependence between $[Cu_4I_4(py)_4]$ and the reciprocal of the lifetime (τ^{-1}). The slope of this plot gives the self-quenching rate constant with $k_q{}^s = 4.5 \pm 0.4 \times 10^9$ M^{-1} s^{-1} and an intercept ($\tau_0{}^{-1}$) of $2.2 \pm 0.2 \times 10^6$ s^{-1} from which was calculated $\tau_0 = 0.45 \pm 0.04$ μs.

One potential explanation of the self-quenching behavior is that this phenomenon is a reflection of quenching by pyridine liberated by dissociation from I, e.g.,

$$\underset{\mathrm{I}}{\mathrm{Cu_4I_4(py)_4}} \xrightleftharpoons{K_1} \underset{\mathrm{II}}{\mathrm{Cu_4I_4(py)_3}} + \mathrm{py} \qquad (1)$$

For this mechanism to be valid, a K_1 value about 3×10^{-3} M would be required by the data in Figure 2 and the k_q for pyridine (5.9×10^9 M^{-1} s^{-1}). This would lead to [II]/[I] ratios ranging from 83 to 3.1 over the concentrations used in Figure 2, a proposal inconsistent with linear Beer's law plots (e.g., Abs(360 nm) vs [I]) over this concentration range.[9] Thus, since the self-quenching is exclusive to the higher energy MLCT state, we propose that the self-quenching mechanism involves bimolecular energy transfer as illustrated in eq 2.[10] Unfortunately, detection of the enhanced MCC* emission thereby expected is precluded by the small fraction of the total excited state population represented by the MLCT* under these conditions.

$$\mathrm{I^*(MLCT^*) + I \rightarrow I + I^*(MCC^*)} \qquad (2)$$

In summary, two different quenching mechanisms are reported here for the metal-to-ligand charge-transfer excited state of the copper(I) cluster $Cu_4I_4py_4$ in benzene. Quenching by the Lewis base pyridine appears to be operating by complex formation with the Cu(II) center of the MLCT* as previously described for charge-transfer excited states of the mononuclear Cu(I) complex $Cu(dmp)_2{}^+$.[1,2] A competitive mechanism is quenching of the MLCT* by another I, a process proposed to be facile owing to the presence of the MCC* at a lower energy in the manifold of electronic states. In contrast, the MCC emission is not quenched by either mechanism. That the higher energy MLCT* can be quenched by bimolecular pathways, especially the self-quenching mechanism, in competition with unimolecular internal conversion to the MCC state represents a particularly dramatic demonstration of the poor coupling between these two types of excited states in this cluster.

Acknowledgment. This work was supported by Grant No. CHE87-22561 from the National Science Foundation.

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(7) Murov, S. L. *Handbook of Photochemistry*; Marcel Dekker, Inc.: New York, 1973; pp 20 and 35.

(8) The observation that quenching also occurs with Lewis bases such as methanol and tetrahydrofuran is consistent with the proposed exciplex mechanism.

(9) (a) Linear Beer's law behavior would also preclude significant contributions from equilibria between the Cu_4 cluster and other copper species of lower nuclearity. These data would not eliminate an equilibrium between the step and cube forms of $Cu_4I_4py_4$.[9b] (b) That the MLCT* and MCC* emissions arise solely from the cube form of $Cu_4I_4py_4$ has been demonstrated by solid-state emission spectroscopy. Both emissions are still present in samples which have been shown by crystallography to be *closo*-$Cu_4I_4py_4$.[9c] (c) Raston, C. L.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1976**, 2153.

(10) Qualitative studies demonstrate that biphenyl with a triplet state energy of 23 000 cm^{-1}, which is close to the 0–0 energy of the MLCT state, quenches the MLCT emission lifetime but not that of the MCC state.

Preparation, Crystal Structures, and Spectroscopic Characterization of Diaminochalcogenophosphonium Cations[1]

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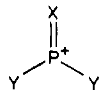
Received January 27, 1989

We view the tricoordinate phosphonium electronic environment **1** (isovalent to the carbon center in ethene) as a fundamental key to the development of group 15 chemistry. However, examples of **1** are rare, and characterization is incomplete. Phosphoryl chloride is postulated to autoionize giving **1a**,[4] and the nitrogen **1b**,[5] carbon **1c**,[6] and thio **1d**[4b,7] analogues of **1** have recently been identified spectroscopically in solution. Alternative covalent structures involving phosphoryl–[4] and thiophosphoryl–Lewis acid adducts[8] have also been studied. Here we report attempts to investigate diaminothiophosphonium and tetraethyldiaminoselenophosphonium cations and reveal them to adopt dimeric ring structures **2** in the solid state. The derivatives of **2** represent the first examples of heterocyclic chalcogen–phosphorus cations. In addition, we present new spectroscopic evidence for the solution behavior of the chalcogenophosphonium systems.



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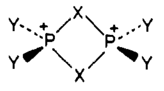

2

a, X = O; Y = Cl
b, X = NR; Y = NR_2
c, X = CR_2; Y = NR_2
d, X = S; Y = Ph, Y = NR_2
e, X = S; Y = NEt_2;
e′, Y = NMe_2
f, X = Se; Y = NEt_2

Reactions of Y_2XPCl (**e**, **e′**,[9] and **f**[10]) with $AlCl_3$ in CH_2Cl_2 at room temperature provided good yields (**e**, 86%; **e′**, 77%; **f**, 95%) of crystalline solids (**e**, **e′**, white; **f**, yellow) with the empirical formula $1AlCl_4{}^-$.[11] The ionic nature of these extremely air-

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(1) This work has been supported by grants from the Natural Sciences and Engineering Research Council of Canada (N.B.), the donors of the Petroleum Research Fund, administered by the American Chemical Society (N.B. and R.D.R.), the U.S. National Science Foundation's Chemical Instrumentation Program (R.D.R.) and Dalhousie University (N.B.).

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(3) Address correspondence regarding crystallography to this author.

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