agement, and to Dr. Katsuhiko Miyoshi and Dr. Ushio Sakaguchi for valuable discussions.

References and Notes

(1) Part 5 of Stereoselectivity in Ion-Pair Formation.[2]

(2) Part 4: T. Taura, H. Tamada, and H. Yoneda, *Inorg. Chem.*, 17, 3127 (1978).

(3) K. Ogino and U. Saito, *Bull. Chem. Soc. Jpn.*, **40**, 826 (1967).

(4) B. Norden, *Acta Chem. Scand.*, **26**, 111 (1972).

(5) H. Yoneda, K. Miyoshi, S. Suzuki, and T. Taura, *Bull. Chem. Soc. Jpn.*, **47**, 1661 (1974).

(6) H. Yoneda and T. Taura, *Chem. Lett.*, 63 (1977).

(7) T. Taura and H. Yoneda, *Chem. Lett.*, 71 (1977).

(8) T. Taura and H. Yoneda, *Inorg. Chem.*, 17, 1495 (1978).

(9) K. G. R. Pachler, *Z. Anal. Chem.*, **224**, 211 (1967).

(10) J. S. Mariano and V. N. S. Gil, *Mol. Phys.*, 17, 313 (1969).

(11) H. Ishizuka, T. Yamamoto, Y. Arata, and S. Fujiwara, *Bull. Chem. Soc. Jpn.*, **46**, 468 (1973).

(12) M. Kainosho and K. Ajisaka, *J. Am. Chem. Soc.*, **97**, 5630 (1975).

(13) L. Eberson, "The Chemistry of Carboxylic Acids and Esters", S. Patai, Ed., Wiley, New York, 1969, p 211.

(14) H. N. K. Rordam, *J. Chem. Soc.*, 2933 (1932).

(15) A. McKenzie, *J. Chem. Soc.*, 1196 (1912).

(16) W. L. F. Armarego and T. Kobayashi, *J. Chem. Soc. C*, 1635 (1969).

(17) H. Nohira, T. Kakegawa, M. Kurokawa, and N. Katsuta, presented at the 36th Annual Meeting of the Chemical Society of Japan, 1974, Abstract II, 3T22.

(18) K. G. R. Pachler, *Spectrochim. Acta*, **20**, 581 (1964).

(19) The CD spectrum upon addition of thiomalate was measured but this spectrum increased in magnitude with time because of the reaction between the complex ion and thiomalate. The CD change, which was measured soon after the preparation of the sample solution, was similar to these for the other monosubstituted succinates in shape and magnitude.

(20) The CD changes for Λ- and Δ-$[Co(en)_3]^{3+}$ were the same in magnitude within the limits of experimental errors in the cases of optically active malate, aspartate, chlorosuccinate, and bromosuccinate. Phenylsuccinate and methylsuccinate used were racemates.

(21) R. E. Cramer and R. L. Harris, *Inorg. Chem.*, **13**, 2208 (1974).

(22) (a) J. J. M. Rowe, J. Hinton, and K. L. Rowe, *Chem. Rev.*, **70**, 1 (1970); (b) J. R. Cavanaugh, *J. Am. Chem. Soc.*, **89**, 1558 (1967).

(23) The CD changes for Λ- and Δ-$[Co(en)_3]^{3+}$ were different from each other in the cases of optically active tartrate and *trans*-1,2-cyclohexanedicarboxylate. However, these difference were small in comparison with the differences between the meso and *dl* isomers. Therefore, this result was not discussed in this paper.

(24) The meso isomer of dimethylsuccinate was examined on the CD change. This dianion should behave like a corresponding meso dibromosuccinate dianion because of the repulsion between the two methyl groups. In fact, the CD change pattern was similar to that for the meso dibromosuccinate, that is, to that for a singly charged anion.

(25) Crystal structure studies have been shown that, in the solid state, *trans*-1,2-CHD acid exists in the diequatorial conformation (gauche conformation). However, the repulsion of two carboxyl groups should partially convert the conformation from diequatorial (gauche) to diaxial (trans) in going from the solid state to solution. See (a) E. Benedetti, P. Corradini, C. Pedone, and B. Post, *J. Am. Chem. Soc.*, **91**, 4072 (1969); (b) *ibid.*, **91**, 4075 (1969); (c) G. Montando and C. G. Overberger, *ibid.*, **91**, 753 (1969).

(26) J. F. J. Dippy, S. R. C. Hughes, and A. Rozanski, *J. Chem. Soc.*, 2492 (1959).

(27) L. D. Pettit and J. L. M. Swash, *J. Chem. Soc., Dalton Trans.*, 286 (1978).

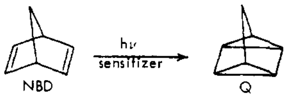
Photobehavior of Copper(I) Compounds. Role of Copper(I)–Phosphine Compounds in the Photosensitized Valence Isomerization of Norbornadiene

Paul A. Grutsch and Charles Kutal*

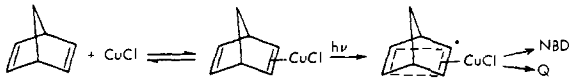
Contribution from the Department of Chemistry, University of Georgia, Athens, Georgia 30602. *Received September 11, 1978*

Abstract: The valence isomerization of norbornadiene to quadricyclene can be photosensitized with high quantum efficiency by certain copper(I)–phosphine compounds. Sensitization yields in the presence of $Cu(PPh_3)_2BH_4$ and $Cu(PPh_2Me)_3BH_4$ attain limiting values of 0.76 and 0.54, respectively, at high norbornadiene concentrations. In contrast, $Cu(diphos)BH_4$ (diphos is 1,2-bis(diphenylphosphino)ethane), which contains a bidentate phosphine ligand, is decidely less effective. The mechanism of sensitization by these copper(I)–phosphine compounds is fundamentally different from that exhibited by simple cuprous salts in that no ground-state coordination to the metal center occurs. A pathway involving the bimolecular interaction of the photoexcited Cu(I) compound with a ground-state norbornadiene molecule is better able to accommodate the available data. Electronic absorption and emission studies reveal some interesting differences between the spectral properties of effective vs. noneffective sensitizers.

Previous studies[1,2] from this laboratory have focused upon the use of transition-metal compounds to photosensitize the energy-storing valence isomerization of norbornadiene (NBD) to quadricyclene (Q) (eq 1). Particular attention has been afforded simple copper(I) salts, since their role as sensitizers in a wide variety of olefin photoreactions is well documented.[3,4] Thus we recently reported that cuprous chloride effectively sensitizes the production of Q via a pathway (eq 2) involving a photoactive ClCu-NBD complex.[5] Minimally, complex formation shifts the spectrum of the system to longer wavelengths and thereby enhances absorption of the irradiating light. Moreover, the possibility exists that the complex provides a sterically or electronically favorable path to Q which is inaccessible to the uncoordinated olefin.



(1)



(2)

Our quest for new classes of Cu(I) sensitizers led us to investigate the series $Cu(PPh_3)_2BH_4$, $Cu(PPh_2Me)_3BH_4$, and $Cu(diphos)BH_4$ (diphos is 1,2-bis(diphenylphosphino)ethane). Preliminary studies[6] revealed that the first two members efficiently sensitize the NBD to Q conversion but by a mechanism which appears to be fundamentally different from the complexation pathway noted above. This seminal finding, plus the observation of some intriguing structural and spectral characteristics, prompted us to examine the detailed behavior of these Cu(I) compounds. The results of our investigations are described in the present article.

Experimental Section

A. Reagents. Norbornadiene (Aldrich) was purified by passage through a glass column packed with 8-in. layers of alumina (80–200

0002-7863/79/1501-4228$01.00/0

mesh) and silica gel (60–200 mesh), followed by three successive distillations from potassium metal under a nitrogen atmosphere. Analytically pure samples of $Cu(PPh_3)_2BH_4$, $Cu(PPh_2Me)_3BH_4$, and $Cu(diphos)BH_4$ were prepared from CuCl and the appropriate phosphine by the general procedure of Lippard and Ucko.[7] Quinine bisulfate (NF grade from New York Quinine and Chemical Works) was recrystallized three times from ethanol. Spectral grade solvents were employed in all spectral and photochemical studies.

B. Spectral Measurements. Electronic absorption spectra were recorded on a Cary 15 spectrophotometer. Emission spectra were obtained on a Perkin-Elmer MPF-4 spectrofluorimeter equipped with a corrected spectra attachment. Lifetime determinations were performed on an Ortec time-resolved spectrometer whose output pulse duration is ~2 ns at half of the maximum intensity and ~5 ns at the one-tenth level. Samples were degassed by bubbling with nitrogen for 10 min prior to taking luminescence or lifetime measurements.

Emission quantum yields, ϕ_e, were determined by the following procedure. The absorbances of the sample and a standard, quinine bisulfate in 0.1 N H_2SO_4 ($\phi_e = 0.55$[8]), were matched at the excitation wavelength (313 nm). Corrected emission spectra were then measured and the data replotted on an energy scale. The areas, A, under the curves were determined with a planimeter. The emission yield can be calculated from the equation

$$\phi_{e,2} = \phi_{e,1}\left(\frac{A_2}{A_1}\right)\left(\frac{n_2^2}{n_1^2}\right) \qquad (3)$$

where n is refractive index[9] and the subscripts 1 and 2 denote the standard and sample, respectively. Errors in ϕ_e of 30–40% are possible owing to (1) the difficulty in accurately measuring the weak emission signals and (2) the unequal absorbance of the sample and standard at wavelengths other than 313 nm.

^{31}P NMR spectra were obtained on a JEOL PFT-100 spectrometer. Infrared spectra were run on a Perkin-Elmer 621 grating spectrometer.

C. Photochemical Studies. Nitrogen-purged benzene solutions containing NBD and sufficient sensitizer to absorb >99% of the incident light were irradiated in 1-cm quartz cells using a 450-W medium-pressure mercury-arc lamp mounted in a merry-go-round apparatus. The region centered at 313 nm was isolated using a combination of a Corning 7-54 filter and a circulating solution of 10^{-3} M K_2CrO_4–1% K_2CO_3.[10] Sample temperatures during irradiation typically were 30–31 °C. Light intensity was measured by ferrioxalate actinometry.[11]

Aliquots of the irradiated solutions were analyzed for NBD and Q by gas chromatography using a Varian 2700 gas chromatograph equipped with a flame ionization detector and containing either a 14 ft × 1/8 in. column packed with 5% SF-96/1% Apiezon L on Chromosorb W (60/80 mesh) or a 6 ft × 1/8 in. column packed with 1.5% OV-101 on Chromosorb G HP (80/100 mesh). The operating temperatures of the instrument follow: injector, 135–140 °C; detector, 295 °C; column, 85 °C (for SF-96) or 45–120 °C (for OV-101, temperature programmed with pre-, post-, and cooldown times of 2, 3, and 4 min, respectively). Flow rates of nitrogen carrier gas of 25–30 mL/min were employed. Percent conversion to Q was determined by comparing the gas chromatographic peak area of the irradiated sample with that of an unirradiated reference. Measurements taken at various times following irradiation reveal that the Q produced is thermally stable over a period of at least several hours. Routine control experiments indicate that 313-nm irradiation of NBD solutions in the absence of a sensitizer affords no Q; likewise, no thermal conversion could be detected.

Decomposition of triphenylphosphine was monitored by gas chromatography using a 6 ft × 1/8 in. stainless steel column packed with 3.5% OV-101 on Chromosorb G HP (80/100 mesh). The operating temperatures of the instrument follow: injector, 315 °C; detector, 320 °C; column, 250 °C. The flow rate of nitrogen carrier gas was 40 mL/min.

Results and Discussion

A. Structural Characteristics and Solution Behavior. Lippard et al. have determined the molecular geometry of $Cu(PPh_3)_2BH_4$ by single-crystal X-ray diffraction.[12,13] The compound crystallizes as monomeric units with structure I (Figure 1), which features the copper atom surrounded in a quasi-tetrahedral fashion by the P atoms of two triphenylphosphine molecules and two bridging H atoms from the tetrahydroborate group. This structural unit persists upon dissolving the compound in benzene or chloroform as evidenced by the qualitative similarity of the solid state and solution infrared spectra.[7] The absence of ligand dissociation in solution is confirmed by the excellent agreement between the calculated (603) and observed (580 in chloroform, 604 in benzene[14]) molecular weights.

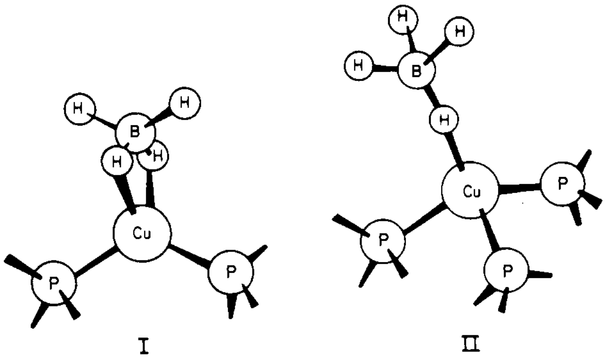
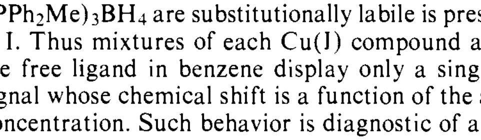


Figure 1. Two coordination environments found in $Cu(phosphine)_nBH_4$ compounds. Structure I occurs for $Cu(PPh_3)_2BH_4$ and $Cu(diphos)BH_4$ in solution and the solid state and for $Cu(PPh_2Me)_3BH_4$ in solution. Structure II obtains for $Cu(PPh_2Me)_3BH_4$ in the solid state.

While $Cu(diphos)BH_4$ has not been characterized by diffraction techniques, its solid state and solution infrared spectra are both consonant with structure I (Figure 1). Thus the bands assigned as B–H stretching and BH_2 deformation fall within the frequency regions suggested by Marks and Kolb[15] for bidentate BH_4^- coordination. Moreover, molecular weight data (calculated 477, observed 468[14]) indicate that the compound is undissociated in chloroform.

A recent X-ray diffraction study has revealed that $Cu(PPh_2Me)_3BH_4$ possesses structure II (Figure 1) in the solid state.[16] The copper atom resides in a distorted tetrahedral environment consisting of the P atoms of three PPh_2Me ligands and a single H atom from the tetrahydroborate group. This novel monodentate attachment of BH_4^- does not survive dissolution of the compound in benzene, however, as evidenced by the pronounced infrared spectral changes which attend this process.[16,17] In addition, the low observed molecular weight (calculated 679, observed 381 in benzene[16]) is indicative of extensive ligand dissociation. Both observations can be interpreted in terms of the equilibrium shown in eq 4, wherein a



$$(PPh_2Me)_3Cu{-}H{-}BH_3 \rightleftharpoons (PPh_2Me)_2Cu(\mu\text{-}H)_2BH_2 + PPh_2Me \qquad (4)$$

PPh_2Me group dissociates in solution and its coordination site is occupied by a second H atom from BH_4^-. A key consequence of this behavior is that *$Cu(PPh_2Me)_3BH_4$ exists predominantly as structure I under the conditions employed in the solution photochemical studies* (vide infra).

Evidence that the coordinated phosphines in $Cu(PPh_3)_2BH_4$ and $Cu(PPh_2Me)_3BH_4$ are substitutionally labile is presented in Table I. Thus mixtures of each Cu(I) compound and its respective free ligand in benzene display only a single ^{31}P NMR signal whose chemical shift is a function of the added ligand concentration. Such behavior is diagnostic of a rapid interchange between coordinated and uncoordinated phosphines.[18]

B. Absorption and Emission Spectra. Table II summarizes the salient absorption features of the compounds investigated in the present study.[19] The dominant band in the ultraviolet spectra of aryl-containing phosphines arises from the transfer

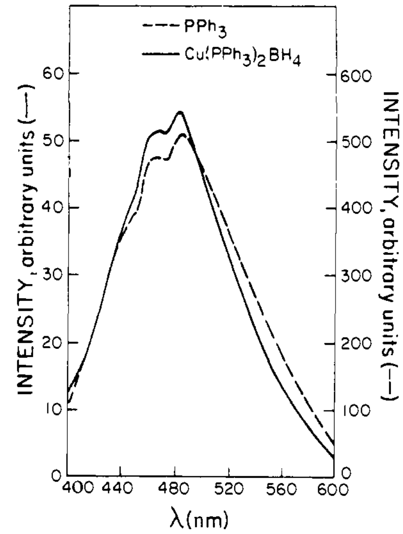


Figure 2. Emission spectra of $Cu(PPh_3)_2BH_4$ and PPh_3 in benzene at room temperature. Note different intensity scales.

Table I. ^{31}P NMR Data

sample	chemical shift[a]
$Cu(PPh_3)_2BH_4$	
$Cu(PPh_3)_2BH_4$ (0.04 M)	+2.2
PPh_3 (0.08 M)	+5.8
$Cu(PPh_3)_2BH_4$ (0.02 M) + PPh_3 (0.07 M)	+4.8
$Cu(PPh_3)_2BH_4$ (0.02 M) + NBD (0.27 M)	+2.2
$Cu(PPh_3)_2BH_4$ (0.02 M) + NBD (1.5 M)	+2.0
$Cu(PPh_2Me)_3BH_4$	
$Cu(PPh_2Me)_3BH_4$ (0.05 M)	+22.1
PPh_2Me (0.1 M)	+27.7
$Cu(PPh_2Me)_3BH_4$ (0.05 M) + PPh_2Me (0.1 M)	+24.1
$Cu(PPh_2Me)_3BH_4$ (0.05 M) + NBD (1 M)	+22.0

[a] Values in parts per million (ppm) relative to external 85% H_3PO_4.

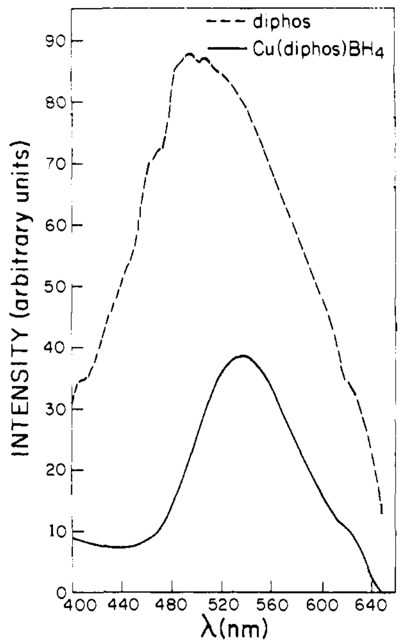


Figure 3. Emission spectra of $Cu(diphos)BH_4$ and diphos in benzene at room temperature.

Table II. Electronic Absorption Characteristics of Several Phosphines and Their Corresponding Cu(I) Compounds

compd	λ_{max}, nm; ϵ, L mol^{-1} cm^{-1} [a]
PPh_3	262; 1.06×10^4 ~271 (sh)
PPh_2Me	251; 8.8×10^3[b]
diphos	252; 1.83×10^4
$Cu(PPh_3)_2BH_4$	257; 1.70×10^4 ~271 (sh)
$Cu(PPh_2Me)_3BH_4$	250; 2.15×10^4
$Cu(diphos)BH_4$	265; 6.47×10^3 ~300 (sh)

[a] Spectra measured in cyclohexane which had been passed down an alumina column. [b] Owing to the air sensitivity of this compound, the reported extinction coefficient may be somewhat low.

of a lone-pair electron on phosphorus to an empty antibonding orbital of π origin centered on a phenyl ring.[20-22] Of the various assignments which have been suggested for this type of transition, the l-a_π designation of Kasha and Rawls seems most appropriate.[23] These workers noted that the phosphorus orbital, l, containing the lone pair can engage in π bonding with the attached aromatic groups, depending upon the twist angle between the axis of l and the axis of the adjacent carbon $2p_\pi$ orbital. While the importance of this π interaction is difficult to gauge, there is evidence that variations in the twist angle can affect the spectral properties of arylphosphines[22,24] (vide infra).

The slight shoulder in the spectrum of PPh_3 has been assigned as a π-π* transition localized on a phenyl ring.[20,21] Although this transition is not discernible in the spectra of PPh_2Me or diphos, it is presumably buried under the intense l-a_π band.

Upon coordination of a phosphine to copper, the energy levels of the ligand are affected to varying degrees. Minimally, the electron pair which resided in the l orbital on phosphorus becomes involved in σ bonding to the metal; thus the transfer of an electron from this σ-type orbital to a π-antibonding orbital centered on a phenyl ring is properly designated as a σ-a_π transition. Moreover, the π system in the phosphine molecule may be perturbed by interaction with appropriate metal d orbitals.

Some idea as to the importance of these effects can be ascertained from the spectral data in Table II. In comparing PPh_3 and $Cu(PPh_3)_2BH_4$, we note the following features: (1) The change in the orbital nature of the most intense transition from l-a_π (free ligand) to σ-a_π (coordinated ligand) causes a relatively minor shift in peak position. (2) The π-π* transition is not noticeably affected by coordination of the ligand. (3) The emitting levels in the two compounds are nearly isoenergetic (Figure 2). We infer from these results that the energies of the electronic states localized on PPh_3 are not significantly altered upon formation of $Cu(PPh_3)_2BH_4$.

A more complicated situation obtains for $Cu(PPh_2Me)_3BH_4$ in that it is extensively dissociated in solution (eq 4). Thus the observed absorption spectrum is, in actuality, a composite of those of the parent compound, $Cu(PPh_2Me)_2BH_4$, and PPh_2Me. Nonetheless, the marked similarity of this composite spectrum to that of pure PPh_2Me again suggests that coordination has only a slight effect upon the energy levels of the phosphine molecule.

In comparing diphos and $Cu(diphos)BH_4$, we encounter distinctly different behavior from that noted above. Thus one or more transitions (presumably σ-a_π) appear in the absorption spectrum of the Cu(I) compound at appreciably longer wavelengths than the l-a_π transition in the free ligand (Table II). Likewise the emission maximum of $Cu(diphos)BH_4$ is considerably red shifted from that of the ligand (Figure 3). Both observations indicate that the energies of the electronic states in diphos are strongly perturbed upon coordination of the ligand to copper.

A possible rationale for the distinctive spectral behavior of

Table III. Emission Yield and Lifetime Data[a]

compd	emission yield, ϕ_e	lifetime, ns
PPh_3	3.3×10^{-3}	<10
$Cu(PPh_3)_2BH_4$	3.4×10^{-4}	<10
diphos	8.6×10^{-4}	<10
$Cu(diphos)BH_4$	2.3×10^{-4}	130

[a] Measured in benzene at room temperature; for the lifetime determinations, the solvent was purified by photolysis in the presence of Cl_2 (D. I. Schuster, M. D. Goldstein, and P. Bane, *J. Am. Chem. Soc.*, **99**, 187 (1977)).

Table IV. Quantum Yields for the Sensitized Conversion of NBD to Q upon 313-nm Irradiation

data set	sensitizer	[NBD], M	ϕ_{sen}[a,b]
A	PPh_3	0.1	<0.01
B	PPh_2Me	0.1	<0.04
C	diphos	0.1	<0.01
D	$Cu(PPh_3)_2BH_4$	0.055	0.13 ± 0.01 (4 values)
E	$Cu(PPh_3)_2BH_4$	0.07	0.20 ± 0.03 (6 values)
F	$Cu(PPh_3)_2BH_4$	0.1	0.23 ± 0.05 (11 values)
G	$Cu(PPh_3)_2BH_4$[c]	0.1	0.22 (1 value)
H	$Cu(PPh_3)_2BH_4$[d]	0.1	0.17 (1 value)
I	$Cu(PPh_3)_2BH_4$	0.2	0.34 ± 0.09 (6 values)
J	$Cu(PPh_3)_2BH_4$	0.5	0.56 ± 0.12 (15 values)
K	$Cu(PPh_2Me)_3BH_4$	0.053	0.25 ± 0.07 (7 values)
L	$Cu(PPh_2Me)_3BH_4$	0.1	0.32 ± 0.05 (10 values)
M	$Cu(PPh_2Me)_3BH_4$	0.32	0.45 ± 0.03 (4 values)
N	$Cu(PPh_2Me)_3BH_4$	0.5	0.48 ± 0.03 (9 values)
O	$Cu(diphos)BH_4$	0.1	<0.01
P	$Cu(diphos)BH_4$	0.3	<0.03

[a] Values of ϕ_{sen} were determined at short (≤3 h) irradiation times. [b] Where quoted, error limits represent standard deviation of the mean. [c] Sample contained 9.6×10^{-4} M PPh_3. [d] Intensity of incident light was 4.8 times less than in other runs.

$Cu(diphos)BH_4$ is suggested by the observation that the energy of the l-a_π transition in arylphosphines is lowered by alkyl substitution at the ortho positions of the aromatic ring.[22,24] This effect was related to the magnitude of the twist angle about the phosphorus-phenyl bond which, in turn, was shown to depend upon the steric properties of the aryl group. In an analogous fashion, the steric constraint imposed by formation of the five-membered chelate ring in $Cu(diphos)BH_4$ may change the twist angle from its characteristic value in free diphos and thus be responsible for the shift of the absorption and emission spectra to lower energies. Furthermore, the splitting observed in the absorption spectrum of $Cu(diphos)BH_4$ suggests that the equivalence of the two phenyl groups attached to each phosphorus atom in diphos has been destroyed by coordination to the metal center.[25] Consequently, transitions to the antibonding orbitals of each aromatic ring can occur with different energies.[20] We are currently gathering additional structural and spectral data on related Cu(I)-phosphine compounds in hopes of testing these suggestions.

C. Emission Quantum Yields and Lifetimes. The observation of luminescence from Cu(I) compounds in room temperature fluid solution is, to our knowledge, quite rare. Accordingly, we are prompted to report our initial studies of the emission characteristics of $Cu(PPh_3)_2BH_4$, $Cu(diphos)BH_4$, and the respective free phosphine molecules. The actual spectra (Figures 2 and 3) have already been discussed, while the results of quantum yield and lifetime measurements are summarized in Table III.

A few points merit brief comment. Thus radiative decay is clearly a low-probability pathway for the excited states of these compounds. We find it especially interesting that the emission yields for PPh_3 and $Cu(PPh_3)_2BH_4$ differ by a factor of 10 despite the close similarity of the corresponding spectra. Coordination of PPh_3 to copper has evidently altered one or more of the rate constants for population or depopulation of the emitting state *without* appreciably perturbing its energy.

The emission lifetimes fall into two categories. Those of $Cu(PPh_3)_2BH_4$, PPh_3, and diphos are sufficiently short that we cannot accurately distinguish the luminescence signal from the excitation lamp profile. In contrast, the red-shifted emission of $Cu(diphos)BH_4$ is more than an order of magnitude longer lived.

D. Photochemical Studies. Quantum yields, ϕ_{sen}, for the sensitized conversion of norbornadiene to quadricyclene are compiled in Table IV. Quite clearly, compounds whose electronic or structural characteristics are superficially akin can differ considerably in their sensitization behavior. Thus, although PPh_3 and $Cu(PPh_3)_2BH_4$ possess similar absorption (Table II) and emission (Figure 2) spectra, they exhibit quite different ϕ_{sen} values. Furthermore, the imposition of a CH_2-CH_2 bridge between the two phosphorus atoms in $Cu(diphos)BH_4$ drastically reduces its effectiveness as a sensitizer relative to $Cu(PPh_2Me)_3BH_4$.

Some photodegradation of $Cu(PPh_3)_2BH_4$ and $Cu(PPh_2Me)_3BH_4$ is evident during the course of the sensitization experiments.[26] To avoid the complications (secondary photolysis, inner filter effects) which might arise from this process, the measurements of ϕ_{sen} reported in Table IV were taken at short (≤3 h) irradiation times. A more fundamental problem, however, relates to the identity of the *actual* sensitizer in these systems, since it is conceivable that the active species may be generated photochemically from the parent Cu(I) compounds. To investigate this possibility, we determined the time dependence of ϕ_{sen} for solutions originally charged with $Cu(PPh_3)_2BH_4$ or $Cu(PPh_2Me)_3BH_4$. During the initial 2-3 h of irradiation, plots of quadricyclene production vs. time are linear (ϕ_{sen} remains constant) and pass through the origin (sensitization exhibits no induction period). Such behavior is incompatible with the in situ photogeneration of a sensitizer from the parent compounds. Consequently, the photoinstability of $Cu(PPh_3)_2BH_4$ and $Cu(PPh_2Me)_3BH_4$ constitutes a pathway which competes with, rather than leads to, sensitization of the NBD to Q conversion.

A few experiments were conducted at long irradiation times to test the catalytic nature of the sensitization process. Catalytic factors (mol of Q produced per mol of sensitizer present) of >10 were observed for both $Cu(PPh_3)_2BH_4$ and $Cu(PPh_2Me)_3BH_4$ at NBD concentrations ≥0.2 M.

Since triphenylphosphine has been reported to undergo a photochemical reaction in benzene solution,[27] we investigated the possibility that its ineffectiveness as a sensitizer results from a high quantum efficiency for this competing process. In a typical experiment, a degassed benzene solution containing 5×10^{-3} M PPh_3 and 0.5 M NBD was irradiated at 313 nm for 30 min. Under these conditions the quantum yield for disappearance of PPh_3 is ~0.07.[28] Photodecomposition of PPh_3 is thus a relatively minor excited-state pathway.

E. Mechanistic Considerations. Our earlier finding[5] that simple CuX (X is Cl, Br, I, or $C_2H_3O_2$) salts sensitize the conversion of norbornadiene to quadricyclene via a mechanism involving the photoexcitation of a preformed XCu-NBD complex (eq 2) prompted us to investigate the possibility that a similar pathway may be available to $Cu(PPh_3)_2BH_4$ and $Cu(PPh_2Me)_3BH_4$. Since tetracoordinate Cu(I) compounds containing monodentate or bidentate ligands invariably are coordinatively saturated,[29] complex formation in these latter systems would necessarily involve the replacement by NBD of one or more of the ligands originally bound to the metal center. Accordingly, we have considered the feasibility of

Table V. Parameters Derived from Stern-Volmer Plots of $1/\phi_{\rm sen}$ vs. $1/[\rm NBD]$

	$Cu(PPh_3)_2BH_4$	$Cu(PPh_2Me)_3BH_4$
slope, M	0.31 ± 0.02	0.14 ± 0.02
intercept	1.32 ± 0.2	1.86 ± 0.2
$k_{\rm SV}^{\rm (sen)}$, M^{-1} [a]	4.3	13.1
$\phi_{\rm sen}^{\rm lim}$ [b]	0.76	0.54

[a] Stern-Volmer constant for sensitization, defined by intercept/slope. [b] Limiting sensitization yield, defined by 1/intercept.

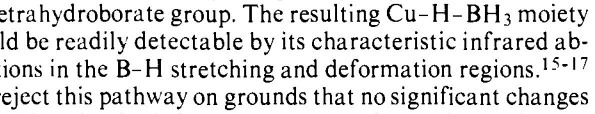
several routes (depicted in Scheme I) by which this ligand substitution process could occur.

In path A one of the substitutionally labile phosphine ligands is displaced from the metal by NBD. Two lines of evidence militate against the occurrence of this process. Thus the single ^{31}P NMR resonance exhibited by solutions of $Cu(PPh_3)_2BH_4$ or $Cu(PPh_2Me)_3BH_4$ should undergo a high-field shift, indicative of an increased concentration of uncoordinated phosphine, upon addition of NBD. Contrary to this expectation, we find that even a large excess of NBD has essentially no effect upon the position of the signal (Table I). Furthermore, addition of excess PPh_3 to a solution containing $Cu(PPh_3)_2BH_4$ and NBD should repress the formation of the photoactive complex and thus decrease the observed sensitization yield. A comparison of data sets F and G in Table IV reveals that within typical experimental uncertainty this situation does not obtain.

An alternative mechanism in path B involves coordination of NBD at a site originally occupied by a hydrogen atom from the tetrahydroborate group. The resulting $Cu\text{-}H\text{-}BH_3$ moiety should be readily detectable by its characteristic infrared absorptions in the B-H stretching and deformation regions.[15-17] We reject this pathway on grounds that no significant changes are evident in the infrared spectrum of $Cu(PPh_2Me)_3BH_4$ upon addition of excess NBD. Moreover, since the BH_4^- group in $Cu(diphos)BH_4$ appears to be equally susceptible to this type of process, it would be difficult to rationalize the low sensitization yields observed for this compound.[30]

A final possibility in path C involves the photochemical production of a Cu-NBD complex which subsequently absorbs a second photon to yield Q. This type of sequential, two-photon process seems untenable, however, in view of the constancy of $\phi_{\rm sen}$ at short irradiation times and the absence of an induction period for sensitization (see discussion in preceding section). The insensitivity of $\phi_{\rm sen}$ to a fivefold variation of the incident light intensity (data sets F and H in Table IV) or the presence of excess triphenylphosphine (data sets F and G in Table IV) buttresses this conclusion.

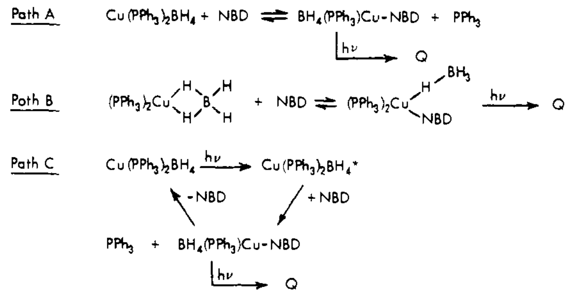
The studies cited above strongly suggest that the mechanism of sensitization by $Cu(PPh_3)_2BH_4$ and $Cu(PPh_2Me)_3BH_4$ is *fundamentally different* from that of simple CuX salts in that no ground-state coordination of NBD to the copper atom occurs. The alternative pathway in eq 5 involving interaction of



$$Cu(PPh_3)_2BH_4 \xrightarrow{h\nu} Cu(PPh_3)_2BH_4^* \xrightarrow{NBD} [Cu(PPh_3)_2BH_4^*, NBD] \rightarrow Cu(PPh_3)_2BH_4 + Q \qquad (5)$$

the photoexcited copper compound with NBD, presumably via electronic energy transfer or excited state complex (exciplex) formation,[31] thus deserves serious consideration. As required by this simple scheme, the dependence of $\phi_{\rm sen}$ upon NBD concentration obeys a Stern-Volmer type relationship for both $Cu(PPh_3)_2BH_4$ and $Cu(PPh_2Me)_3BH_4$. Plots of $1/\phi_{\rm sen}$ vs. $1/[\rm NBD]$ are linear and give rise to the parameters listed in Table V. The intercept/slope ratio defines the Stern-Volmer constant for sensitization, $k_{\rm SV}^{\rm (sen)}$, whereas the reciprocal of the intercept is the limiting (maximum) quantum yield, $\phi_{\rm sen}^{\rm lim}$. The substantial values obtained for $\phi_{\rm sen}^{\rm lim}$ indicate that sensitization can be the dominant pathway for deactivating the excited states of $Cu(PPh_3)_2BH_4$ and $Cu(PPh_2Me)_3BH_4$.

Scheme I[a]



[a] For illustrative purposes, each path is shown for the specific case of $Cu(PPh_3)_2BH_4$.

Several important features of the sensitization process remain to be established. Quite clearly, the key interaction between NBD and the photoexcited Cu(I) compound (eq 5) needs to be defined more precisely. Moreover, while we have learned that the rates of population and/or depopulation of the excited states localized on a phosphine molecule can be perturbed appreciably upon coordination to copper (section C), the nature of this perturbation and its effect upon the efficiency of sensitization (i.e., why $Cu(PPh_3)_2BH_4$ is a better sensitizer than PPh_3) are not well understood at present. Finally, the extent to which the eccentric spectral and lifetime properties of $Cu(diphos)BH_4$ contribute to its low sensitization yield remains to be resolved. Studies aimed at probing these related questions are underway in our laboratory.

F. Concluding Remarks. The series of compounds $Cu(PPh_3)_2BH_4$, $Cu(PPh_2Me)_3BH_4$, and $Cu(diphos)BH_4$ possess several interesting structural and electronic properties. Particularly noteworthy is the ability of the first two members to efficiently photosensitize the valence isomerization of norbornadiene to quadricyclene. Beside broadening the rather limited selection of Cu(I) compounds which have been examined in this context, the present study provides evidence for the operation of a sensitization mechanism that is fundamentally different from that exhibited by the well-studied class of simple CuX salts. Thus the *photoexcited* Cu-phosphine compound undergoes a bimolecular interaction with a ground-state NBD molecule. The occurrence of this pathway as well as our observation of luminescence from $Cu(PPh_3)_2BH_4$ and $Cu(diphos)BH_4$ in room temperature, fluid solution adds to the increasing weight of evidence[32-34] that Cu(I) compounds can possess fundamentally interesting and potentially useful excited-state behavior.

Acknowledgment. The authors acknowledge the support of this work by the Department of Energy and by the National Science Foundation. We also wish to thank Drs. R. R. Hautala, A. C. Capomacchia, and J. T. Stewart for access to the emission and lifetime equipment.

References and Notes

(1) C. Kutal, D. P. Schwendiman, and P. Grutsch, *Sol. Energy*, **19**, 651 (1977).
(2) C. Kutal, *Adv. Chem. Ser.*, **168**, 158 (1978).
(3) R. G. Salomon, A. Sinha, and M. F. Salomon, *J. Am. Chem. Soc.*, **100**, 520 (1978).
(4) C. Kutal and P. A. Grutsch, *Adv. Chem. Ser.*, **173**, 325 (1979).
(5) D. P. Schwendiman and C. Kutal, *J. Am. Chem. Soc.*, **99**, 5677 (1977).
(6) P. A. Grutsch and C. Kutal, *J. Am. Chem. Soc.*, **99**, 6460 (1977).
(7) S. J. Lippard and D. A. Ucko, *Inorg. Chem.*, **7**, 1051 (1968).
(8) J. N. Demas and G. A. Crosby, *J. Phys. Chem.*, **75**, 991 (1971).
(9) Values of the refractive index (1.498 for benzene and 1.333 for 0.1 N H_2SO_4) were taken from J. A. Riddick and W. B. Bunger, "Organic Solvents", 3rd ed., Wiley-Interscience, New York, 1971.

(10) In addition to the predominant 313-nm Hg line, small amounts of the 297-, 302-, and 334-nm lines are transmitted by this filter combination.
(11) C. G. Hatchard and C. A. Parker, *Proc. R. Soc. London, Ser. A*, **235**, 518 (1956).
(12) S. J. Lippard and K. M. Melmed, *Inorg. Chem.*, **6**, 2223 (1967).
(13) J. T. Gill and S. J. Lippard, *Inorg. Chem.*, **14**, 751 (1975).
(14) F. Cariati and L. Naldini, *Gazz. Chim. Ital.*, **95**, 3 (1965).
(15) T. J. Marks and J. R. Kolb, *Chem. Rev.*, 77, 263 (1977).
(16) C. Kutal, P. A. Grutsch, J. L. Atwood, and R. D. Rogers, *Inorg. Chem.*, 17, 3558 (1978).
(17) J. C. Bommer and K. W. Morse, *J. Chem. Soc., Chem. Commun.*, 137 (1977).
(18) F. Klanberg, E. L. Muetterties, and L. J. Guggenberger, *Inorg. Chem.*, 7, 2272 (1968).
(19) The absorption spectra of $Cu(PPh_3)_2BH_4$, $Cu(diphos)BH_4$, and the corresponding free phosphine molecules are displayed in ref 6.
(20) W. R. Cullen and R. M. Hochstrasser, *J. Mol. Spectrosc.*, **5**, 118 (1960).
(21) G. Shaw, J. K. Becconsall, R. M. Canadine, and R. Murray, *Chem. Commun.*, 425 (1966).
(22) B. I. Stepanov, A. I. Bokanov, and V. I. Svergun, *J. Gen. Chem. USSR (Engl. Transl.)*, **41**, 526 (1971).
(23) M. Kasha and H. R. Rawls, *Photochem. Photobiol.*, 7, 561 (1968).
(24) E. J. Halpern and K. Mislow, *J. Am. Chem. Soc.*, **89**, 5224 (1967).
(25) Recent X-ray structural studies of $Rh(diphos)(1,5\text{-cyclooctadiene})^+$ (personal communication from W. S. Knowles) and $[Cu(diphos)(PPh_2)]_2 \cdot 2C_6H_6$ (T. Greiser and E. Weiss, *Chem. Ber.*, 111, 516 (1978)) reveal that the two phenyl rings attached to each P atom of the coordinated diphos ligand possess nonequivalent environments.
(26) Degassed benzene solutions of $Cu(PPh_3)_2BH_4$ or $Cu(PPh_2Me)_3BH_4$ and excess NBD undergo no discernible spectral changes when kept in the dark for a period of several hours. Upon irradiation at 313 nm, however, the solutions gradually change from colorless to yellow. Attempts to characterize the photoproducts spectrally have proven inconclusive.
(27) M. L. Kaufman and C. E. Griffin, *Tetrahedron Lett.*, **12**, 769 (1965). The major products resulting from the homolysis of an aryl–phosphorus bond are diphenylphosphine and biphenyl.
(28) We encountered difficulty in obtaining reproducible quantum yields, presumably because of adventitious traces of oxygen which can cause a facile photooxidation of PPh_3 to its oxide: G. L. Geoffroy, D. A. Denton, and C. W. Eigenbrot, Jr., *Inorg. Chem.*, **15**, 2310 (1976). To the extent that this competing process occurs, our reported disappearance quantum yield will be high.
(29) F. H. Jardine, *Adv. Inorg. Chem. Radiochem.*, 17, 115 (1975). Some novel five-coordinate Cu(I) compounds have been reported recently, but they contain a rigid, tetradentate macrocyclic ligand: R. R. Gagné, J. L. Allison, R. S. Gall, and C. A. Koval, *J. Am. Chem. Soc.*, **99**, 7170 (1977).
(30) At the suggestion of a referee, we measured the ^1H NMR spectra of norbornadiene in the presence and absence of $Cu(PPh_3)_2BH_4$. The two spectra were found to be experimentally indistinguishable, in accord with other evidence that thermally induced complex formation between NBD and the Cu(I) sensitizer (e.g., paths A and B in Scheme I) plays no role in the mechanism of sensitization.
(31) Both pathways have been reported for the quenching of aromatic carbonyl triplets by norbornadiene and substituted analogues: A. J. G. Barwise, A. A. Gorman, R. L. Leyland, P. G. Smith, and M. A. J. Rogers, *J. Am. Chem. Soc.*, **100**, 1814 (1978).
(32) G. Ferraudi, *Inorg. Chem.*, 17, 1370 (1978).
(33) D. D. Davis, K. L. Stevenson, and C. R. Davis, *J. Am. Chem. Soc.*, **100**, 5344 (1978).
(34) B. -T. Ahn and D. R. McMillin, *Inorg. Chem.*, 17, 2253 (1978).

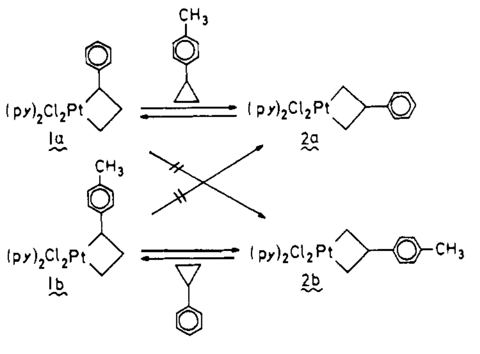
Mechanism of Rearrangement of Platinacyclobutanes

Charles P. Casey,* Daniel M. Scheck, and Alan J. Shusterman

Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706. *Received December 22, 1978*

Abstract: No crossover products were observed when the rearrangement of dichlorobis(pyridine)(1-phenylpropane-1,3-diyl)platinum(IV) (**1a**) to dichlorobis(pyridine)(2-phenylpropane-1,3-diyl)platinum(IV) (**2a**) was carried out in the presence of either *p*-tolylcyclopropane or *p*-methylstyrene. Preparation of dichlorobis(pyridine)(*cis*-1-phenylpropane-*3-d*$_1$-1,3-diyl)platinum(IV) (**5a**) from *cis*-phenylcyclopropane-*2-d*$_1$ and rearrangement of **5a** to the β-phenylplatinacyclobutane **6** both proceeded with complete retention of stereochemistry.

The olefin metathesis reaction[1] has been proposed to proceed via interconversion of metal–alkene–carbene complexes and metallacyclobutanes.[2] This proposal is supported both by studies of the reactions of metal carbene complexes with alkenes[3] and by labeling experiments which show that the olefin metathesis reaction proceeds in a nonpairwise manner.[4] Our interest in the metathesis reaction has led us to study the rearrangement of platinacyclobutanes which was first discovered by Puddephatt.[5] Puddephatt found that the initially formed α-phenylplatinacyclobutane **1a** formed by ring opening of phenylcyclopropane rearranges to a mixture of α- and β-phenylplatinacyclobutanes **1a** and **2a** on heating. Initially it seemed possible that this rearrangement proceeded by a mechanism closely related to that proposed for olefin metathesis. Here we present the results of mechanistic studies of the rearrangement of platinacyclobutanes.



Results

The possibility that the rearrangement of the α-phenylplatinacyclobutane **1a** to the β-phenyl isomer **2a** proceeded via elimination and readdition of phenylcyclopropane was seriously considered since thermal decomposition of **1a** or **2a** gives some phenylcyclopropane[5,6] and since reaction of **1a** or **2a** with $P(C_6H_5)_3$ gives a high yield of phenylcyclopropane.[7] Rearrangement of **1a** to a 1:2 equilibrium mixture of **1a**:**2a** in the presence of *p*-tolylcyclopropane led to no formation of α- or β-(*p*-tolyl)platinacyclobutanes **1b** or **2b**. Similarly, rearrangement of α-(*p*-tolyl)platinacyclobutane **1b** in the presence of phenylcyclopropane gave a 1:4 equilibrium mixture of **1b**:**2b** and no phenylplatinacyclobutanes **1a** or **2a**.

Heating a mixture of dichlorobis(pyridine)(1-hexylpropane-1,3-diyl)platinum(IV) (**1c**) and the corresponding 2-hexyl derivative, **2c**, in the presence of phenylcyclopropane at 50 °C for several hours gave no **1a** or **1b**. Puddephatt has reported that the rearrangement of alkyl-substituted platinacyclobutanes is substantially faster than that of aryl-substituted platinacyclobutanes.[8] Our experiment helps establish that coordination of the phenyl ring to platinum is not the means of maintaining the intramolecularity of the rearrangement.

The possibility that the rearrangement of **1a** to **2a** proceeded by fragmentation to styrene and a $Pt{=}CH_2$ species was

0002-7863/79/1501-4233$01.00/0