the chemical and spectroscopic properties of complex **1** and related tetrameric complexes will prove to be fruitful in elucidating the structure and mechanism of the water-oxidizing complex in green plants.

Acknowledgment. We gratefully acknowledge the assistance of Professor J. W. Faller with the solution of the crystal structure. G.W.B. acknowledges receipt of a Camille and Henry Dreyfus Teacher-Scholar award and an A. P. Sloan research fellowship.

Supplementary Material Available: Summary of crystallographic data and tables of positional parameters and B(eq) values, intramolecular bond distances and angles, torsion angles, and U values (13 pages); a listing of F_o vs F_c values (24 pages). Ordering information is given on any current masthead page.

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Articles

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Photobehavior of Copper(I) Compounds. 4.[1a] Role of the Triplet State of (Arylphosphine)copper(I) Complexes in the Photosensitized Isomerization of Dienes

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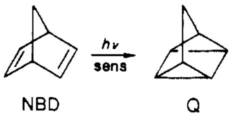
Photoisomerization of *cis*- and *trans*-piperylene can be sensitized with high quantum efficiency by Cu(diphos)BH_4 (diphos is 1,2-bis(diphenylphosphino)ethane) and Cu(prophos)BH_4 (prophos is 1,3-bis(diphenylphosphino)propane). Sensitization is accompanied by quenching of the emissive ${}^3(\sigma\text{–}a_\pi)$ excited state in each copper(I) complex, and the two processes occur with identical Stern–Volmer kinetics. Measurements of the trans/cis diene ratio at the photostationary state can be used to estimate the triplet-state energy as 60–61 kcal for Cu(diphos)BH_4 and >61 kcal for Cu(prophos)BH_4; additional evidence suggests that 66–67 kcal is a reasonable value for the latter complex. Collectively, the results support the assignment of triplet–triplet energy transfer as the primary mechanism for sensitization and quenching in these systems. This mechanism also can accommodate earlier reports that Cu(diphos)BH_4 and Cu(prophos)BH_4 sensitize the valence isomerization of norbornadiene to quadricyclene with markedly different quantum efficiencies.

Introduction

Copper(I) complexes of general formula CuP_nX, where P is a monodentate or polydentate arylphosphine, X is a uninegative group such as Cl^-, Br^-, or BH_4^-, and n = 1–3, possess a number of interesting spectral and photochemical properties.[1a,2,3] Exemplary in this respect is the behavior of the triphenylphosphine, diphos (1,2-bis(diphenylphosphino)ethane), and prophos (1,3-bis(diphenylphosphino)propane) complexes pictured in Figure 1. As summarized in Table I, each member of this series luminesces in room-temperature fluid solution and also functions as a photosensitizer, with limiting quantum efficiency $\phi^\infty{}_{\text{isom}}$, for the valence isomerization of norbornadiene (NBD) to quadricyclene (Q) (eq 1). A detailed investigation of the Cu$(PPh_3)_2BH_4$/NBD system



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led us to propose that sensitization arises from the bimolecular interaction of the photoexcited copper(I) complex (denoted by an asterisk) with the ground-state diene molecule (eq 2).[2a,b] Direct

$$^*Cu(PPh_3)_2BH_4 + NBD \rightarrow \underset{\text{encounter pair}}{[^*Cu(PPh_3)_2BH_4,NBD]} \rightarrow Cu(PPh_3)_2BH_4 + Q \quad (2)$$

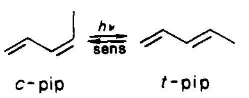
Table I. Properties of (Arylphosphine)copper(I) Complexes[a]

complex	λ_{em},[b] nm	τ,[c] μs	$\phi^\infty{}_{\text{isom}}$[d]
Cu$(PPh_3)_2BH_4$	475	<0.01	0.76
Cu(diphos)BH_4	537	1.1[e,f]	<0.01
Cu(prophos)BH_4	510	3.9[e]	0.88

[a] Measured in benzene at 25 °C; unless noted otherwise, data were taken from ref 2b,c. [b] Wavelength of luminescence maximum. [c] Luminescence lifetime. [d] Limiting quantum yield for sensitized isomerization of NBD to Q. [e] Measured in this study. [f] This lifetime is considerably longer than the one reported in ref 2b.

support for this proposal came from a related study in which it was observed that quenching of the phosphorescence of Cu(prophos)BH_4 by NBD and sensitized production of Q (eq 1) occur concurrently and with identical Stern–Volmer kinetics.[2c] The simplest interpretation of this parallel behavior is that both processes result from the bimolecular encounter of the organic substrate with the emissive triplet state of the copper(I) complex.

Since relatively little is known about the bimolecular chemistry of (arylphosphine)copper(I) excited states, we have undertaken additional studies of the triplet-state behavior of the two model complexes Cu(diphos)BH_4 and Cu(prophos)BH_4 in the presence of isomerizable dienes. Our primary goal has been to characterize the key excited-state interaction responsible for quenching and sensitization in these systems. In this report we investigate the use of the two copper(I) complexes as photosensitizers for the isomerization of *cis*- and *trans*-piperylene (hereafter abbreviated as *c*-pip and *t*-pip, respectively (eq 3)). The well-characterized



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interconversion of these acyclic 1,3-dienes proceeds efficiently upon population of the lowest triplet state of either isomer and thereby

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(1) (a) Part 3: Borsub, N; Chang, S.-C.; Kutal, C. *Inorg. Chem.* **1982**, *21*, 538. (b) Permanent address: Department of Chemistry, University of the Witwatersrand, Johannesburg 2001, South Africa.

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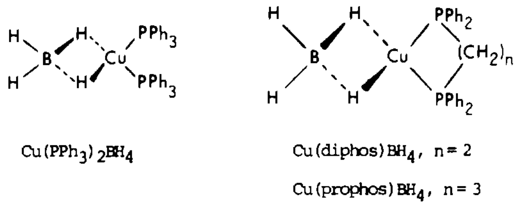

Figure 1. Structures of three (arylphosphine)copper(I) complexes.

provides a convenient monitor of triplet–triplet interaction between sensitizer and substrate.[4] Moreover, measurement of the trans/cis ratio at the photostationary state (where the forward and reverse photochemical rates of eq 3 are equal) affords a reasonably accurate estimate of the triplet energy of the sensitizer. Finally, knowledge of the photostationary-state composition and quantum yield of sensitized isomerization can be used to determine the efficiency of populating the sensitizer triplet state.

Experimental Section

(a) Reagents. (1,3-Bis(diphenylphosphino)propane)copper(I) tetrahydroborate, Cu(prophos)BH_4, was prepared by a modification of the procedure reported by Cariati and Naldini.[5] To 50 mL of benzene containing dissolved prophos (0.9 g, 2.2 mmol) was added cuprous chloride (0.099 g, 1.0 mmol) that had been recrystallized from concentrated acetic acid. The resulting solution was stirred for 2 h, whereupon 10 mL of a freshly prepared and filtered solution of sodium tetrahydroborate (0.079 g, 2.1 mmol) in ethanol was added dropwise. After being stirred for an additional 3 h, the solution was filtered and the volume of the filtrate reduced on a rotary evaporator to a point (<10 mL) where cloudiness developed. The mixture was then left to sit overnight at room temperature. The following day a white crystalline solid was filtered off, washed with several portions of ethanol and diethyl ether, and freed of trapped solvents by mechanical pumping. Anal. Calcd for $C_{27}H_{30}P_2BCu$: C, 66.07; H, 6.16; P, 12.63; Cu, 12.94. Found: C, 66.51; H, 6.35; P, 12.57; Cu, 12.69. (1,2-Bis(diphenylphosphino)ethane)copper(I) tetrahydroborate, Cu(diphos)BH_4, was prepared by an analogous procedure. Anal. Calcd for $C_{26}H_{28}P_2BCu$: C, 65.49; H, 5.92; P, 12.99. Found: C, 65.9; H, 5.9; P, 12.6. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

Samples of *cis*-piperylene (Chemical Samples Co.) and *trans*-piperylene (Aldrich) were purified immediately prior to use by refluxing with lithium aluminum hydride under a nitrogen atmosphere for 1–2 h and then distilling. Gas chromatographic analysis of the dienes indicated a purity of >99%. Solvents employed in the synthetic work were reagent grade and used as received. Spectral grade benzene (Burdick and Jackson) was used in the luminescence and photochemical experiments, while IR Spectranalyzed *n*-pentane (Fisher) was used as an internal standard in gas chromatographic analyses.

(b) Equipment and Techniques. Electronic absorption spectra were recorded on a Cary 15 spectrophotometer. Emission spectra were measured at 25 °C on a Perkin Elmer MPF-44B spectrofluorimeter. Luminescence lifetime measurements at 25 °C were obtained by time-correlated single-photon-counting techniques with an Ortec 9200 nanosecond fluorescence spectrometer. A Spex $^1/_4$-m monochromator was used to isolate emission wavelengths at 500 and 530 nm for Cu(prophos)BH_4 and Cu(diphos)BH_4, respectively. Least-squares treatment of the emission decay as a single exponential function typically afforded a correlation coefficient above 0.99.

Photochemical experiments were conducted with a 200-W high-pressure mercury-arc lamp whose output was passed through a high-intensity monochromator to isolate the 313-nm Hg line. Incident light intensity at this wavelength was determined by ferrioxalate actinometry.[6] Solutions containing the copper(I) sensitizer, *cis*- or *trans*-piperylene, and *n*-pentane were degassed by five freeze–pump–thaw cycles. Irradiated and dark (control) samples were analyzed for isomeric composition of the dienes by gas chromatography. The apparatus consisted of a Varian 2700 chromatograph equipped with a flame-ionization detector and containing a 12 ft × 1/8 in. stainless-steel column packed with 20% β,β-oxydipropionitrile on Chrom W. The column was maintained close to ambient temperature, and the flow rate of nitrogen carrier gas was 10–15 mL/min. Gas chromatographic peak areas were integrated with a Perkin-Elmer Sigma 10 data system. Typically, 4–5 analyses were performed on each sample and the values averaged.

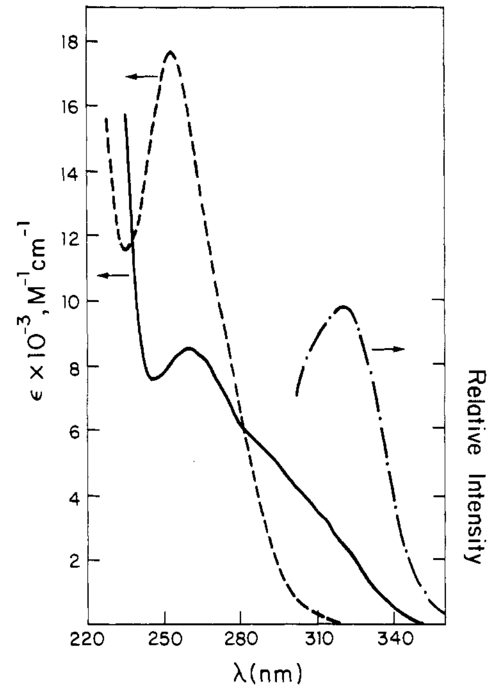

Figure 2. Absorption spectra of prophos (- -) and Cu(prophos)BH_4 (—) in cyclohexane; phosphorescence excitation spectrum of Cu(prophos)BH_4 (-··-) in benzene.

Since the photosensitized interconversion of *cis*- and *trans*-piperylene (eq 3) is a reversible process, the extent of conversion used to calculate the quantum yield was corrected for the contribution of the back reaction. Correction was made using eq 4,[4b] where β is the percentage conversion

$$\beta = (2.303\alpha) \log [\alpha/(\alpha - \beta')] \qquad (4)$$

(cis → trans or trans → cis) in the absence of back reaction, α is the conversion at the photostationary state, and β' is the experimentally measured conversion.

Results

Figure 2 displays the electronic absorption spectra of prophos and Cu(prophos)BH_4 in room-temperature cyclohexane solution. The spectrum of the uncoordinated phosphine molecule contains a band at 252 nm ($\epsilon = 1.76 \times 10^4$ M^{-1} cm^{-1}), which is characteristic of the entire $Ph_2P(CH_2)_nPPh_2$ series; thus the corresponding transition occurs at 251 nm ($\epsilon = 1.82 \times 10^4$ M^{-1} cm^{-1}) and 252 nm ($\epsilon = 1.83 \times 10^4$ M^{-1} cm^{-1}), respectively, in the spectra of the $n = 1$ and $n = 2$ (diphos) analogues. A more complicated spectral pattern results upon coordination of the phosphine to copper. The absorption spectrum of Cu(prophos)BH_4 possesses a band with a maximum at 259 nm ($\epsilon = 8.5 \times 10^3$ M^{-1} cm^{-1}) and a clearly discernible shoulder on the long-wavelength side. Similarly, the spectrum of Cu(diphos)BH_4 contains a peak at 265 nm ($\epsilon = 6.5 \times 10^3$ M^{-1} cm^{-1}) accompanied by a pronounced shoulder at ~300 nm (see ref 2a).

Both Cu(diphos)BH_4 and Cu(prophos)BH_4 exhibit a broad, rather featureless phosphorescence (vide infra) in benzene solution at 25 °C when excited at 313 nm. Table I summarizes peak positions and lifetimes, while Figure 3 illustrates the detailed spectrum of the prophos complex. Measurement of the phosphorescence excitation spectrum presented several experimental difficulties. Thus the limited solubility of the weakly emitting complexes in cyclohexane resulted in samples that absorbed too little of the exciting light to yield a detectable emission signal. While this problem could be ameliorated by the use of more concentrated solutions of the complexes in benzene, the higher absorbance values (>0.1) tended to distort the spectrum and competitive absorption by solvent effectively restricted the range of excitation wavelengths to >300 nm. Because of these shortcomings, the excitation spectrum of Cu(prophos)BH_4 presented in Figure 2 must be regarded as approximate. Nevertheless, it

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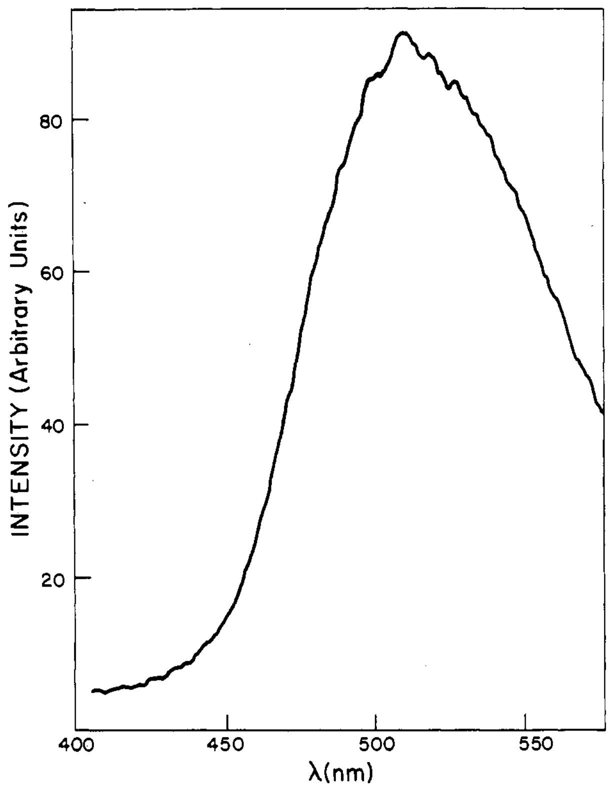

Figure 3. Corrected phosphorescence spectrum of Cu(prophos)BH_4 in benzene at 25 °C.

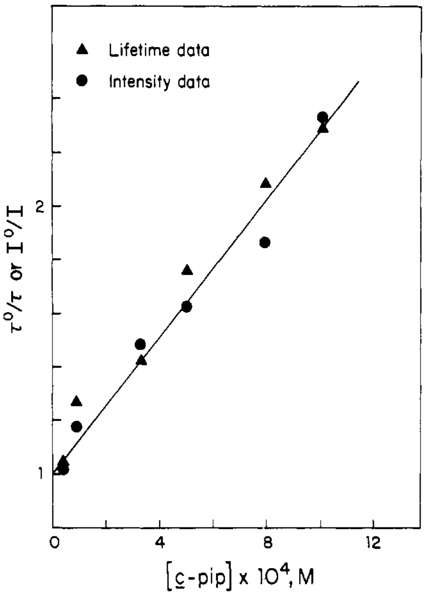

Figure 4. Stern–Volmer plot for quenching of the phosphorescent excited state of Cu(prophos)BH_4 by *c*-pip in benzene at 25 °C: (●) luminescence intensity quenching, (▲) luminescence lifetime quenching.

clearly differs in appearance from the absorption spectrum of the complex.

Quenching of the emissive triplet state of Cu(prophos)BH_4 in benzene solution occurs upon addition of *c*-pip. Lifetime and steady-state intensity measurements obey the Stern–Volmer relationship given by eq 5, where τ° and I° denote the lifetime and

$$\frac{\tau^\circ}{\tau} = \frac{I^\circ}{I} = 1 + K_{SV}[c\text{-pip}] \qquad (5)$$

emission intensity, respectively, of the copper complex in the absence of quencher, τ and I represent the corresponding quantities in the presence of quencher, and K_{SV} is the Stern–Volmer quenching constant. As shown in Figure 4, plots of τ°/τ and I°/I vs [*c*-pip] are linear with a common slope of (1.2 ± 0.1) × 10^3 M^{-1}. Such behavior establishes that *c*-pip quenches the triplet state via a dynamic, collisional process. Since K_{SV} equals $k_q\tau^\circ$, where k_q is the bimolecular quenching rate constant, a simple calculation gives $k_q = (3.1 \pm 0.5) \times 10^8$ M^{-1} s^{-1}.

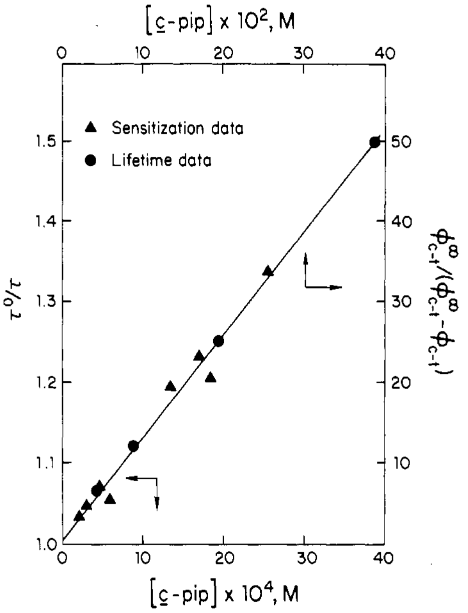

Figure 5. Stern–Volmer plot for quenching of the phosphorescent excited state of Cu(diphos)BH_4 by *c*-pip and concomitant sensitized production of *t*-pip in benzene at 25 °C: (●) luminescence lifetime quenching; (▲) sensitized *t*-pip production.

This quenching of the triplet state of Cu(prophos)BH_4 by *c*-pip is accompanied by sensitized production of *t*-pip. Conventional Stern–Volmer analysis of the sensitization process leads to the double reciprocal relationship in eq 6, where ϕ_{c-t} represents the

$$\frac{1}{\phi_{c-t}} = \frac{1}{\phi^\infty_{c-t}} + \frac{1}{\phi^\infty_{c-t}k_q\tau^\circ[c\text{-pip}]} \qquad (6)$$

experimental quantum yield at any finite concentration of the cis diene and ϕ^∞_{c-t} is the limiting yield reached at high concentrations. Accordingly, a plot of $(\phi_{c-t})^{-1}$ vs $[c\text{-pip}]^{-1}$ should be linear with an intercept of $(\phi^\infty_{c-t})^{-1}$, a slope of $(\phi^\infty_{c-t}k_q\tau^\circ)^{-1}$, and an intercept/slope ratio equal to K_{SV}. Plotting the photochemical data in this manner yields a ϕ^∞_{c-t} value of 0.43 ± 0.01. Unfortunately, the small variation in ϕ_{c-t} over the range of [*c*-pip] concentrations employed in these experiments (i.e. nearly all Cu(prophos)BH_4 triplets were quenched) precludes an accurate determination of K_{SV} from the slope of the double-reciprocal plot. Attempts to determine quantum yields at lower initial concentrations of the cis diene were unsuccessful owing to difficulties in accurately analyzing the small amounts of *t*-pip produced.

Phosphorescence quenching and sensitized isomerization also occur in benzene solutions of Cu(diphos)BH_4 and *c*-pip. Figure 5 depicts a Stern–Volmer plot of the lifetime quenching data (eq 5) from which a value of $K_{SV} = (1.3 \pm 0.0) \times 10^2$ M^{-1} can be obtained. The double-reciprocal plot of the quantum yield data (eq 6) affords values of $\phi^\infty_{c-t} = 0.35 \pm 0.01$ and $K_{SV} = (1.3 \pm 0.1) \times 10^2$ M^{-1} (the results are replotted as $\phi^\infty_{c-t}/(\phi^\infty_{c-t} - \phi_{c-t})$ vs [*c*-pip] in Figure 5 to facilitate direct comparison with the lifetime data). Using the average of the K_{SV} values obtained from the two sets of measurements, we calculate $k_q = (1.2 \pm 0.1) \times 10^8$ M^{-1} s^{-1}.

Both Cu(prophos)BH_4 and Cu(diphos)BH_4 sensitize the geometrical isomerization of *t*-pip. Limiting quantum yields, ϕ^∞_{t-c}, were determined for each copper(I) complex from plots of $(\phi_{t-c})^{-1}$ vs $[t\text{-pip}]^{-1}$. These yields, along with the corresponding ϕ^∞_{c-t} values cited above, are compiled in Table II.

Prolonged irradiation of *c*-pip in the presence of Cu(prophos)BH_4 or Cu(diphos)BH_4 produces a photostationary-state mixture of cis and trans dienes. Table II reports the percentage

Table II. Photochemical Quantum Yields and Photostationary-State Results for the Isomerization of *cis*- and *trans*-Piperylene Sensitized by Cu(prophos)BH_4 and Cu(diphos)BH_4

sensitizer	$\phi^{\infty}{}_{c-t}{}^{a}$	$\phi^{\infty}{}_{t-c}{}^{a}$	% trans (cis)[b] at pss	(trans/cis)$_{pss}$[c]
Cu(prophos)BH_4	0.43 ± 0.01	0.34 ± 0.01	54.7 (45.3)	1.21
Cu(diphos)BH_4	0.35 ± 0.01	0.23 ± 0.01	59.9 (40.1)	1.49

[a] Limiting quantum yield for sensitized isomerization of *c*-pip to *t*-pip (c–t) or *t*-pip to *c*-pip (t–c) at 313 nm. [b] Percentage composition of *t*-pip and *c*-pip at the photostationary state. [c] Estimated accuracy of this ratio is ±5%.

composition of this mixture for each copper(I) complex and the corresponding trans/cis isomeric ratio. Attempts to determine the photostationary-state compositions of samples initially containing pure *t*-pip were unsuccessful owing to the long irradiation times involved and the consequent decomposition of the copper(I) sensitizers.

Discussion

Before considering the excited-state properties of Cu(diphos)BH_4 and Cu(prophos)BH_4, we review some pertinent information about the spectral characteristics of the corresponding uncoordinated phosphine molecules. At present, two alternative assignments exist for the intense band located at 252 nm in the absorption spectra of diphos and prophos (Figure 2). The chief point of contention centers upon the extent to which the lone-pair electrons residing on the phosphorus atom participate in the transition responsible for this band. Several workers have characterized the transition as l–a_π,[2b,7,8] reflecting the view that it involves the promotion of an electron from the lone-pair orbital (l) to an empty antibonding orbital of π origin (a_π) situated on a phenyl ring. Fife et al.,[9] on the other hand, have argued that a phenyl-localized π–π^* assignment better accommodates the properties of this transition and that the lowest energy l–a_π transition actually occurs as a weak band buried beneath the long-wavelength tail of the π–π^* band.

Both of these transition types (l–a_π and π–π^*) will be affected to varying degrees upon coordination of the phosphine molecule to copper. The electron pair that resided in the l orbital now engages in σ bonding to the metal. Consequently, the transfer of an electron from this σ orbital to a π-antibonding orbital centered on a phenyl ring is properly designated as a σ–a_π transition.[2b] The π system of the phosphine ligand may also be perturbed via interaction with metal d orbitals of appropriate symmetry. Metal–phosphorus d_π–d_π back-bonding has been described,[10] and evidence exists that the phosphorus d orbitals may mix with the π^* orbitals of the phenyl group.[11] Thus a mechanism exists for delocalization of π-electron density over the entire copper–phosphine unit.[3a]

Spectroscopic assignments for the electronic absorption and emission bands of (arylphosphine)copper(I) complexes have been proposed by us and by Fife et al.[2b,3a] Both groups agree that the lowest energy singlet and triplet excited states in these complexes are of σ–a_π orbital character. Thus the pronounced shoulder appearing at ~300 nm in the spectra of Cu(diphos)BH_4 and Cu(prophos)BH_4 (Figure 2) can be associated with a spin-allowed σ–a_π transition. The broad emission exhibited by each complex (e.g. Figure 3) in room-temperature fluid media decays with a microsecond lifetime characteristic of a spin-forbidden transition, and accordingly, it has been assigned as a phosphorescence from the lowest σ–a_π triplet state.[2d] Intersystem crossing from the lowest singlet σ–a_π excited state to this emissive triplet proceeds relatively efficiently as evidenced by the maximum in the excitation spectrum at 320 nm (Figure 2). In contrast, the drop in emission intensity at shorter excitation wavelengths suggests that higher energy singlet excited states, such as the one associated with the absorption maximum at ~260 nm (Figure 2), decay via pathways that avoid the lowest σ–a_π triplet. The orbital nature of this 260-nm peak is still contentious with both σ–a_π and π–π^* assignments being suggested.[2b,3a] The present study does not resolve this question, and it will not be considered further. Instead, we shall focus our attention upon the properties of the lowest singlet and triplet σ–a_π excited states, since they will be the predominant species produced, either directly or via intersystem crossing, by the 313-nm excitation employed in the luminescence and photochemical experiments.

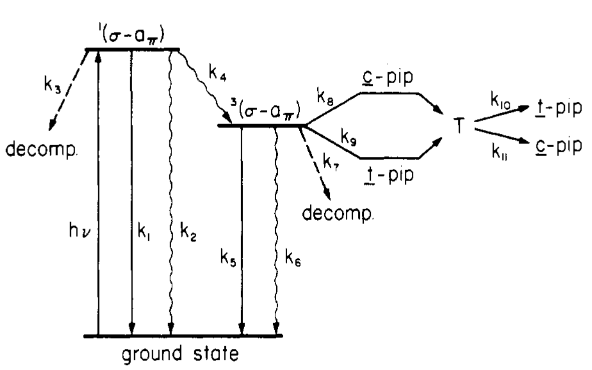

Figure 6. Scheme showing the processes that occur upon 313-nm excitation of Cu(prophos)BH_4 and Cu(diphos)BH_4 in the presence of the isomeric piperylenes. $^1(\sigma$–$a_\pi)$ and $^3(\sigma$–$a_\pi)$ are excited states of the copper(I) complex while T denotes the diene triplet state. Rate constants refer to fluorescence (k_1), internal conversion (k_2), photochemical decomposition (k_3 and k_7), intersystem crossing (k_4 and k_6), phosphorescence (k_5), energy transfer (k_8 and k_9), and relaxation of T to products (k_{10} and k_{11}).

Table III. Compilation of Quenching Rate Constants, Triplet Energies, and Oxidation Potentials for a Series of Quenchers

quencher	k_q,[a] M^{-1} s^{-1}	E_T, kcal	E_{ox}, V vs SCE (Ag/AgCl)
c-pip	3.1×10^8	56.9[b]	(1.48)[c]
NBD	1.2×10^6	70[d]	1.56[e] (1.62)[c]
Q	$<3 \times 10^5$	>70[d]	0.91[e]

[a] Rate constant for quenching of $^3(\sigma$–$a_\pi)$ state of Cu(prophos)BH_4; value for NBD from ref 2c and value for Q from unpublished work of S. W. Orchard. [b] From ref 4a. [c] Peak potential on glassy-carbon electrode in CH_3CN; isomeric purity not specified. From: Baltes, H.; Steckhan, E.; Schäfer, H. J. *Chem. Ber.* **1978**, *111*, 1294. [d] Estimated from quenching data reported in Barwise, A. J. G.; Gorman, A. A.; Leyland, R. L.; Smith, P. G.; Rodgers, M. A. J. *J. Am. Chem. Soc.* **1978**, *100*, 1814. [e] Half-wave potential on Pt electrode in CH_3CN; from Gassman, P.; Yamaguchi, R.; Koser, G. F. *J. Org. Chem.* **1978**, *43*, 4392.

Since conventional triplet–triplet energy transfer is the primary mechanism by which numerous organic molecules sensitize the cis–trans isomerization of the piperylenes,[4] we propose as a working hypothesis that a similar pathway operates for Cu(prophos)BH_4 and Cu(diphos)BH_4. The scheme depicted in Figure 6 then provides a convenient framework for analyzing the phosphorescence quenching and sensitization data obtained in the present study. In brief, the absorption of a 313-nm photon excites the copper(I) complex to the lowest σ–a_π singlet state. Unimolecular deactivation of this state can occur (with rate constant indicated in parenthesis) by fluorescence emission (k_1), internal conversion (k_2) to the ground state, chemical reaction (k_3), and intersystem crossing (k_4) to the lowest σ–a_π triplet state. This triplet state, in turn, may decay via phosphorescence emission (k_5), intersystem crossing (k_6) to the ground state, and chemical reaction (k_7). In addition, bimolecular energy transfer to *c*-pip (k_8) and *t*-pip (k_9) can occur with the consequent formation of the diene triplet state T. Decay of T to the ground state of either isomer (k_{10} and k_{11}) yields the observed product mixture.

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Several lines of evidence can be cited in support of this mechanistic scheme. For example, the identical kinetics of phosphorescence quenching and *t*-pip production (Figure 5) establish the direct involvement of the emissive σ–a_π triplet state of Cu(diphos)BH_4 in the sensitized isomerization of *c*-pip. Though less definitive, the concurrence of quenching and sensitization in the Cu(prophos)BH_4/*c*-pip system suggests a similar key role for the σ–a_π triplet of this copper(I) complex. Data summarized in Table III reveal an inverse relationship between the rate constant for phosphorescence quenching of Cu(prophos)BH_4 and the triplet state energy, E_T, of the quencher. Such behavior is clearly consistent with the assignment of triplet–triplet energy transfer as the predominant interaction between the sensitizer and quencher. In contrast, the lack of a correlation between k_q and the oxidation potential, E_{ox}, of the quencher effectively argues against any mechanism involving complete or partial transfer of an electron from the quencher to the photoexcited copper(I) complex.[12]

Earlier studies of the photosensitized interconversion of *cis*- and *trans*-piperylene revealed that the isomeric composition at the photostationary state exhibits a complicated dependence upon the triplet energy, E_T, of the sensitizer employed.[4a] Sensitizers having energies above ~61 kcal yield a constant photostationary-state ratio, $(\text{trans/cis})_{\text{pss}}$, of 1.22 ± 0.05. As E_T drops from 61 to 56 kcal, this ratio rises to a maximum, and then, below 56 kcal, it begins to decrease. Such behavior can be interpreted by reference to eq 7,[4] which expresses the photostationary-state ratio in terms

$$\left(\frac{\text{trans}}{\text{cis}}\right)_{\text{pss}} = \left(\frac{k_8}{k_9}\right)\left(\frac{k_{10}}{k_{11}}\right) \tag{7}$$

of the rate constants for activation (k_8 and k_9) and decay (k_{10} and k_{11}) of the piperylene triplet state T (Figure 6). For sensitizers whose energies exceed 61 kcal, energy transfer to *c*-pip (E_T = 56.9 kcal)[4a] and *t*-pip (E_T = 58.8 kcal)[4a] is an exoergic process that should occur at a near-diffusion-controlled rate. In this "high-energy" regime, $k_8 = k_9$ and the photostationary state ratio attains a constant value that directly reflects the intrinsic decay characteristics of T. As the sensitizer energy drops below 61 kcal, energy transfer to *t*-pip becomes measurably inefficient, $k_9 < k_8$, and the preferential excitation of *c*-pip results in a trans-rich photostationary state. For sensitizers having E_T values below 56 kcal, energy transfer to both isomers is inefficient and factors other than energetics become important in determining the photostationary-state composition.

Comparison of the photostationary-state ratios listed in Table II with those reported for a series of sensitizers of known E_T[4a] allows us to estimate the previously unknown triplet energies of Cu(diphos)BH_4 and Cu(prophos)BH_4. Thus, a ratio of 1.49 places the triplet state of the diphos complex in the vicinity of 60–61 kcal. The prophos complex, on the other hand, yields a ratio characteristic of a "high-energy" sensitizer having E_T > 61 kcal. Taking the difference between the phosphorescence maxima of Cu(diphos)BH_4 and Cu(prophos)BH_4 (~3 kcal; see Table I) as an approximate measure of the energy difference between the corresponding triplet states, we tentatively suggest an E_T value of ~64 kcal for the latter complex. Interestingly, the rate constants for quenching of the $^3(\sigma$–$a_\pi)$ states of the two copper(I) complexes by *c*-pip (Table II) are well below the diffusion-controlled constant ($k_{\text{dif}} \sim 1 \times 10^{10}$ M^{-1} s^{-1} at 25 °C in benzene), even though triplet–triplet energy transfer should be exoergic by some 3–7 kcal. Similar behavior observed for the triplet-state quenching of $Cu(PPh_2Me)_3Cl$ (E_T = 76 kcal) by NBD has been attributed to poor orbital overlap between the $^3(\sigma$–$a_\pi)$ state of the (arylphosphine)copper(I) complex and the organic quencher.[3a,13]

Since the sum of the limiting quantum yields for sensitized cis–trans and trans–cis isomerization, $\phi^\infty{}_{c\text{-}t} + \phi^\infty{}_{t\text{-}c}$, is considerably below unity for both Cu(diphos)BH_4 and Cu(prophos)BH_4 (Table II), apparently not all of the complexes initially excited with 313-nm radiation decay to the lowest $^3(\sigma$–$a_\pi)$ state. One possible cause of this behavior has already been mentioned in connection with the phosphorescence excitation spectrum of Cu(prophos)BH_4. Recall that comparison of this spectrum with the absorption spectrum of the complex (Figure 2) indicates that population of $^3(\sigma$–$a_\pi)$ occurs more efficiently from the lowest $^1(\sigma$–$a_\pi)$ excited state than from higher energy states. To the extent that these higher lying states competitively absorb the 313-nm excitation, the quantum yield of triplet sensitized isomerization will be diminished. Likewise, any inefficiency in intersystem crossing from $^1(\sigma$–$a_\pi)$ to $^3(\sigma$–$a_\pi)$ will lower the value of $\phi^\infty{}_{c\text{-}t} + \phi^\infty{}_{t\text{-}c}$. Data compiled in Table II can be used to calculate ϕ_{isc}, the quantum efficiency of intersystem crossing, by the method of Lamola and Hammond.[4b] Under conditions of complete quenching of the $^3(\sigma$–$a_\pi)$ state of Cu(prophos)BH_4 by *c*-pip, eq 8 applies, where

$$\phi^\infty{}_{c\text{-}t} = \eta\phi_{\text{isc}} \tag{8}$$

η is the fraction of piperylene triplet states that decay to the trans isomer (in terms of Figure 6, $\eta = k_{10}/(k_{10} + k_{11})$. Using $\phi^\infty{}_{c\text{-}t}$ = 0.43 and η = 0.55, we obtain ϕ_{isc} = 0.78. A similar calculation yields ϕ_{isc} = 0.64 for Cu(diphos)BH_4. It should be emphasized that these values represent lower limits to the true efficiency of intersystem crossing from $^1(\sigma$–$a_\pi)$ to $^3(\sigma$–$a_\pi)$ since, as noted above, competitive absorption by higher lying excited states can lower the measured value of $\phi^\infty{}_{c\text{-}t}$. Indeed the finding that $\phi^\infty{}_{\text{isom}}$ = 0.88 ± 0.06 for the conversion of NBD to Q sensitized by the $^3(\sigma$–$a_\pi)$ state of Cu(prophos)BH_4[2c] suggests that ϕ_{isc} for this complex is somewhat higher than 0.78.

Having considered the evidence that supports the assignment of triplet energy transfer as the primary mechanism by which Cu(diphos)BH_4 and Cu(prophos)BH_4 sensitize the isomerization of the piperylenes, let us now inquire whether a similar pathway is operative for the sensitized conversion of NBD to Q.[2b,c] We begin by noting that energy transfer from the lowest $^3(\sigma$–$a_\pi)$ state of either complex to the lowest triplet of NBD would be an endoergic process. Nonetheless, it should occur essentially irreversibly owing to the short lifetime (i.e. high reactivity) of the diene triplet.[14] The energy deficiency, ΔE, between the donor and acceptor states can be treated as an activation energy to be supplied by the surroundings, and the energy-transfer rate constant, k_{ET}, falls below some optimum value, $k^{\max}{}_{ET}$, which is generally assumed to be close or equal to the diffusion-controlled limit. The relationship between k_{ET} and the degree of endoergicity is given by eq 9,[15] where R is the gas constant and T is the absolute

$$\log \frac{k^{\max}{}_{ET}}{k_{ET}} = \frac{\Delta E}{2.3RT} \tag{9}$$

temperature. Using our earlier estimate of 64 kcal for the available triplet-state energy of Cu(prophos)BH_4 and taking $k^{\max}{}_{ET} = 1 \times 10^{10}$ M^{-1} s^{-1} yield ΔE = 6 kcal and $k_{ET} = 4 \times 10^5$ M^{-1} s^{-1}. This predicted value of the rate constant for energy transfer from the $^3(\sigma$–$a_\pi)$ state of Cu(prophos)BH_4 to the triplet of NBD agrees moderately well with the experimental value of 1.2×10^6 M^{-1} s^{-1}. This agreement, however, must be at least partly the fortuitous result of equating $k^{\max}{}_{ET}$ with the rate constant for diffusion. As noted previously, exoergic energy transfer from the $^3(\sigma$–$a_\pi)$ states of (arylphosphine)copper(I) complexes to organic substrates generally occurs with a rate constant 10–100 times below the diffusion limit. If we make the more realistic assumption that $k^{\max}{}_{ET}$ can be no greater than the measured rate constant for quenching of the phosphorescence of Cu(prophos)BH_4 by *c*-pip (3×10^8 M^{-1} s^{-1}), the predicted value of k_{ET} in the Cu(prophos)BH_4/NBD system (keeping ΔE = 6 kcal) falls to 1.5×10^4 M^{-1} s^{-1}. In order to bring the predicted k_{ET} into concordance with the experimental value, it is necessary to raise our estimate of the energy of the $^3(\sigma$–$a_\pi)$ state in the copper(I) complex to 66–67 kcal

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[12] For example, see: Grutsch, P. A.; Kutal, C. *J. Am. Chem. Soc.* **1986**, *108*, 3108.

[13] For a thorough discussion of the relationship between donor–acceptor orbital overlap and the rate of exchange energy transfer, see: Balzani, V.; Bolleta, F.; Scandola, F. *J. Am. Chem. Soc.* **1980**, *102*, 2152.

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(i.e. ΔE = 3–4 kcal). This slightly higher value of E_T does not appear unreasonable (e.g. it is consonant with the 430-nm onset of the phosphorescence band of Cu(prophos)BH_4[2d]), and we conclude that endoergic energy transfer from the lowest triplet of Cu(prophos)BH_4 to NBD can adequately account for the efficient, sensitized production of Q.

In the case of Cu(diphos)BH_4, the low triplet energy of 60–61 kcal results in a predicted rate constant for energy transfer to NBD of $<10^4\ M^{-1}\ s^{-1}$. This value is sufficiently small that triplet energy transfer cannot compete successfully with the other processes, with total rate constant of $\sim 10^6\ s^{-1}$, which deactivate the $^3(\sigma\text{–}a_\pi)$ excited state. Consequently, the complex is ineffective (Table I) as a sensitizer for the NBD to Q conversion.

Concluding Remarks

This investigation of the triplet-state properties of Cu(diphos)BH_4 and Cu(prophos)BH_4 has yielded information that can be used to characterize the bimolecular quenching and sensitization processes of these complexes in the presence of dienes. The key findings and their implications can be summarized as follows.

(1) Both Cu(diphos)BH_4 (E_T = 60–61 kcal) and Cu(prophos)BH_4 (E_T = 66–67 kcal) possess triplet-state energies that fall well below the average value of 76 kcal reported for a series of $Cu(PPh_3)_xCl$ and $Cu(PPh_2Me)_xCl$ (x = 1–3) complexes.[3a] By comparison, the triplet energies of all the corresponding free phosphine ligands lie in the 75–77 kcal range.[9] Thus, while coordination of a monodentate phosphine to copper produces relatively little perturbation in the energy of the lowest $^3(\sigma\text{–}a_\pi)$ state, chelation of a bis(phosphine) causes a marked energy decrease. A possible explanation for this latter behavior is provided by the observation that the energy of the $l\text{–}a_\pi$ transition in arylphosphines drops upon the introduction of alkyl groups at the ortho position of the aromatic ring.[7,8,16] It is thought that steric crowding by these substituents alters the C–P–C valence angle and/or the twist angle (angle between the axis of the phosphorus l orbital and the axis of the adjacent carbon $2p_\pi$ orbital) from the characteristic value(s) in the uncoordinated phosphine and thereby affects the transition energy. In a similar fashion, steric constraints imposed by formation of the five- and six-membered chelate rings in Cu(diphos)BH_4 and Cu(prophos)BH_4 may cause changes in one or both angles with an accompanying lowering of the triplet state energy. Detailed structural and spectroscopic studies of a series of copper(I) complexes containing chelated phosphines of varying ring size are needed to test this suggestion.

(2) Both Cu(diphos)BH_4 and Cu(prophos)BH_4 undergo intersystem crossing from $^1(\sigma\text{–}a_\pi)$ to $^3(\sigma\text{–}a_\pi)$ with high quantum efficiency ($\phi_{isc} \geq 0.64$ and ≥ 0.78, respectively). Highly efficient ($\phi_{isc} \sim 1$) intersystem crossing has also been reported for the series of $Cu(PPh_2Me)_3X$ (X = Cl^-, Br^-, I^-) complexes.[3a] Interestingly, however, only the diphos and prophos complexes phosphoresce in room-temperature fluid solution (note also that the luminescence of $Cu(PPh_3)_2BH_4$ appears to be fluorescence rather than phosphorescence[2d]). This apparent disparity in phosphorescence yields cannot be attributed to significant differences in the nonradiative rate constants of the respective $^3(\sigma\text{–}a_\pi)$ states (k_6 and k_7 in Figure 6), since all of the complexes possess comparable triplet lifetimes under these conditions. Instead, it appears that the chelated phosphine complexes possess larger phosphorescence rate constants (k_5 in Figure 6) than their nonchelated counterparts; such behavior could again be indicative of differences in the twist angle about the phosphorus–phenyl bond.[17]

(3) Triplet–triplet energy transfer is the principal mechanism by which Cu(diphos)BH_4 and Cu(prophos)BH_4 sensitize the interconversion of *cis*- and *trans*-piperylene and the valence isomerization of NBD to Q. The process is exoergic for both complexes as donors and the piperylenes as acceptors. Energy transfer from Cu(prophos)BH_4 to NBD, on the other hand, is endoergic by 3–4 kcal; nonetheless, the long lifetime of the $^3(\sigma\text{–}a_\pi)$ excited state permits the complex to acquire sufficient thermal energy from the surroundings to overcome this deficit and energy transfer occurs with high quantum efficiency. In the Cu(diphos)BH_4/NBD system, the endoergicity rises to $\sim$9 kcal and energy transfer can no longer compete with the other deactivation processes of the $^3(\sigma\text{–}a_\pi)$ state.

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Registry No. Cu(diphos)BH_4, 19681-25-5; Cu(prophos)BH_4, 81432-70-4; *cis*-piperylene, 1574-41-0; *trans*-piperylene, 2004-70-8.

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Palladium(II) Complexes of Diphenylvinyl- and Phenyldivinylphosphine

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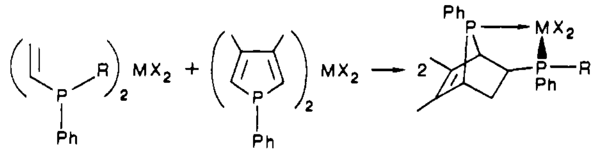
Palladium(II) complexes of the ligands L = $Ph_2PCH{=}CH_2$ and $PhP(CH{=}CH_2)_2$ have been prepared and characterized by elemental analysis, infrared spectroscopy, and ^1H, $^1H\{^{31}P\}$, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$, and $^1H/^{13}C$ HETCOR nuclear magnetic resonance spectroscopy. These complexes exist as temperature-dependent equilibrium mixtures of cis and trans isomers in solution. Equilibrium thermodynamics for the isomerization process *cis*-$L_2PdX_2 \rightleftharpoons$ *trans*-L_2PdX_2, determined by variable-temperature $^{31}P\{^1H\}$ NMR spectroscopy, demonstrate that the cis isomers are in general thermodynamically more stable than the trans isomers. However, the relative isomer stabilities are anion dependent with the trans isomer becoming more stable in the order Cl < Br < I. Coordination of a vinylphosphine to palladium(II) strongly polarizes the C=C double bond as evidenced by ^{13}C NMR data.

Introduction

We have recently reported[1] the synthesis of novel rigid asymmetric bidentate phosphines by intramolecular Diels–Alder cycloaddition reactions of metal phosphole complexes with metal vinylphosphine complexes. For M = Pd and Pt reaction 1 occurs. The rates of these reactions are a function of the metal, the halide, and the phosphine. In order to gain greater understanding regarding the factors that influence these reactions we have com-



(1)

M = Pt, Pd; R = CH=CH_2, Ph; X = Cl, Br, I

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