0.500-g sample of PCl_3 (3.65 mmol) were combined under vacuum and allowed to stand at 25 °C. After 72 h the materials were fractionated by trap-to-trap distillation. The more volatile fraction was 0.500 g of PCl_3. In a second experiment $P(CN)_3$ (~2 mmol) was combined with PCl_3 (~2 mmol) in 2.5 cm^3 of dry CD_3CN. The reaction was followed by ^{31}P NMR. Only signals for starting materials were ever detected.

In the second process the reaction between $(C_2H_5)_2NP(CN)_2$ and HCl was carried out on the vacuum line of a 100-mL flask. A 5.00-g sample of $P(CN)_2N(C_2H_5)_2$ (32.7 mmol) was frozen with a 65.4-mmol sample of HCl at −196 °C and then allowed to warm to 25 °C. After 0.5 h the volatiles were removed, fractionated, and identified by infrared spectroscopy. Only PCl_3 and a trace of HCN could be identified.

The third process involved the reaction of $P(CN)_3$ with HCl. In a 100-mL flask was frozen a 0.72-g sample of $P(CN)_3$ (6.6 mmol) (−196 °C) with a 7.3-mmol sample of HCl. The system was warmed to −78 °C, allowed to stand 10 min at −78 °C, and then fractionated through a trap at −196 °C to remove the volatiles. Trapped volatiles were identified by IR as PCl_3, HCl, and HCN. Finally, the nonvolatile residue was identified as $P(CN)_3$.

Reactions of $P(CN)_2N(C_2H_5)_2$ and $P(CN)_3$ with B_2H_6. A 0.18-g sample of $P(CN)_3$ (1.4 mmol) was frozen (−196 °C) with a 0.77-mmol sample of B_2H_6 on the vacuum line. The system was warmed to 25 °C, allowed to sit for 18 h, and then fractionated on the vacuum line. A 0.74-mm sample of B_2H_6 was recovered unchanged.

A 0.520-g sample of $P(CN)_2N(C_2H_5)_2$ (3.35 mmol) was frozen (−196 °C) on the vacuum line with a 1.83-mmol sample of B_2H_6. The system was warmed to 25 °C and allowed to stand for 18 h, and then the volatiles were removed. A 0.100-mmol sample of B_2H_6 was identified as the volatile component by IR. Thus, a 1.73-mmol sample of B_2H_6 had reacted with 3.35 mmol of $P(CN)_2N(C_2H_5)_2$.

Reactions of Cyanophosphines with Pyridine and BF_3. Approximately a 2.0-mmol sample of the desired cyanophosphine was dissolved in 2.5 mL of $CDCl_3$ in an NMR tube. In a separate tube a similar solution of the cyanophosphine in $CDCl_3$ was treated with either 2.0 mmol of pyridine or 2.0 mmol of BF_3. NMR spectra were then run on the samples.

Acknowledgment. Support of this research by the National Science Foundation through Grant No. CHE 77-01013 is gratefully acknowledged.

Registry No. $P(CN)_3$, 1116-01-4; $P(CN)_2(Ph)$, 2946-59-0; $P(CN)(Ph)_2$, 4791-48-4; $P(CN)_2N(C_2H_5)_2$, 33326-16-8; $K[P(CN)_4]$, 73104-89-9; pyridine, 110-86-1; BF_3, 7637-07-2; B_2H_6, 19287-45-7; $P(CN)_3$·py, 73104-90-2.

Contribution from the Department of Chemistry,
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Photoconversion of Norbornadiene to Quadricyclene in the Presence of a Copper(I) Carbonyl Compound[1]

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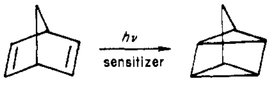
Received October 2, 1979

A detailed study of the thermal and photochemical behavior of $Cu[HB(pz)_3](CO)$ [$HB(pz)_3^-$ is hydrotris(1-pyrazolyl)borate] in the presence of norbornadiene (NBD) is reported. In solution NBD displaces CO from the coordination sphere of copper to produce a new complex formulated as $Cu[HB(pz)_3](NBD)$. This ground-state process is readily discernible by a shift in the absorption spectrum of the system to longer wavelengths. Irradiation of the complex with 313-nm light induces the valence isomerization of norbornadiene to quadricyclene with high quantum efficiency. The occurrence of this pathway is explicable in terms of the bonding changes that result from populating an excited state possessing Cu–NBD charge-transfer character.

Introduction

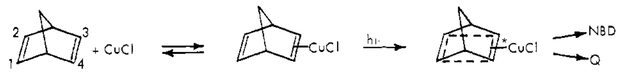
The photosensitized valence isomerization of norbornadiene, NBD, to quadricyclene, Q (eq 1), continues to be of interest



NBD Q (1)

as a model for photochemical energy storage.[2] Recently we reported that simple copper(I) salts, most notably cuprous chloride, function as effective sensitizers for this transformation.[3] Detailed spectral and mechanistic studies led us to assign a 1:1 ClCu–NBD complex as the key photoactive species in the system. As depicted in Scheme I, the immediate consequence of irradiating the intense metal–olefin charge-transfer band in the complex is to weaken the bonding between carbon atom pairs C_1–C_2 and C_3–C_4 while enhancing that between C_1–C_4 and C_2–C_3.[4] These photoinduced changes generate a reactive organic substrate which, upon relaxation, returns to NBD or completes the structural reorganization necessary to form Q.

Scheme I



In searching for new types of Cu(I) sensitizers for the NBD to Q conversion, we became intrigued by the reported properties of $Cu[HB(pz)_3](CO)$[5,6] [Figure 1; $HB(pz)_3^-$ is hydro-

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(1) Photobehavior of Copper(I) Compounds. 2. Part 1: Grutsch, P. A.; Kutal, C. *J. Am. Chem. Soc.* **1979**, *101*, 4228.

(2) Hautala, R. R.; King, R. B.; Kutal, C. In "Solar Energy: Chemical Conversion and Storage"; Hautala, R. R., King, R. B., Kutal, C., Eds.; Humana Press: Clifton, NJ, 1979; pp 333–69.

(3) (a) Schwendiman, D. P.; Kutal, C. *J. Am. Chem. Soc.* **1977**, *99*, 5677. (b) In the present context, a sensitizer is a compound which enhances the rate of the photoconversion of NBD to Q, with at least one photon being required per product molecule formed. The detailed mechanism of sensitization will depend upon the nature of the sensitizer involved. Grutsch, P. A.; Kutal, C. *Adv. Chem. Ser.* **1979**, *No. 173*, 325.

(4) These bonding changes occur regardless of the direction (metal to olefin or olefin to metal) of charge transfer: (a) Hoffmann, R. *Acc. Chem. Res.* **1971**, *4*, 1; (b) Schwendiman, D. P.; Kutal, C. *Inorg. Chem.* **1977**, *16*, 719; (c) Jones, G.; Chiang, S.-H.; Xuan, P. T. *J. Photochem.* **1979**, *10*, 1.

(5) Bruce, M. I; Ostazewski, A. P. P. *J. Chem. Soc., Dalton Trans.* **1973**, 2433.

(6) Churchill, M. R.; DeBoer, B. G.; Rotella, F. J.; Abu Salah, O. M; Bruce, M. I. *Inorg. Chem.* **1975**, *14*, 2051.

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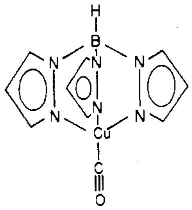

Figure 1. Structure of Cu[HB(pz)$_3$](CO).

tris(1-pyrazolyl)borate]. Most notable is the presence of a reasonably stable Cu–CO bond.[7] This feature of Cu[HB(pz)$_3$](CO) has been ascribed to the high σ-donating character of HB(pz)$_3^-$ which, in turn, enhances the back-donation from copper to the π-accepting CO ligand.[5] Although the compound persists intact when dissolved in noncoordinating solvents (e.g., ligroin, acetone), it reacts with a variety of uncharged ligands, L, including phosphines, arsines, isocyanides, and *olefins*, to yield Cu[HB(pz)$_3$](L) with the concomitant evolution of CO.[5] When L is NBD, a species analogous to the photoactive ClCu–NBD complex (Scheme I) should thus be formed. To explore this interesting possibility, we undertook a detailed investigation of the thermal and photochemical behavior of Cu[HB(pz)$_3$](CO) in the presence of NBD. A full account of our results is reported here.

Experimental Section

(a) Reagents. Samples of CuCl[8] and K[HB(pz)$_3$][9] were prepared by literature procedures. The following modification of previous synthetic schemes[5,10] affords a satisfactory yield of Cu[HB(pz)$_3$](CO).[11] A three-necked flask containing 30 mL of deionized water and 40 mL of pentane was placed in an ice bath and the solvent mixture bubbled with a brisk stream of carbon monoxide for 50 min. Addition of 0.24 g of K[HB(pz)$_3$] and 0.1 g of CuCl produces a suspension which is stirred for 60 min while being bubbled with CO. Virtually all of the solid material has dissolved at this point. The organic layer is then removed with a syringe and the aqueous layer extracted with two 10-mL portions of cold ligroin (boiling range 30–50 °C) saturated with CO. The combined pentane–ligroin fractions are dried by stirring with 1 g of anhydrous sodium sulfate for 15 min, after which the solution is filtered through a Schlenk-type funnel by using a positive pressure of CO. Evaporation of the light blue filtrate to dryness was achieved by passing a stream of CO over its surface; this procedure yields white, shiny crystals intermingled with a few particles of a blue substance. Extraction of the crude product with 5 mL of cold, CO-saturated ligroin, followed by filtration and evaporation of the filtrate as described above, affords white crystals of Cu[HB(pz)$_3$](CO). Anal. Calcd: C, 39.42; H, 3.31. Found: C, 39.60; H, 3.45. Analyses were performed by Galbraith Laboratories. The infrared spectrum of the complex dissolved in hexane exhibits the reported[5] B–H (~2465 cm^{-1}) and C–O (2083 cm^{-1}) stretching modes.

Norbornadiene (Aldrich) was obtained in ≥99% purity by three successive distillations from potassium metal under a nitrogen atmosphere. It was stored under nitrogen at ~0 °C and freshly distilled prior to each use. Quadricyclene was prepared by the method of Smith[12] and stored at 0 °C. Hexane was purified by a standard procedure[13] and was freshly distilled under nitrogen prior to each thermal or photochemical experiment.

(b) Spectral Studies. Reproducible extinction coefficients for the air-sensitive complex Cu[HB(pz)$_3$](CO) were obtained by the following procedure. A sample of the complex was weighed on a Cahn microbalance enclosed in a nitrogen-purged glovebag. The solid was then placed in a volumetric flask and dissolved in hexane. An aliquot of the resulting solution was transferred by syringe to an absorption cell which could be tightly stoppered, and the electronic spectrum was recorded on a Cary 15 spectrophotometer. A similar procedure was employed to obtain the spectrum of the complex in neat NBD. Infrared spectra were measured on Perkin-Elmer 621 or 599 spectrometers using matched 0.5-mm NaCl solution cells.

(c) Thermal Studies. All solutions were prepared under a nitrogen atmosphere in a glovebag. A sample of Cu[HB(pz)$_3$](CO) was dissolved in hexane and its concentration determined by transferring an aliquot to a spectrophotometer cell and measuring the absorbance at 275 nm (where $\epsilon = 4.2 \times 10^3$ M^{-1} cm^{-1}). A stock solution 4.0×10^{-3} M in complex could then be prepared by appropriate dilution of the original solution. Four 5-mL volumetric flasks were filled to the mark with the stock solution, and a predetermined amount of neat NBD was added with a microliter syringe to obtain the desired final concentration (0.1–0.5 M) of the diene.[14] The flasks were stoppered, shaken for 10 s, and finally unstoppered to release any pressure buildup resulting from liberated carbon monoxide. A disposable pipet was used to transfer a portion of each sample to an infrared cell. The IR spectrum (run in the absorbance mode) was then recorded in the region encompassing the C–O stretching band at 2083 cm^{-1}. Comparison of the area of this band (determined by planimetry) with a calibration curve prepared from standard solutions [$(0.8–4.0) \times 10^{-3}$ M] of Cu[HB(pz)$_3$](CO) yielded the concentration of the parent complex still remaining in the sample. Following each spectral run, the IR cell was flushed with hexane and rinsed with a portion of the next sample solution.

(d) Photochemical Studies. Solutions containing 4.0×10^{-3} M Cu[HB(pz)$_3$](CO) and varying amounts of NBD were prepared by the procedure described in the preceding section. In a typical photochemical run, a 3-mL aliquot of the sample solution was transferred by syringe to a 1-cm rectangular quartz cell fitted with a ground-glass stopper. Irradiations were performed by using a 450-W medium-pressure mercury-arc lamp mounted in a merry-go-round apparatus similar to one described in the literature.[15] The wavelength region centered at 313 nm was isolated with a 23-nm bandwidth by using a combination of a Corning 7-54 filter and a circulating solution of 10^{-3} M K_2CrO_4–1% K_2CO_3.[16] Light intensity was measured by ferrioxalate actinometry.[17]

Irradiated samples were analyzed for NBD and Q by gas chromatography using a Varian Model 2700 gas chromatograph equipped with a flame-ionization detector and containing a 10 ft × $^1/_8$ in. stainless-steel column packed with 5% OV-101 on Chromosorb G HP (80–100 mesh). The operating temperatures of the instrument were as follows: injector, 130–140 °C; column, 50–70 °C (isothermal); detector, 240 °C. The flow rate of the nitrogen carrier gas was 20 mL/min. Gas chromatographic data (retention times, peak areas) were collected and analyzed by a Perkin-Elmer Sigma 10 data system. The area of the Q peak was converted to concentration units by comparison with a calibration curve constructed from standard Q solutions. Measurements taken at various times following irradiation reveal that the Q produced is thermally stable over a period of at least several hours.

Identification of carbon monoxide evolved from solutions of Cu[HB(pz)$_3$](CO) was accomplished by using a gas-analysis apparatus recently described in the literature.[18] An authentic sample of the gas was employed as a standard.

Results and Discussion

(a) Thermal Behavior of Cu[HB(pz)$_3$](CO). Solid Cu[HB(pz)$_3$](CO) dissolves in neat NBD with clearly discernible

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[7] Several other examples of reasonably stable Cu–CO bonds have been reported in recent years: (a) Tsuda, T.; Habu, H.; Horiguchi, S.; Saegusa, T. *J. Am. Chem. Soc.* **1974**, *96*, 5930; (b) Gagné, R. R.; Allison, J. L.; Gall, R. S.; Koval, C. A. *Ibid.* **1977**, *99*, 7170; (c) Pasquali, M.; Marchetti, F.; Floriani, C. *Inorg. Chem.* **1978**, *17*, 1684.

[8] Brauer, G. "Handbook of Preparative Inorganic Chemistry", 2nd ed.; Riley, R. F., Translation Ed.; Academic Press: New York, 1963.

[9] Trofimenko, S. *J. Am. Chem. Soc.* **1967**, *89*, 3170.

[10] Mealli, C.; Arcus, C. S.; Wilkinson, J. L.; Marks, T. J.; Ibers, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 711.

[11] All manipulations must be carried out under an atmosphere of carbon monoxide or argon to prevent the facile oxidation of Cu(I).

[12] Smith, C. D. *Org. Synth.* **1971**, *51*, 133.

[13] Riddick, J. A.; Bunger, W. B. "Organic Solvents", 3rd ed.; Wiley: New York, 1971.

[14] The small (<5%) volume change resulting from the addition of NBD was neglected.

[15] Moses, F. G.; Liu, R. S. H.; Monroe, B. M. *Mol. Photochem.* **1969**, *1*, 245.

[16] 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.

[17] Hatchard, C. G.; Parker, C. A. *Proc R. Soc. London, Ser. A* **1956**, *235*, 518.

[18] King, A. D.; King, R. B.; Yang, D. B. *J. Am. Chem. Soc.* **1980**, *102*, 1028.

Table I. Percentage of Coordinated CO Released from $Cu[HB(pz)_3](CO)^a$ as a Function of Added NBD

[NBD], M	% CO released^b	[NBD], M	% CO released^b
0.10	27 ± 2	0.35	45 ± 8
0.25	37 ± 6	0.50	59 ± 8

[a] Initial concentration of $Cu[HB(pz)_3](CO)$ is 4×10^{-3} M; the solvent is hexane. [b] Error limits represent mean deviation of three or more runs.

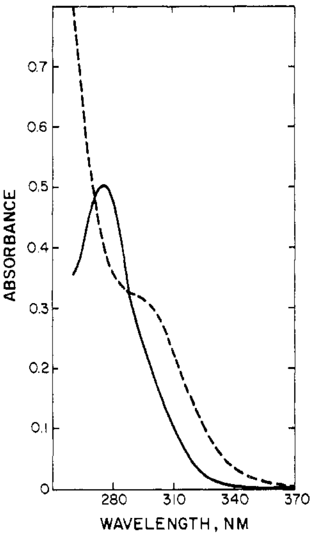
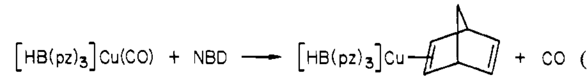


Figure 2. Spectral change accompanying the conversion of $Cu[HB(pz)_3](CO)$ to $Cu[HB(pz)_3](NBD)$ in a two-component spectrophotometer cell: —, spectrum observed when hexane solutions of $Cu[HB(pz)_3](CO)$ and NBD occupy separate compartments; ----, spectrum resulting when the two solutions are mixed.

effervescence. Gas chromatographic analysis of the evolved gas establishes its identity as carbon monoxide. Moreover, the distinctive C–O stretching band at 2083 cm^{-1} in the original compound is absent in the IR spectrum of the NBD solution. Collectively, these qualitative observations indicate that CO is displaced from the coordination sphere of copper by NBD (eq 2). We favor the 1:1 formulation of the resulting product on the grounds that (1) $Cu[HB(pz)_3](L)$ complexes are isolated in high yields upon mixing $Cu[HB(pz)_3](CO)$ with an assortment of uncharged ligands, L[5], (2) a coordination number exceeding four (e.g., $Cu[HB(pz)_3](NBD)_2$) is exceedingly rare for Cu(I),[7b,19] and (3) NBD seemingly prefers monodentate (exo) over bidentate (endo) coordination to Cu(I).[20]



(2)

By monitoring the peak area of the C–O stretching band in $Cu[HB(pz)_3](CO)$, we can directly determine the percent conversion of this complex to $Cu[HB(pz)_3](NBD)$. The results compiled in Table I reveal that appreciable concentrations of the olefin are needed to completely displace the coordinated CO group. By comparison, as little as 0.062 M triphenylphosphine effects a quantitative conversion to $Cu[HB(pz)_3](PPh_3)$. These and earlier observations[5] suggest that the affinity of the coordinatively unsaturated $Cu[HB(pz)_3]$ moiety for uncharged ligands follows the order $PPh_3 > CO > NBD$.

The electronic absorption spectrum of $Cu[HB(pz)_3](CO)$ in hexane displays peaks at 275 (ϵ $(4.2 \pm 0.1) \times 10^3$ M^{-1} cm^{-1}) and 215 nm. On the basis of its similarity to the spectra of $K[HB(pz)_3]$[21] and $Zn[HB(pz)_3]_2$[22] (also a d^{10} system), we assign the short-wavelength feature as a π–π^* transition localized on the pyrazolylborate ligand. Since the 275-nm band disappears upon displacement of coordinated CO from the parent complex by NBD (Figure 2), it most likely arises from a charge-transfer transition characteristic of the Cu–CO moiety.[23] The spectrum of the resulting product, $Cu[HB(pz)_3](NBD)$, displays a strong new absorption (with a shoulder at ~293 nm) that extends beyond 360 nm. We attribute this absorption to a Cu–NBD charge-transfer transition in the $Cu[HB(pz)_3](NBD)$ complex on the grounds that neither of the individual components ($Cu[HB(pz)_3]$ or NBD) absorbs appreciably above 260 nm. A similar feature in the electronic spectrum of ClCu–NBD has likewise been assigned as a metal–olefin charge-transfer transition.[4b]

Table II. Quantum Yields for the 313-nm Photoisomerization of NBD to Q in the Presence of $Cu[HB(pz)_3](CO)^a$

[NBD], M	$\phi_{obsd}{}^{b,c}$	$\phi_{in}{}^d$
0.10	0.37 ± 0.01^e	0.60
0.25	0.40 ± 0.02	0.56
0.35	0.44 ± 0.00	0.56
0.50	0.51 ± 0.04	0.58
9.86 (neat)	0.65 ± 0.07	

[a] Initial concentration of $Cu[HB(pz)_3](CO)$ is 4×10^{-3} M; the solvent is hexane. [b] Experimentally observed quantum yield. [c] Error limits represent mean deviation of two or more runs. [d] Intrinsic quantum yield calculated by using eq 3. [e] ϕ_{obsd} is independent of the time (15, 30, 45, 60 min) of irradiation.

(b) Photochemical Behavior of $Cu[HB(pz)_3](CO)$. The key photochemical observations (Table II) can be summarized as follows. (i) Q is produced upon 313-nm irradiation of hexane solutions originally charged with $Cu[HB(pz)_3](CO)$ and NBD. (ii) The observed quantum efficiency (ϕ_{obsd}) of this process rises with increasing NBD concentration. (iii) ϕ_{obsd} exhibits no dependence upon the time of irradiation. (iv) Catalytic factors (moles of Q produced/mole of $Cu[HB(pz)_3](CO)$ initially added) of ≥65 are attainable.

Comparison of the thermal and photochemical data in Tables I and II, respectively, reveals that the rise in the quantum efficiency of Q production with increasing NBD concentration parallels the conversion of the parent carbonyl complex to $Cu[HB(pz)_3](NBD)$. In the limiting case (e.g., pure NBD) where this conversion is complete, ϕ_{obsd} attains its highest value. We conclude from this behavior that $Cu[HB(pz)_3](NBD)$ is the *key photoactive species leading to Q production.*

The smaller ϕ_{obsd} values measured at NBD concentrations ≤0.5 M arise from the competitive and unproductive absorption of the incident radiation by the original complex, $Cu[HB(pz)_3](CO)$, remaining in solution. To correct for this factor, we employ the relationship in eq 3, where ϕ_{in} is the

$$\phi_{obsd} = \phi_{in}\left(\frac{A_{Cu\text{-}NBD}}{A_{Cu\text{-}NBD} + A_{Cu\text{-}CO}}\right) \qquad (3)$$

intrinsic quantum efficiency with which photoexcited $Cu[HB(pz)_3](NBD)$ produces Q, and $A_{Cu\text{-}NBD}$ and $A_{Cu\text{-}CO}$ denote the absorbances of the indicated complexes at 313 nm. Since

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(19) Jardine, F. H. *Adv. Inorg. Chem. Radiochem.* **1975**, *17*, 115.

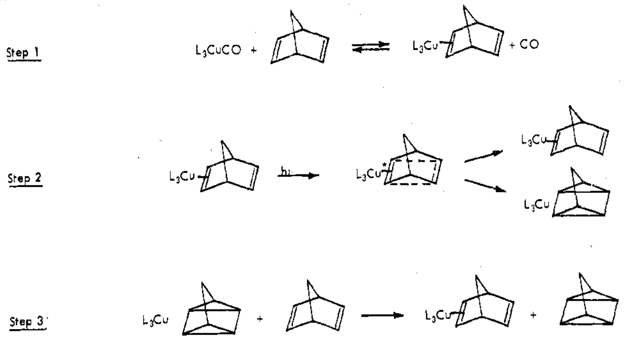
(20) Baenziger, N. C.; Haight, H. L.; Doyle, J. R. *Inorg. Chem.* **1964**, *3*, 1535. Salomon, R. G.; Kochi, J. K. *J. Am. Chem. Soc.* **1973**, *95*, 1889.

(21) The absorption spectrum of $K[HB(pz)_3]$ in ethanol contains a band at 216 nm.

(22) Jesson, J. P.; Trofimenko, S.; Eaton, D. R. *J. Am. Chem. Soc.* **1967**, *89*, 3148.

(23) As additional support for this assignment, we note that a hexane solution of $Cu[HB(pz)_3](CO)$ left to sit overnight at −10 °C experiences a decrease in the intensity of the 275-nm band. This behavior apparently arises from a loss of coordinated CO, since the original absorption spectrum can be regenerated upon bubbling the solution with carbon monoxide.

Scheme II[a]



[a] L_3Cu denotes the $[HB(pz)_3]Cu$ moiety.

the fraction of light absorbed by the photoactive complex (given by the term in parentheses in eq 3) tends toward unity with increasing NBD concentration, the limiting value of ϕ_{obsd} should approach ϕ_{in}. Using the 313-nm extinction coefficients for $Cu[HB(pz)_3](NBD)$ (ϵ 2.2 × 10^3 M^{-1} cm^{-1}) and $Cu[HB(pz)_3](CO)$ (ϵ 5.0 × 10^2 M^{-1} cm^{-1}), the concentrations of the two complexes obtainable from Table I, and the values of ϕ_{obsd} listed in Table II, we can calculate ϕ_{in} as a function of NBD concentration (last column in Table II).[24] Both the constancy of ϕ_{in} (0.58 ± 0.02) and its acceptable agreement with the limiting value of ϕ_{obsd} measured in pure NBD (0.65 ± 0.07) corroborate our assignment of $Cu[HB(pz)_3](NBD)$ as the photoactive species in solution.

The insensitivity of ϕ_{obsd} to the time of irradiation establishes that little, if any, $Cu[HB(pz)_3](NBD)$ is generated photochemically. The thermal substitution process in eq 2 thus appears to be the only important pathway leading to this photoactive species. Parenthetically, we note that the validity of the relationship in eq 3 hinges upon this result, since the concentrations of $Cu[HB(pz)_3](NBD)$ and $Cu[HB(pz)_3](CO)$ used to calculate absorbance values were derived from the thermal data in Table I.

(c) Mechanism of Sensitization by $Cu[HB(pz)_3](CO)$. At the outset we may anticipate that the mechanism of sensitization by CuCl (Scheme I) should provide a reasonable model for the behavior of $Cu[HB(pz)_3](CO)$ observed in the present study. Both compounds form a ground-state complex with NBD as evidenced by a shift of their electronic absorption spectra to longer wavelengths upon addition of the diene. Such spectral behavior reflects the creation within the complex of one or more low-lying excited states possessing metal–olefin charge-transfer character. Upon photoexcitation of the complex to this type of state, changes occur within the π-bonding framework of the coordinated NBD molecule which facilitate its rearrangement to Q.[4]

Guided by these general considerations, we feel that the sequence of steps in Scheme II represents an attractive formulation of the mechanism of sensitization by $Cu[HB(pz)_3](CO)$. Since several of the experimental observations supporting this mechanism have already been discussed, we need only summarize the more salient features here.

Step 1 involves the thermal displacement of CO from the parent compound by NBD.[25] Irradiation with 313-nm light in step 2 excites $Cu[HB(pz)_3](NBD)$ to a metal–olefin charge-transfer excited state. The consequent redistribution of electron density generates a reactive species that can partition between relaxation pathways leading to NBD or Q. Since Q has little affinity for Cu(I),[3a] it readily diffuses away from the immediate vicinity of the $Cu[HB(pz)_3]$ moiety. Regeneration of the photoactive $Cu[HB(pz)_3](NBD)$ complex in step 3 then occurs and accounts for the catalytic role of Cu(I) in the sensitization process.

(d) Concluding Remarks. The finding that $Cu[HB(pz)_3](CO)$ sensitizes the valence isomerization of norbornadiene to quadricyclene via formation of a photoactive Cu–NBD complex establishes that this mechanism is not limited to simple CuX (X = Cl, Br, etc.) salts. More generally, the present study suggests that monomeric, four-coordinate Cu(I) compounds containing a single substitutionally labile ligand constitute an interesting and potentially useful class of inorganic sensitizers for olefin photoreactions. We suspect, for example, that the ready accessibility of only one coordination site about copper should make these compounds effective as sensitizers for intramolecular rearrangements of olefins. Conversely, oligomerization processes that require the close proximity of two or more olefin molecules at a single metal center would be retarded. The latter pathway becomes more likely, on the other hand, for Cu(I) compounds (e.g., $Cu(O_3SCF_3)$[26]) which are prone to such multiple coordination of olefins. In optimal cases, it may prove possible to dictate the preferred course of an olefin photoreaction by judicious selection of the Cu(I) sensitizer.[3b]

Acknowledgment. The authors acknowledge the generous financial support of the Department of Energy. We also wish to thank Drs. A. D. King, Jr., and M. I. Bruce for their helpful advice and Dr. D. B. Yang for his technical assistance.

Registry No. $Cu[HB(pz)_3](CO)$, 52374-64-8; NBD, 121-46-0; $Cu[HB(pz)_3](NBD)$, 73116-63-9; Q, 278-06-8.

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(24) Since the filter combination employed in the photochemical studies transmits small amounts of light at wavelengths other than 313 nm,[16] we repeated the calculation of ϕ_{in} taking this factor into account. The resulting values of ϕ_{in} were ~5% higher than those reported in Table II.

(25) Formation of the photoactive species, $Cu[HB(pz)_3](NBD)$, from the parent carbonyl complex in step 1 is written as a reversible process, since we find that bubbling the solution with CO drives the system to the left with a concomitant decrease in ϕ_{obsd}.

(26) Salomon, R. G.; Kochi, J. K. *J. Am. Chem. Soc.* **1974**, *96*, 1137. Evers, J. T. M.; Mackor, A. *Tetrahedron Lett.* **1978**, 2317.