and the CD band shapes differ in the two cases.

The general theory of the interference effects in CD spectra resulting from the superposition of a sharp transition upon a broad continuous excitation has been investigated for chiral molecules with C_2 point symmetry.[23] The application of the theory to IV, and analogous complexes with C_2 symmetry, indicates that the line-shape function, L_{CD}, expected for the CD spectra in the region of the frequency ν_{01} of a C–H stretching fundamental has the form

$$L_{CD} = \rho(\epsilon^2 + \delta^2)^{-1}\{R_{01} + \epsilon[\mu_{01}\cdot\mathbf{m}_{dd} + \mu_{dd}\cdot\mathbf{m}_{01}] + \epsilon^2 R_{dd}\} \quad (7)$$

where ρ is the state density of the broad manifold of the d–d transition, with the rotational strength, R_{dd}, in the frequency region of the sharp vibrational transition, with the rotational strength, R_{01}. In eq 7, ϵ and δ are dimensionless scaled quantities, respectively representing the frequency region centered upon ν_{01} and the width, $\Delta\nu_{01}$, of the vibrational fundamental, in units of the potential, V_{ev}, between the electronic and the vibrational transition charge distributions, namely

$$\epsilon = hc(\bar{\nu} - \bar{\nu}_{01})/V_{ev} \quad (8)$$

$$\delta = hc\Delta\bar{\nu}_{01}/2V_{ev} \quad (9)$$

The coupling term, V_{ev}, corresponds to the Coulombic potential between the electric hexadecapole moment of the d–d transition (Figure 4) and the electric dipole of the C–H stretching vibration transition, governed by a geometric tensor analogous to that of eq 2.

The rotational strength of the C–H stretching vibration transitions, R_{01}, measured by the CD band areas observed for the d^{10} complex $[Zn(l\text{-sp})Cl_2]$ over the 2800–3000-cm^{-1} region,[24] is small and makes only a minor contribution to the CD line shape found for the analogous cobalt(II) complexes over the same wavenumber region (Figure 3). The first of the two cross terms in eq 7, $[\mu_{01}\cdot\mathbf{m}_{dd}]$, is the more important, since the C–H stretching transition and the d–d transition are primarily electric dipole and magnetic dipole allowed, respectively. This term contributes a dispersive line shape to the CD curve,[23] as is particularly evident in the case of complex IV and its bromo analogue in the region of both the symmetric and the antisymmetric stretching modes of the CH_2 groups in ligand II, at 2855 and 2940 cm^{-1}, respectively (Figure 3). The final term of eq 7, dependent upon the rotational strength of the d–d transition, contributes an interference feature to the CD line shape, a resonance or an antiresonance, dependent upon the positive or the negative sign of the ratio R_{01}/R_{dd}, with an amplitude proportional to the magnitude of that ratio.[23] A comparison of the CD spectra of the zinc(II) and cobalt(II) complexes $[M^{II}(l\text{-sp})Cl_2]$ over the 2800–3000-cm^{-1} range[24] shows that the ratio is small, $\sim 10^{-2}$, and the interference features are not so evident as the dispersion effect arising from the first cross term of eq 7 (Figure 3).

Acknowledgment. We thank the U.K. Science Research Council for support.

Registry No. Co(l-α-isp)Cl_2, 71392-82-0; Co(l-α-isp)Br_2, 79357-60-1; Co(l-α-isp)I_2, 79390-70-8.

Contribution from the Department of Chemistry,
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Ligand Control of the Mechanism of Photosensitization by Copper(I) Compounds[1]

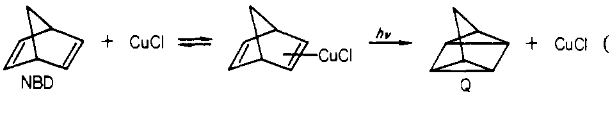
NOPADOL BORSUB, SHI-CHING CHANG, and CHARLES KUTAL*

Received March 23, 1981

Formation of a ground-state complex between $CuBr(py)(PPh_3)$ (py is pyridine) and norbornadiene (NBD) occurs upon mixing the compounds in benzene. Irradiation of the complex with 313-nm light generates the valence isomer quadricyclene (Q) with moderate observed quantum efficiency. This efficiency varies with the nature and concentration of excess ligands present in solution. Spectral studies reveal that this behavior arises from the creation of new Cu(I) species whose sensitization properties differ from those of $CuBr(py)(PPh_3)$. Thus a sufficient excess of triphenylphosphine converts the parent compound to $CuBr(PPh_3)_3$. The latter species functions as an effective sensitizer for Q production but by a pathway involving bimolecular interaction of photoexcited $CuBr(PPh_3)_3$ with ground-state NBD. These results demonstrate that the mechanism of sensitization by Cu(I) can be controlled by the judicious addition of ligands to the system.

Introduction

Recent work from this laboratory has established that copper(I) compounds can sensitize the photoisomerization of norbornadiene (NBD) to quadricyclene (Q) via two distinct mechanisms.[2] The first, summarized in eq 1, features the



(1)

formation of a ground-state copper(I)–norbornadiene complex that, upon the absorption of a photon, generates the highly strained Q molecule. Simple CuX salts[3] and $Cu[HB(pz)_3]CO$[4] function as sensitizers in this manner. An alternative pathway followed by $Cu(PPh_3)_2BH_4$ and $Cu(PPh_2Me)_3BH_4$[5] is depicted in eq 2. Here sensitization results from the bimolecular

$$Cu(PPh_3)_2BH_4 \xrightarrow{h\nu} Cu(PPh_3)_2BH_4^* \xrightarrow{NBD} Cu(PPh_3)_2BH_4^*{,}NBD \rightarrow Cu(PPh_3)_2BH_4 + Q \quad (2)$$

interaction of the photoexcited copper(I) compound with ground-state NBD.

A combination of structural and electronic factors will determine which of the two sensitization mechanisms predominates for a particular Cu(I) compound.[6] The ready availability of a vacant coordination site about copper clearly favors the first pathway. Conversely, sensitization via the second mechanism will become more prominent among coordinatively saturated Cu(I) compounds whose ligands are not

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(1) Photobehavior of Copper(I) Compounds. 3. Part 2: Sterling, R. F.; Kutal, C. *Inorg. Chem.* **1980**, *19*, 1502.

(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) Schwendiman, D. P.; Kutal, C. *J. Am. Chem. Soc.* **1977**, *99*, 5677.

(4) Reference 1; $HB(pz)_3^-$ is hydrotris(1-pyrazolyl)borate.

(5) Grutsch, P. A.; Kutal, C. *J. Am. Chem. Soc.* **1979**, *101*, 4228.

(6) Grutsch, P. A.; Kutal, C. *Adv. Chem. Ser.* **1979**, *No. 173*, 325.

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readily displaced by NBD and whose low-lying electronic excited states are capable of undergoing significant energy-transfer and/or charge-transfer interactions with the diene.

During an investigation of $CuBr(py)(PPh_3)$ (py is pyridine) as a sensitizer for the NBD to Q conversion, we noted an unusual dependence of the observed sensitization efficiency, ϕ_{obsd}, upon the presence of excess ligands in solution. Thus ϕ_{obsd} decreases upon addition of py, whereas the opposite effect can obtain with PPh_3. Closer scrutiny reveals that the first coordination sphere of $CuBr(py)(PPh_3)$ does not remain intact under these conditions. Instead, the compound undergoes ligand addition and/or substitution processes that generate new Cu(I) species whose proclivities for sensitization differ from that of their parent. An intriguing consequence of this behavior is the ability to *alter* the mechanism by which Cu(I) functions as a sensitizer. Our studies of $CuBr(py)(PPh_3)$ and related systems are reported in detail here.

Experimental Section

(a) Reagents. The synthetic procedures of Jardine et al.[7] afford good yields of $CuBr(py)(PPh_3)$ and $CuBr(PPh_3)_3$. Anal. Calcd for $CuBr(py)(PPh_3)$: C, 56.97; H, 4.16; mol wt, 485. Found: C, 56.77; H, 4.18; mol wt, 480 (in chloroform). Anal. Calcd for $CuBr(PPh_3)_3$: C, 69.71; H, 4.87; mol wt, 930. Found: C, 69.81; H, 5.03; mol wt, 608 (0.016 M compound in benzene). Analyses were performed by Galbraith Laboratories. Triphenylphosphine was recrystallized from ethanol and dried under vacuum. Pyridine was distilled prior to use.

Norbornadiene was purified by refluxing the commercially available (Aldrich) material with potassium metal under a nitrogen atmosphere followed by distillation through a 4 ft × $^3/_4$ in. glass column packed with stainless-steel sponge. This procedure was repeated three times and the final distillate stored under nitrogen at 0 °C to minimize peroxide formation. Quadricyclene was prepared by the method of Smith.[8] Reagent-grade benzene was washed repeatedly with concentrated sulfuric acid until the acid layer was not appreciably discolored. The benzene was then washed successively with distilled water, a 1% aqueous solution of sodium bicarbonate, water, and a saturated aqueous solution of sodium chloride. Distillation from P_4O_{10} afforded the dry, high-purity solvent employed in all photochemical studies. Spectral-grade cyclohexane was used as received for the measurement of absorption spectra.

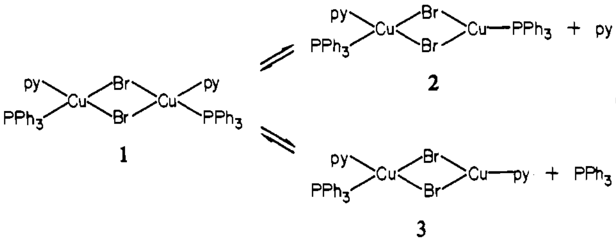
(b) Spectral and Photochemical Studies. Electronic absorption spectra were recorded on Cary 15 and 219 spectrophotometers. Absorbance changes resulting from the addition of various ligands to solutions of $CuBr(py)(PPh_3)$ or $CuBr(PPh_3)_3$ were monitored in a two-compartment cell. Typically, one compartment was filled with a solution of the copper(I) compound while an equal volume of solution containing the ligand was added to the other compartment. Evidence for Cu(I)–ligand interactions was obtained from comparison of the absorption spectra measured before and after mixing (i.e., shaking the cell for 2–3 min) the two solutions.

Nitrogen-purged benzene solutions containing NBD, nonane as internal standard for gas-chromatographic analyses, and sufficient Cu(I) sensitizer to absorb >99% of the incident light were irradiated in 1-cm quartz cells fitted with a ground-glass stopper. Sample temperatures during irradiation typically were 30 ± 1 °C. The photolysis apparatus and filter combination used to isolate the 313-nm Hg line have been described.[1] Light intensity was determined by ferrioxalate actinometry.[9]

Irradiated samples were analyzed for NBD and Q by gas chromatography. The equipment and operational conditions employed were very similar to those reported previously.[1]

Results and Discussion

(a) Solution, Spectral, and Sensitization Properties of $CuBr(py)(PPh_3)$. Jardine et al. investigated the behavior of $CuBr(py)(PPh_3)$ in solution with the aim of assigning the most probable structure.[7] Among the structural formulations considered were (i) ionic species (e.g., $Cu(py)_2(PPh_3)_2^+$-$CuBr_2^-$), (ii) undissociated bromide-bridged dimers (e.g., **1** in eq 3), (iii) discrete three-coordinate monomers, and (iv)



(3)

dimeric species that have undergone complete dissociation of an uncharged ligand (e.g., **2** and **3** in eq 3). Structure i can be discounted on grounds that $CuBr(py)(PPh_3)$ behaves as a nonelectrolyte in nitrobenzene.[7] The close agreement between the calculated and observed molecular weights in chloroform effectively rules out structure ii. The remaining possibilities, iii and iv, appear to be equally compatible with the available evidence, and no clear choice between them can be made. Likewise, a mixture of Cu(I) complexes belonging to these two structural types cannot be discounted.[10] While some uncertainty thus attends the assignment of the structure(s) of $CuBr(py)(PPh_3)$ in solution, it is important to note that each of the possible choices contains a coordinatively unsaturated copper atom which should be susceptible to ligand addition processes (vide infra).

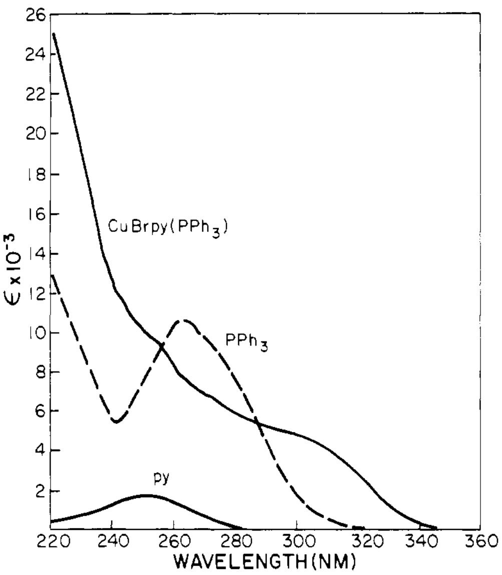


Figure 1. Electronic absorption spectra of $CuBr(py)(PPh_3)$ (2.6×10^{-5} M), triphenylphosphine, and pyridine in cyclohexane.

The electronic absorption spectra of triphenylphosphine, pyridine, and $CuBr(py)(PPh_3)$ in cyclohexane are compared in Figure 1. Each ligand displays a prominent band[11] that

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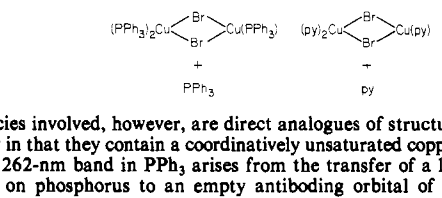
(7) Jardine, F. H.; Rule, L.; Vohra, A. G. *J. Chem. Soc. A* **1970**, 238.

(8) Smith, C. D. *Org. Synth.* **1971**, *51*, 133.

(9) Hatchard, C. G.; Parker, C. A. *Proc. R. Soc. London, Ser. A* **1956**, *235*, 518.

(10) It is possible to devise additional equilibria that are consistent with the observed solution properties of $CuBr(py)(PPh_3)$



The species involved, however, are direct analogues of structure types iii and iv in that they contain a coordinatively unsaturated copper atom.

(11) (a) The 262-nm band in PPh_3 arises from the transfer of a lone-pair electron on phosphorus to an empty antiboding orbital of π origin centered on a phenyl ring (1–a_π transition): Kasha, M.; Rawls, H. R. *Photochem. Photobiol.* **1968**, *7*, 561. (b) The 252-nm band in py has been assigned to a π–π^* transition: Innes, K. K.; Byrne, J. P.; Ross, I. G. *J. Mol. Spectrosc.* **1967**, *22*, 125.

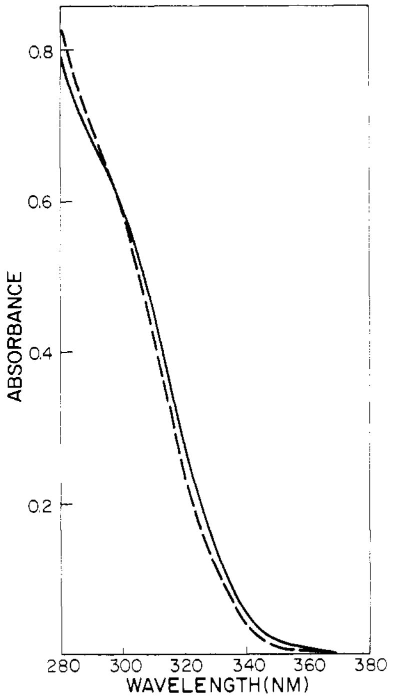


Figure 2. Spectral change that occurs upon mixing a 2.38 × 10^{-4} M solution of CuBr(py)(PPh_3) with an equal volume of a 0.2 M solution of NBD in a two-compartment spectrophotometer cell: (—), spectrum before mixing; (---), spectrum after mixing. The solvent is benzene.

has no obvious counterpart in the Cu(I) compound. We infer from this result that the energies of at least some of the low-lying electronic states localized on PPh_3 and py are perturbed appreciably upon coordination of these ligands to copper. The rather featureless spectrum of CuBr(py)(PPh_3) probably reflects the overlapping of several ligand-centered and metal-ligand charge-transfer bands. Further complicating the task of identifying individual transitions is the aforementioned possibility that more than one Cu(I) species exists in solution. Based upon comparisons with other copper(I)-pyridine compounds,[12] however, it appears reasonable to assign the shoulder at ~310 nm as a Cu → py charge-transfer transition.

Addition of NBD, PPh_3, or py to a benzene solution of CuBr(py)(PPh_3) causes the spectral changes depicted in Figures 2-4. Such behavior constitutes prima facie evidence of ground-state complex formation between the added ligand and Cu(I). The competition between two different ligands for a coordination site on copper was investigated in the following manner. Absorption spectra were measured before and after mixing 0.2 M NBD with a solution containing either (a) 2 × 10^{-4} M CuBr(py)(PPh_3) and 1 × 10^{-3} M PPh_3 or (b) 2 × 10^{-4} M CuBr(py)(PPh_3) and 3 × 10^{-3} M py. No spectral changes result from NBD addition to solution a, indicating that the diene is unable to displace PPh_3 from the first coordination sphere of copper under these conditions. In contrast, added NBD effects a substantial change (Figure 5) in the spectrum of solution b; moreover, the change is just that expected (compare to Figures 2 and 4) if NBD were displacing a coordinated py molecule.

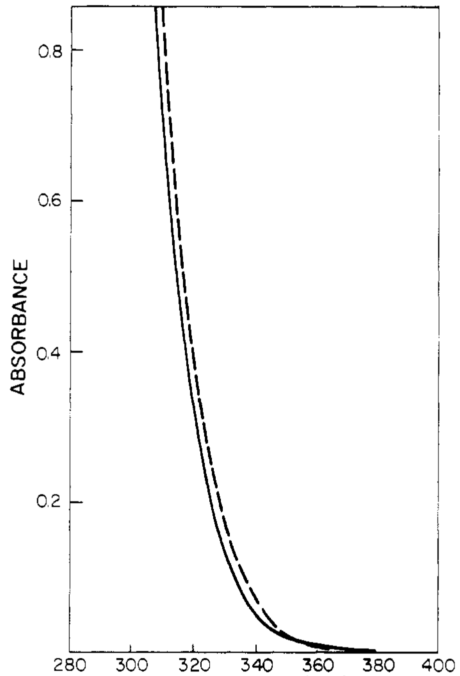


Figure 3. Spectral change that occurs upon mixing a 2.12 × 10^{-4} M solution of CuBr(py)(PPh_3) with an equal volume of a 1.23 × 10^{-3} M solution of PPh_3 in a two-compartment spectrophotometer cell: (—), spectrum before mixing; (---), spectrum after mixing. The solvent is benzene.

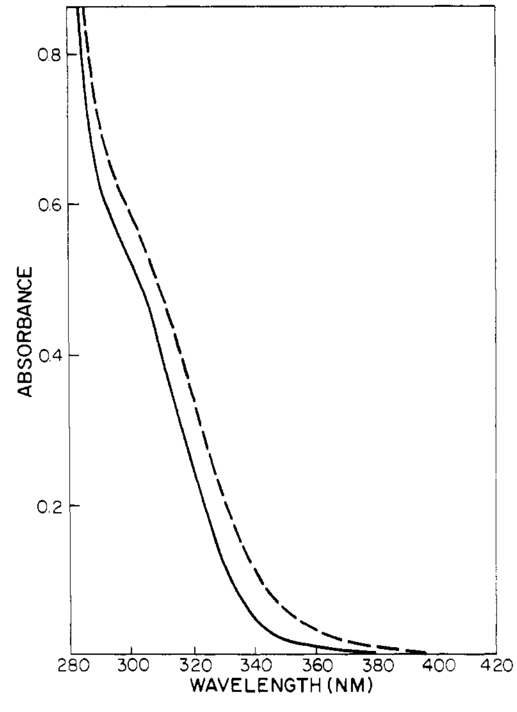


Figure 4. Spectral change that occurs upon mixing a 2.12 × 10^{-4} M solution of CuBr(py)(PPh_3) with an equal volume of a 6.18 × 10^{-3} M solution of py in a two-compartment spectrophotometer cell: (—), spectrum before mixing; (---), spectrum after mixing. The solvent is benzene.

Table I contains a compilation of quantum-yield data for the sensitized conversion of NBD to Q. Several points are worthy of note. (1) Production of Q occurs upon 313-nm irradiation of benzene solutions originally charged with CuBr(py)(PPh_3) and NBD. (2) The observed quantum yield, ϕ_{obsd}, rises with increasing NBD concentration. (3) Catalytic factors (mol of Q produced/mol of CuBr(py)(PPh_3) originally added) of >20 are attainable. (4) At a fixed NBD concentration, the addition of free py depresses ϕ_{obsd}. (5) ϕ_{obsd} exhibits a more complex dependence upon the concentration of added PPh_3, first decreasing, then rising, and finally decreasing once again.

Formation of a ground-state complex between CuBr(py)(PPh_3) and NBD has already been inferred from spectral

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[12] Goher, M. A. S. *Acta Chim. Acad. Sci. Hung.* **1978**, *97*, 235.

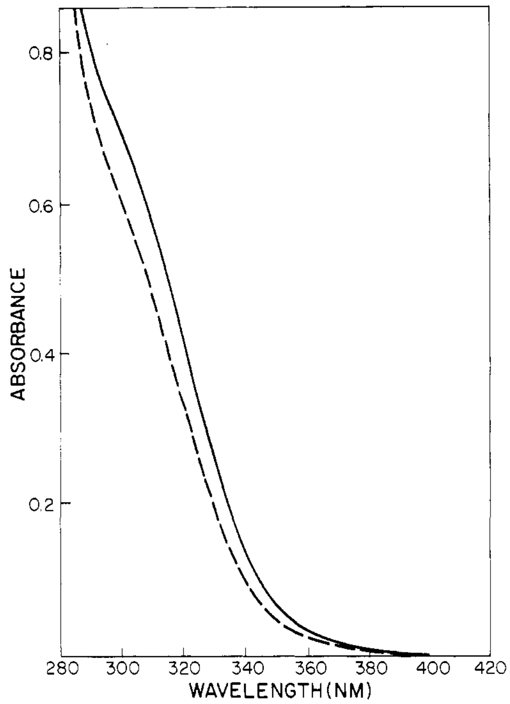


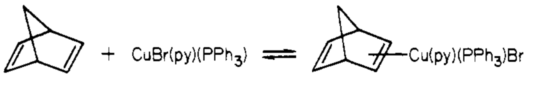
Figure 5. Spectral change that occurs upon mixing a solution originally charged with 2.12 × 10^{-4} M $CuBr(py)(PPh_3)$ and 3.09 × 10^{-3} M py with an equal volume of a 0.2 M solution of NBD in a two-compartment spectrophotometer cell: (—), spectrum before mixing; (---), spectrum after mixing. The solvent is benzene.

Table I. Quantum Yields for the 313-nm Photoisomerization of NBD to Q in the Presence of $CuBr(py)(PPh_3)$ and Added Ligands[a]

[NBD], M	[py] × 10^3, M	$[PPh_3]$ × 10^3, M	ϕ_{obsd}[b,c]	ϕ_{in}[d]
0.1	0	0	0.11 ± 0.00 (2 values)	
0.2	0	0	0.15 ± 0.01 (8 values)[e]	
0.5	0	0	0.19 ± 0.01 (2 values)	
0.2	1.2	0	0.12 ± 0.01 (3 values)	
0.2	4.9	0	0.088 ± 0.003 (3 values)	
0.2	42	0	0.045 ± 0.008 (4 values)	
0.2	0	0.50	0.10 ± 0.01 (2 values)	
0.2	0	0.97	0.10 ± 0.01 (3 values)	
0.2	0	2.0	0.17 ± 0.01 (3 values)	
0.2	0	5.1	0.22 ± 0.01 (2 values)	0.26 ± 0.01
0.2	0	9.7	0.21	0.31
0.2	0	14.8	0.19 ± 0.02 (2 values)	0.34 ± 0.04

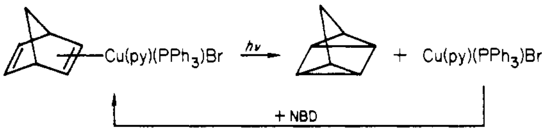
[a] Initial concentration of $CuBr(py)(PPh_3)$ was (1.0–1.1) × 10^{-3} M; the solvent was benzene. [b] Experimentally observed quantum yield; values determined after 3 h of irradiation. [c] Error limits represent mean deviation. [d] Intrinsic quantum yield calculated according to eq 11. [e] ϕ_{obsd} remains unchanged after 7 h of irradiation; after 24 h, however, the value has decreased by ~24%.

evidence (Figure 2). Although not established with certainty, the formulation of this species as a 1:1 adduct (eq 4)[13] seems



(4)

reasonable in light of the coordinatively unsaturated nature of the metal center and the tendency of Cu(I) to possess a maximum coordination number of four.[14] The percent conversion of $CuBr(py)(PPh_3)$ to the complex should increase with increasing NBD concentration. Since ϕ_{obsd} follows a similar trend (Table I), we identify $CuBr(py)(PPh_3)NBD$ as a key photoactive species[15] leading to Q production (eq 5). Because



(5)

the newly formed Q molecule has little affinity for Cu(I),[16] it readily diffuses away from the first coordination sphere of $CuBr(py)(PPh_3)$. Regeneration of $CuBr(py)(PPh_3)NBD$ then occurs and explains the catalytic role of Cu(I) in the sensitization process.

The assignment of $CuBr(py)(PPh_3)NBD$ as a photoactive species also accommodates the decrease in ϕ_{obsd} upon addition of excess py. As shown in eq 6, such behavior reflects the

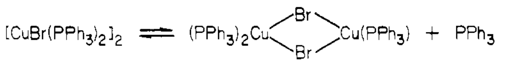
$$CuBr(py)(PPh_3)NBD + py \rightleftharpoons CuBr(py)_2PPh_3 + NBD \tag{6}$$

competition (also see Figure 5) between NBD and py for a coordination site about copper. By displacing coordinated NBD, the added py effectively decreases the concentration of the photoactive complex in the system. By the same token we might expect a diminution in ϕ_{obsd} upon addition of PPh_3, since spectral evidence cited above indicates that $CuBr(py)(PPh_3)$ forms a more stable complex with the phosphine than with NBD. While a decrease is, in fact, observed at low added PPh_3 concentrations, ϕ_{obsd} begins to increase beyond a PPh_3:Cu ratio of ~2:1. This latter behavior is clearly incompatible with the sensitization mechanism outlined in eq 4 and 5. Rather, $CuBr(py)(PPh_3)$ must undergo addition and/or substitution processes leading to new copper(I)–triphenylphosphine species that function as sensitizers without forming a ground-state complex with NBD. We turn next to a detailed examination of $CuBr(PPh_3)_3$ in hopes of gaining some insight about these species and their sensitization properties.

(b) Solution, Spectral, and Sensitization Properties of $CuBr(PPh_3)_3$. Lippard and Mayerle reported a thorough investigation of the equilibria between various $CuBr(PPh_3)_m$ compounds in chloroform at 37 °C.[17] At a PPh_3:Cu ratio of 3:1, only a small amount of $CuBr(PPh_3)_3$ exists in solution. The most abundant Cu(I) species were presumed to be the dissociation products, $CuBr(PPh_3)_2$ and $Cu_2Br_2(PPh_3)_3$, formed according to eq 7–9. Similar types of dissociation processes

$$2CuBr(PPh_3)_3 \rightleftharpoons [CuBr(PPh_3)_2]_2 + 2PPh_3 \tag{7}$$

$$[CuBr(PPh_3)_2]_2 \rightleftharpoons 2CuBr(PPh_3)_2 \tag{8}$$



$$[CuBr(PPh_3)_2]_2 \rightleftharpoons (PPh_3)_2Cu\overset{Br}{\underset{Br}{\diamond}}Cu(PPh_3) + PPh_3 \tag{9}$$

must be occurring in benzene as evidenced by the low observed molecular weight of $CuBr(PPh_3)_3$ in this solvent (Experimental Section).

The electronic absorption spectra of $CuBr(PPh_3)_3$ and PPh_3 in cyclohexane are compared in Figure 6. The close corre-

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(13) Although we depict $CuBr(py)(PPh_3)$ as being monomeric in eq 4, it should be remembered that dimeric species such as **2** and **3** in eq 3 represent equally plausible formulations of the structure in solution. Moreover, we cannot discount the presence of significant amounts of the Cu(I) species discussed in ref 10. Thus while eq 4 is correct to the extent that it indicates ground-state complex formation, it is important to recognize that more than one stoichiometrically distinct Cu(I)–NBD complex may exist in solution. The mechanistic conclusions that pertain to $CuBr(py)(PPh_3)NBD$, however, should apply equally well to these other complexes.

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

(15) While the relatively small spectral change (Figure 2) that accompanies formation of $CuBr(py)(PPh_3)NBD$ provides little clue as to the identity of the photoactive excited state, one likely candidate is a Cu–NBD charge-transfer state.[16]

(16) Schwendiman, D. P.; Kutal, C. *Inorg. Chem.* **1977**, *16*, 719.

(17) Lippard, S. J.; Mayerle, J. J. *Inorg. Chem.* **1972**, *11*, 753.

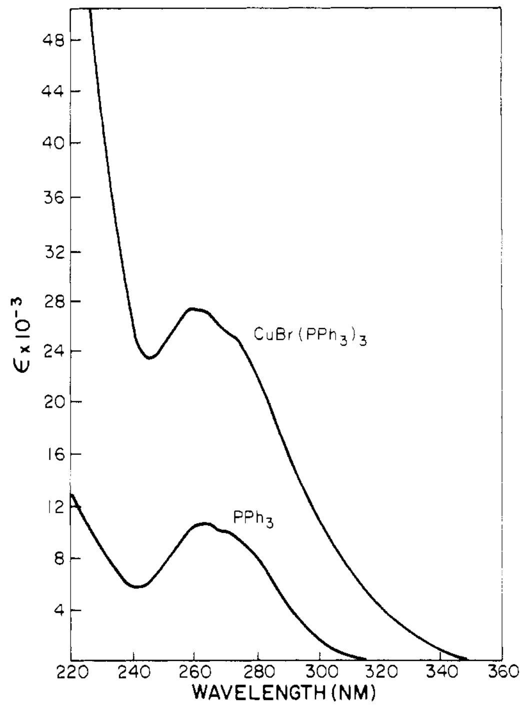

Figure 6. Electronic absorption spectra of $\mathrm{CuBr(PPh_3)_3}$ (1.7×10^{-5} M) and triphenylphosphine in cyclohexane.

Table II. Quantum Yields for the 313-nm Photoisomerization of NBD to Q in the Presence of $\mathrm{CuBr(PPh_3)_3}$ and Added $\mathrm{PPh_3}$

data set	$[\mathrm{CuBr(PPh_3)_3}] \times 10^4$, M[a]	$[\mathrm{PPh_3}] \times 10^3$, M	ϕ_{obsd}[b]	ϕ_{in}[c]
A	4.07–4.22	0	0.10[d]	0.10
B	4.07	1.93	0.16	0.22
C	4.09	4.96	0.18	0.33
D	4.06	9.87	0.13	0.34
E	10.3	9.61	0.18	0.30
F	9.85	10.1	0.17	0.29
G	9.85	10.1	0.20	0.34
H	0	7.7	0.003	

[a] Initial concentration of $\mathrm{CuBr(PPh_3)_3}$ dissolved in benzene; the concentration of NBD was 0.2 M in all runs. [b] Experimentally observed quantum yield; values determined after 3 h of irradiation. [c] Intrinsic quantum yield calculated according to eq 11. [d] Average value of three determinations with a mean deviation of 4.2%.

spondence of the band maxima indicates that the relative energies of the low-lying electronic states of $\mathrm{PPh_3}$ are not altered to any significant extent upon coordination of the ligand to copper.[18] Addition of NBD to a benzene solution of $\mathrm{CuBr(PPh_3)_3}$ causes no discernible change in the absorption spectrum, thus discounting the occurrence of ground-state Cu–NBD complex formation. A similar result obtains when NBD is added to a solution containing $\mathrm{CuBr(PPh_3)_3}$ and excess $\mathrm{PPh_3}$.

Irradiation of solutions initially charged with $\mathrm{CuBr(PPh_3)_3}$ and NBD results in production of Q with moderate observed quantum efficiency. As seen in Table II, ϕ_{obsd} displays an interesting dependence upon added $\mathrm{PPh_3}$, first increasing and then decreasing as the phosphine concentration is increased at fixed NBD and Cu(I) concentrations (data sets A–D). We propose that two effects are operative here. The first, competitive and unproductive (data set H) absorption by free $\mathrm{PPh_3}$ ($\epsilon_{313\mathrm{nm}} = 446$ $\mathrm{M^{-1}\ cm^{-1}}$), reduces the amount of light available to any Cu(I) sensitizer in solution and thus acts to inhibit sensitization. This inner filter effect probably accounts for the decrease in ϕ_{obsd} at higher $\mathrm{PPh_3}$ concentration.

The second effect of added $\mathrm{PPh_3}$ is to suppress the dissociation of $\mathrm{CuBr(PPh_3)_3}$ (eq 7) and thereby increase the effective concentration of this species in solution. Since ϕ_{obsd} rises under the same conditions, we assign $\mathrm{CuBr(PPh_3)_3}$ as the dominant Cu(I) sensitizer responsible for Q production (eq 10). At sufficiently high $\mathrm{PPh_3}$ concentrations all of the Cu(I)

$$\mathrm{CuBr(PPh_3)_3} \xrightarrow{h\nu} \mathrm{CuBr(PPh_3)_3^*} \xrightarrow{\mathrm{NBD}} \mathrm{CuBr(PPh_3)_3^*,NBD} \rightarrow \mathrm{CuBr(PPh_3)_3} + \mathrm{Q} \qquad (10)$$

in solution should exist in this form. Under these circumstances the intrinsic quantum efficiency, ϕ_{in}, for sensitization by $\mathrm{CuBr(PPh_3)_3}$ can be obtained from the relationship in eq 11, where $A_{\mathrm{CuBr(PPh_3)_3}}$ and $A_{\mathrm{PPh_3}}$ denote the absorbances of the

$$\phi_{\mathrm{obsd}} = \phi_{\mathrm{in}}\left(\frac{A_{\mathrm{CuBr(PPh_3)_3}}}{A_{\mathrm{CuBr(PPh_3)_3}} + A_{\mathrm{PPh_3}}}\right) \qquad (11)$$

indicated compounds at 313 nm. Substituting in the appropriate absorbance values,[19] we can calculate ϕ_{in} as a function of $\mathrm{PPh_3}$ concentration (last column in Table II). The constancy of ϕ_{in} at higher $\mathrm{PPh_3}$ concentrations (data sets C–G) supports the premise that $\mathrm{CuBr(PPh_3)_3}$ is the key sensitizer in these solutions.[20]

With this information in hand, we are in a position to reconsider the sensitization behavior of $\mathrm{CuBr(py)(PPh_3)}$ in the presence of added $\mathrm{PPh_3}$. At low (≤ 1) $\mathrm{PPh_3}$:Cu ratios, the decrease in ϕ_{obsd} presumably reflects the presence of a species such as $\mathrm{CuBr(py)(PPh_3)_2}$, which is an intrinsically poor sensitizer (vide infra). The rise in ϕ_{obsd} at higher $\mathrm{PPh_3}$:Cu ratios must then result from the formation of a more effective Cu(I) sensitizer. The assignment of this new sensitizer as $\mathrm{CuBr(PPh_3)_3}$ is supported by two lines of evidence. First, under the assumption that the overall formation of $\mathrm{CuBr(PPh_3)_3}$ proceeds according to eq 12, the 313-nm extinction coefficient

$$2\mathrm{PPh_3} + \mathrm{CuBr(py)(PPh_3)} \rightleftharpoons \mathrm{CuBr(PPh_3)_3} + \mathrm{py} \qquad (12)$$

of this species can be determined from absorbance measurements of solutions originally charged with $\mathrm{CuBr(py)(PPh_3)}$ and varying concentrations of $\mathrm{PPh_3}$. The necessary relationship is given by eq 13, where A_{tot} is the measured total absorbance

$$\epsilon_{313\mathrm{nm}} = \frac{A_{\mathrm{tot}} - A_{\mathrm{PPh_3}}}{[\mathrm{Cu(I)}]l} \qquad (13)$$

of the solution, $A_{\mathrm{PPh_3}}$ is the calculated absorbance due to free $\mathrm{PPh_3}$ (concentration of added $\mathrm{PPh_3}$ − 2[Cu(I)]), [Cu(I)] is the concentration of added $\mathrm{CuBr(py)(PPh_3)}$, and l is the cell path length. The extinction coefficient determined in this manner, $(6.72 \pm 0.23) \times 10^3$ $\mathrm{M^{-1}\ cm^{-1}}$ (five determinations), agrees closely with the value obtained for an authentic sample

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(18) To the extent that $\mathrm{CuBr(PPh_3)_3}$ dissociates in cyclohexane (recall eq 7–9), the observed absorption spectrum will be a composite of those of the parent compound and any dissociation products. Thus if two or more Cu(I)–$\mathrm{PPh_3}$ species are present in appreciable concentrations, they must possess similar spectra.

(19) The value of $A_{\mathrm{CuBr(PPh_3)_3}}$ is obtained by subtracting the calculated (i.e., Beer's law) absorbance due to free $\mathrm{PPh_3}$ from the measured total absorbance. The 313-nm extinction coefficient of $\mathrm{CuBr(PPh_3)_3}$ can then be determined on the basis of the concentration of Cu(I) originally added. This procedure yields a value of $\epsilon_{313\mathrm{nm}} = (6.45 \pm 0.04) \times 10^3$ $\mathrm{M^{-1}\ cm^{-1}}$ for solutions containing a 10- to 25-fold excess of $\mathrm{PPh_3}$. The constancy of the extinction coefficient at different $\mathrm{PPh_3}$:Cu ratios validates the assumption that all of the Cu(I) in solution exists as $\mathrm{CuBr(PPh_3)_3}$.

(20) The smaller ϕ_{in} values at lower $\mathrm{PPh_3}$ concentrations presumably reflects the presence in solution of other Cu(I) species (e.g., eq 7–9) that are appreciably less effective as sensitizers than $\mathrm{CuBr(PPh_3)_3}$. The reason for this disparity in sensitization behavior is not clear.

of $CuBr(PPh_3)_3$, (6.45 ± 0.04) × 10^3 M^{-1} cm^{-1}.[19]

Quantum-yield data provide the second source of information about the nature of the sensitizer formed upon $CuBr(py)(PPh_3)$. of a several-fold excess of PPh_3 to solutions of $CBr(py)(PPh_3)$. If we again assume that all of the $CuBr(py)(PPh_3)$ originally present is converted to $CuBr(PPh_3)_3$, eq 11 can be used to calculate the intrinsic quantum yield of sensitization (last column in Table I). Both the reasonable constancy of ϕ_{in} (0.33 ± 0.03) at PPh_3:Cu ratios ≥10 and the close agreement with the ϕ_{in} values determined for $CuBr(PPh_3)_3$ itself (Table II) substantiate the assignment of this Cu(I) species as the key sensitizer in the system.

(c) Summary Comments. The present study establishes that the mechanism by which Cu(I) sensitizes an olefin photoreaction can be dictated by the addition of suitable ligands to the system. This effect has its origin in the facile[21] ligand addition and/or substitution processes that convert the original copper(I) compound into one or more new species. Thus the addition of NBD to a solution containing $CuBr(py)(PPh_3)$ results in the formation of a ground-state Cu(I)–NBD complex that, upon the absorption of a photon, generates a molecule of Q. This sensitization pathway can be blocked by ligands such as py and PPh_3 that effectively compete with NBD for a coordination site about copper. In the presence of sufficient PPh_3 to form $CuBr(PPh_3)_3$, the predominant mechanism of sensitization changes to one involving bimolecular interaction of the photoexcited Cu(I) compound and ground-state NBD.

The effectiveness of $CuBr(PPh_3)_3$ as a sensitizer stands in sharp contrast to the behavior of $CuBr(py)_2PPh_3$ (eq 6) and $CuBr(py)(PPh_3)_2$ (presumed to be formed upon addition of less than an equimolar amount of PPh_3 to $CuBr(py)(PPh_3)$). It is possible that this disparity reflects differences in orbital parentage of the lowest electronic excited state. This state in $CuBr(PPh_3)_3$ appears to be largely localized on PPh_3, while the py-containing compounds possess low-lying Cu → py charge-transfer states (see Figure 4 and accompanying discussion). Whether the inability of this latter excited state to sensitize the NBD to Q rearrangement reflects its lower energy or an exceedingly rapid deactivation to the ground state remains an interesting question deserving further study.

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Registry No. $CuBr(py)(PPh_3)$, 25753-77-9; $CuBr(PPh_3)_3$, 15709-74-7; NBD, 121-46-0; PPh_3, 603-35-0; py, 110-86-1; Q, 278-06-8.

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[21] Rapid exchange between the first coordination sphere of Cu(I) and bulk solution has been reported for uncharged ligands such as phosphines and olefins: Muetterties, E. L.; Alegranti, C. W. *J. Am. Chem. Soc.* **1970**, *92*, 4114. Salomon, R. G.; Kochi, J. K. *Ibid.* **1973**, *95*, 1889.

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UV Photoelectron Spectroscopic Investigation of Some Polycyclic Group 5A Compounds and Related Acyclic Species. 1. Free and Coordinated Aminophosphines and Related Compounds

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He I ultraviolet photoelectron (UV PES) spectra are reported for $XP(NMeCH_2)_3CMe$ (X = O (**1A**), S (**1B**), Se (**1C**), BH_3 (**1D**)), the rigid tricyclic $XP(NCH_2CH_2)_3$ (X = O (**2A**), S (**2B**), Se (**2C**)), the adamantane-like molecules urotropine (**3**) and $XP(CH_2N)_3(CH_2)_3$ (X = lone pair (**5**), O (**5A**), S (**5B**), Se (**5C**)), $XP(CH_2N)(CH_2)_2(CH_2CH_2)$ (X = lone pair (**6**), O (**6A**)), and $XP(NMe_2)_3$ (X = O (**7A**), S (**7B**), Se (**7C**), BH_3 (**7D**)). The present spectral data are compared to those previously recorded for $P(NMeCH_2)_3CMe$ (**1**), $MeC(CH_2NCH_2)_3$ (**4**), and $P(NMe_2)_3$ (**7**).

Introduction

Ultraviolet photoelectron spectroscopy (UV PES) has been shown to be a useful tool for studying molecular conformation and bonding in the gas phase.[2] The utility of the UV PES experiment in these respects stems largely from the patterns that are associated with the ionizations from orbitals possessing appreciable lone-pair character.[3] Interpretational difficulties can arise with this approach, however, particularly when several conformations are possible and/or the lone-pair orbitals of the various heteroatoms are close in energy. A case in point concerns the acyclic aminophosphines,[2a,d,f,h] where doubts persist not only about the UV PES assignments but also about the ground-state structures. The present work was carried out in an attempt to resolve these residual uncertainties (a) by broadening the scope of our previous UV PES work[2f] on rigid, polycyclic PN_3 systems possessing either well-established structures or geometries that can be confidently inferred and (b) by examining the spectral changes that ensue upon coordination of the phosphorus lone pair to various Lewis acids. A subsequent paper will be concerned with similar studies of phosphite, arsenite, and thiophosphite esters.

Results and Discussion

The UV PES data for the compounds studied are summarized in Table I. The data and assignments pertain primarily to lone-pair ionizations; however, other ionizations have been

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[1] (a) The University of Texas at Austin. (b) Southern Methodist University. (c) Iowa State University.

[2] See, for example: (a) Cowley, A. H.; Dewar, M. J. S.; Goodman, D. W.; Schweiger, J. R. *J. Am. Chem. Soc.* **1973**, *95*, 6506. (b) Cowley, A. H.; Dewar, M. J. S.; Goodman, D. W.; Padolina, M. C. *Ibid.* **1974**, *96*, 2648. (c) Ames, D. L.; Turner, D. W. *J. Chem. Soc., Chem. Commun.* **1975**, 179. (d) Lappert, M. F.; Pedley, J. B.; Wilkins, B. T.; Stelzer, O.; Unger, E. *J. Chem. Soc., Dalton Trans.* **1975**, 1207. (e) Cowley, A. H. *Phosphorus Sulfur* **1976**, 2, 282. (f) Cowley, A. H.; Goodman, D. W.; Kuebler, N. A.; Sanchez, M.; Verkade, J. G. *Inorg. Chem.* **1977**, *16*, 854. (g) Cowley, A. H.; Lattman, M.; Montag, R. A.; Verkade, J. G. *Inorg. Chim. Acta* **1977**, *25*, L151. (h) Hargis, J. H.; Worley, S. D. *Inorg. Chem.* **1977**, *16*, 1686. (i) Cowley, A. H.; Dewar, M. J. S.; Lattman, M.; Mills, J. L.; McKee, M. *J. Am. Chem. Soc.* **1978**, *100*, 3349. (j) Yarbrough, L. W.; Hall, M. B. *Inorg. Chem.* **1978**, *17*, 2269. (k) Cowley, A. H.; Lattman, M.; Walker, M. *J. Am. Chem. Soc.* **1979**, *101*, 4074. (l) Chisholm, M. H.; Cowley, A. H.; Lattman, M. *Ibid.* **1980**, *102*, 46.

[3] For a review, see: Hoffman, R. *Acc. Chem. Res.* **1971**, *4*, 1.

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