

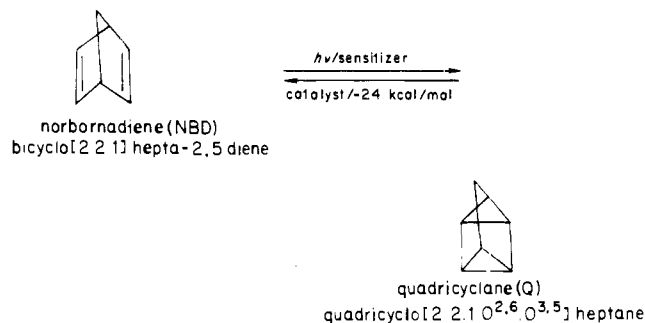
Photosensitized Isomerization of Norbornadiene to Quadricyclane with (Arylphosphine)copper(I) Halides[†]

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Abstract: The (arylphosphine)copper(I) halides [(Ph₃P)₃CuX, (MePh₂P)₃CuX, (Ph₂PCH₂CH₂PPh₂)CuCl; X = Cl, Br, I] were studied as sensitizers in the photoisomerization side of a solar energy storage cycle based on the interconversion of norbornadiene (NBD) and quadricyclane (Q). The lowest electronic excited state of these compounds can be effective triplet energy sensitizers as evidenced by a maximum quantum yield of 1.0 with (MePh₂P)₃CuX. The efficiency of the (MePh₂P)₃CuX sensitizers is unprecedented compared to other reported inorganic complexes used as sensitizers for the NBD/Q system. The (MePh₂P)₃CuCl sensitizer has an intersystem crossing triplet yield of 1.0 with a triplet lifetime in benzene at room temperature of 3.3 μs. The triplet energy transfer rate constant with NBD is $8 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$. While the L₃CuX (L = Ph₃P, MePh₂P) species are the most efficient sensitizers in solution, dissociation of the ligand from the metal in dilute solution detracts from their otherwise attractive features. The much lower quantum efficiency observed for the (Ph₃P)₃CuX compared to the MePh₂P sensitizer is attributed to this extensive ligand dissociation. The coordinately unsaturated (arylphosphine)copper(I) halides produced by ligand dissociation appear to have extremely short lifetimes while the free ligand undergoes photodecomposition. Ground-state complexation of NBD with the coordinately unsaturated (arylphosphine)copper(I) halides is shown to occur in the presence of a large excess of NBD. Photoexcitation of NBD-(MePh₂P)₂CuCl (C1) and NBD-(MePh₂P)₂CuCl (C2) complexes can produce Q, but with quantum efficiencies less than one.

The photoisomerization of norbornadiene (NBD) to quadricyclane (Q) has received considerable attention as a solar energy storage process.¹⁻⁵ The high-energy product, Q, may be catalytically converted to starting material with a corresponding release of stored energy.^{1-3,6-7} Norbornadiene itself does not absorb light



in the region of solar radiation,^{8,9} therefore, the current research effort reported in the literature has involved a search for suitable compounds which could absorb sunlight and still sensitize the NBD to Q isomerization.³⁻⁵ The photoreaction does occur in the presence of an appropriate triplet sensitizer with an overall efficiency of Q production approaching 100%.^{10,11} Hammond and co-workers¹⁰ established the mechanism of sensitization by organic carbonyl compounds as an electronic energy transfer from the triplet state of the sensitizer to NBD. Other work has verified that the conversion of NBD to Q proceeds via the lowest triplet state of NBD.¹² Several problems exist with these systems. One is that the carbonyl sensitizers showing efficient conversion are only weak absorbers of solar radiation. An even greater problem is the fact that side reactions consume the sensitizer.⁶ Sensitization of the NBD/Q system has also been shown to occur by transition metals.^{3,13} These sensitizers are generally weak absorbers of solar radiation, inefficient, or prone to decomposition. Of the transition metal sensitizers studied for the NBD/Q system, copper(I) compounds have shown the most promising possibilities.³ Evidence has been presented for two different sensitization mechanisms: (1) photoexcitation of a ground-state complex between the sensitizer and NBD, and (2) bimolecular energy transfer from the

excited sensitizer to ground-state NBD.³

Preliminary experiments by Morse and Bommer¹⁴ showed that (MePh₂P)₃CuI was an excellent sensitizer of the NBD/Q system with quantum yields as high as 0.80 being observed. In order to gain a better understanding of the sensitization process a detailed study of known sensitizers such as (MePh₂P)₃CuI was undertaken. Concentration-dependent efficiencies have permitted evaluation of the ratio of rate constants for the chemical steps compared to the photophysical steps. By competitive quenching experiments a set of absolute rate constants has been established. These results coupled with the photophysical and solution properties of the (arylphosphine)copper(I) halides recently reported¹⁵ have provided

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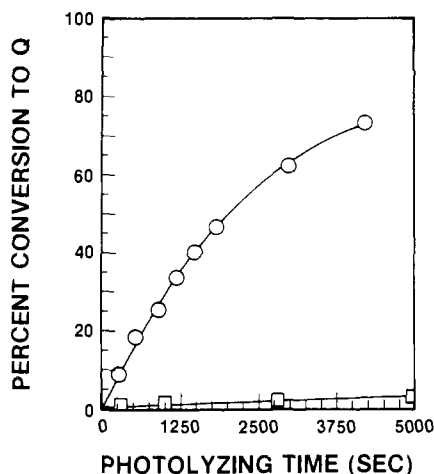


Figure 1. Photosensitized conversion of norbornadiene to quadricyclane. $[\text{NBD}]_0 = 1.63 \times 10^{-2} \text{ M}$. Sensitizers: $(\text{MePh}_2\text{P})_3\text{CuI}$, $1.05 \times 10^{-3} \text{ M}$ (O); $(\text{Ph}_3\text{P})_3\text{CuI}$, $8.4 \times 10^{-4} \text{ M}$ (□). A narrow band of light centered at 313 nm was used for photolyzing solution ($I_0 = 1.4 \times 10^{16}$ quanta/s). Four milliliters of solution photolyzed with solutions absorbing over 99% of irradiation light.

the basis for the development of new concepts which can aid in a rational selection of metals and ligands that could provide greater efficiency for the NBD/Q photoconversion process.

Experimental Procedures.

Materials. The preparation of the (arylphosphine)copper(I) halides was accomplished as previously described.¹⁵ Only spectral grade solvents were used. The drying of benzene with sulfuric acid and distillation did not have an effect on the observed quantum yields; therefore, spectral grade benzene was used without further purification. Norbornadiene and quadricyclane were redistilled prior to a series of experiments. The purity was checked by use of the Hewlett Packard 5880A GC, Hewlett Packard 5992 GC/MS, or the LKB 2091 GC/MS system.

Photoreactor. The photoreactor consisted of a 1000-W Hg(Xe) ozone-free arc lamp at the focal length of a convex quartz lens. During the initial work, the light was filtered with a nickel sulfate solution in conjunction with a narrow band interference filter centered at 313 nm. This was later modified by using a Oriel 7240 monochromator. The light from the arc lamp was passed through a cooled distilled water filter to aid heat removal. After passing through the water filter, the light was focused on the entrance slit of the monochromator. The light beam was then collimated with a focusing lens at the exit slit of the monochromator. With the monochromator set at 313 nm the entrance and exit slits were adjusted to give a narrow band centered at 313 nm with an intensity of 8×10^{15} quanta $\text{s}^{-1} \text{ cm}^{-2}$. Light intensities were determined by ferri-oxalate actinometry¹⁶ and with a thermopile (YSI-Kettering Model 65 Radiometer). The thermopile agreed to within 2% of the actinometer. The photolysis cell consisted of a 10 mm square spectrophotometer cell modified with the addition of a short narrow neck at the top of the cell. The cell was serum rubber stoppered with a syringe needle bubbler and a pressure release inserted through the serum stopper. The photocell was flushed with helium which had passed over hot copper turnings (650–700 °C). After passing through the copper turnings, the helium was bubbled through benzene to alleviate as much as possible any loss of solvent in the photolysis cell. The system was flushed in this manner for 15–30 min. A cell holder was used to reproducibly locate the photolysis cell in the light beam.

Quantum Yields. The solutions were irradiated for a short period while being thoroughly stirred with a miniature magnetic stirring bar. A small sample was analyzed on a GC or GC/MS system. Three different GC systems were used during the research. A Hewlett Packard 5880A GC system equipped with a flame ion detector (12 m fused silica open tubular OV-101 capillary column), Hewlett Packard 5992A GC/MS system (10 ft \times 1/4 in., SP-2100 Supelco glass column), and a LKB 2091 GC/MS system (10 ft \times 1/4 in., 3% OV-101 glass column). The GC/MS was calibrated with standard NBD/Q solutions by monitoring the area of the

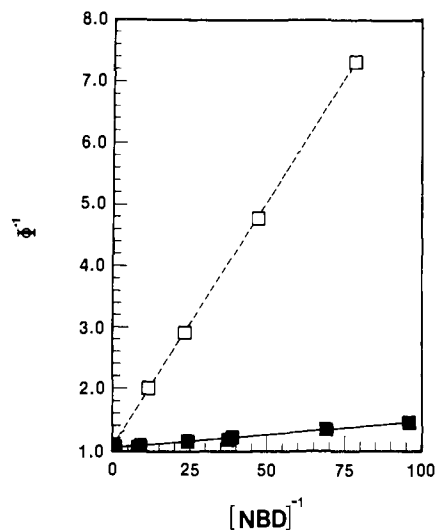


Figure 2. Quantum yield dependence for the isomerization of norbornadiene sensitized by $(\text{MePh}_2\text{P})_3\text{CuCl}$: 10^{-2} M aerobic, intercept = 1.02, slope = 8.0×10^{-2} (□); 10^{-2} M anaerobic, intercept = 1.02, slope = 4.5×10^{-3} (■). (The solid line is for the model using Scheme I and the values from Table II. The dotted line is the least-squares fit of the data.)

91 mass unit peaks. The calibration showed a 1:1 correspondence when a 70 eV ionizing source is used. The GC also showed a 1:1 correspondence between the NBD integrated area and the Q integrated area. During the initial experiments, a percentage of Q produced vs. time was created for each photolysis. Other than Figure 1, the quantum yields reported here were determined by averaging 3 quantum yields calculated with between 1 and 5% Q conversion for the NBD concentration specified. The initial light intensities were obtained as previously described. The solutions in most instances absorbed 99% of the light; however, the thermopile was placed behind the solutions during photolysis so the amount of light absorbed could be determined accurately. All quantum yields reported are for anaerobic (helium flushed) solutions unless otherwise specified. Those solutions photolyzed without flushing with helium (aerobic) are indicated in the results.

Results

Quadricyclane production with L_3CuX ($\text{L} = \text{Ph}_3\text{P}, \text{MePh}_2\text{P}$; $\text{X} = \text{Cl}, \text{Br}, \text{I}$) as sensitizer showed a striking contrast between complexes of the Ph_3P and MePh_2P ligands (Figure 1). The halogen substituent appeared to have no noticeable effect on the quadricyclane yields when the conditions shown in Figure 1 were used. The limiting quantum yield of the $(\text{MePh}_2\text{P})_3\text{CuX}$ compounds were 1.0 as determined from a linear plot of Φ^{-1} vs. $[\text{NBD}]^{-1}$ (Φ is the quantum yield of isomerization). A similar analysis could not be done for the $(\text{Ph}_3\text{P})_3\text{CuX}$ compounds because of the low conversion and discoloration/decomposition which occurred with prolonged photolysis times. The quantum yield at 1.0% conversion to Q with use of the conditions shown in Figure 1 was calculated to be 0.02 for the $(\text{Ph}_3\text{P})_3\text{CuX}$ compounds.

A more detailed concentration-dependent study of the quantum efficiency for the isomerization of NBD to Q was carried out with $(\text{MePh}_2\text{P})_3\text{CuCl}$. Figure 2 shows the data for 10^{-2} M $(\text{MePh}_2\text{P})_3\text{CuCl}$ with and without deaeration. At 10^{-3} M $(\text{MePh}_2\text{P})_3\text{CuCl}$ a sharp deviation occurs from a linear Φ^{-1} vs. $[\text{NBD}]^{-1}$ plot at the higher NBD concentrations ($>0.5 \text{ M}$) (Figure 3). The quantum yields decreased instead of continuing to increase with greater concentrations of NBD. The same result was observed at $4 \times 10^{-4} \text{ M}$ $(\text{MePh}_2\text{P})_3\text{CuCl}$, but the deviation from linearity in the reciprocal plot starts to occur at lower concentrations of NBD. With further dilution to $1 \times 10^{-4} \text{ M}$ $(\text{MePh}_2\text{P})_3\text{CuCl}$, discoloration of the solutions was observed during the photolyzing period. The calculated quantum yields showed considerable variance. The few data points shown in Figure 3 are an average of 5 to 6 observations at the specified concentrations.

The results of the photosensitized isomerization of NBD to Q with $(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2\text{CuCl}$, a 2:1 ratio of MePh_2P to CuCl ,

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Table I. Reciprocal Analysis of Quantum Yield of Isomerization vs. Norbornadiene Concentration (Φ^{-1} vs. $[\text{NBD}]^{-1}$) for Sensitizers Studied in the Photoisomerization of Norbornadiene to Quadricyclane

sensitizer ^a $L_m\text{CuX}$	concn, mM	intercept	slope $\times 10^2$	int/slope (k_q/k_t)	fraction of light absorbed	
					$L_3\text{CuX}$	$L_2\text{CuX}$
(MePh ₂ P) ₃ CuCl	10	1.0	0.44	230	0.95	0.05
aerobic conditions		1.0	8.0	13		
(MePh ₂ P) ₃ CuX (X = Cl, Br, I)	1.0	1.0	0.40 ^b	250	0.84	0.15
(MePh ₂ P) ₃ CuCl	0.40	1.0	0.38 ^b	260	0.75	0.24
(MePh ₂ P) ₂ CuCl	1.3	1.0	3.2	31	0.36	0.63
	3.9	(no)	noticeable	change)		
(Ph ₃ P) ₂ CuCl	1.0	3.6	84	4.3	0	0.60
(DIPHOS)CuCl	0.50	1.5	2.8	0.54		
aerobic conditions		(no)	noticeable	change)		
(MePh ₂ P)CuCl	0.39	3.2	30	11	0	0
	0.11	(no)	noticeable	change)		
Ph ₂ NH	6.0	2.6	0.11	2400		
aerobic conditions		3.3	1.3	250		
Michler's ketone	0.18	1.3	6.2	21		

^a Formulas indicate ratio of ligand to CuCl and not solution structures. ^b Deviation from a linear reciprocal plot observed at $[\text{NBD}]^{-1} < 10$ (see Figure 3).

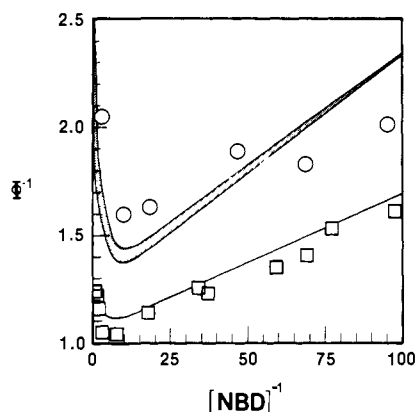


Figure 3. Quantum yield dependence for the isomerization of norbornadiene sensitized by (MePh₂P)₃CuCl at 1.0×10^{-4} M (O) and 1.0×10^{-3} M (□). (The solid lines are for the model using Scheme I and the values from Table II. The shaded area shows the effect of changing Φ_{C_2} from 0.6 to 0.7 holding $K_{C_2} = 10$.)

and a 1:1 ratio of MePh₂P to CuCl are shown in Figures 4 and 5. The efficiency of a 2:1 ratio of Ph₃P to CuCl in the sensitization process was also evaluated. With use of a solution containing 1×10^{-3} M CuCl and 2×10^{-3} M Ph₃P the quantum yields of isomerization were determined for three different NBD concentrations: (1) $[\text{NBD}] = 0.827$, $\Phi = 0.22$; (2) $[\text{NBD}] = 0.157$, $\Phi = 0.11$; (3) $[\text{NBD}] = 0.0785$, $\Phi = 0.070$.

The photoisomerization efficiencies with (MePh₂P)HCl and (MePh₂P)₂ZnCl₂ as sensitizers of the NBD/Q system were extremely low. The 2.5×10^{-3} M (MePh₂P)₂ZnCl₂ solutions with 0.11 to 1.2 M NBD showed a yellow discoloration on photolysis. At 0.5% Q conversion the quantum yield was calculated to be 0.04, showing little variance over the NBD range. (MePh₂P)HCl gave similar results to (MePh₂P)₂ZnCl₂.

Along with the compounds discussed, some known organic triplet sensitizers were also studied to determine the energy transfer efficiency to NBD and to ascertain the ability to predict absolute rate values with the use of competitive oxygen quenching. The two triplet sensitizers studied were 4-4'-bis(*N,N*-dimethylamino)benzophenone commonly referred to a Michler's ketone ($E_T = 61$ kcal/mol) and diphenylamine ($E_T = 72$ kcal/mol). The observed quantum efficiencies of the sensitizers produced a linear Φ^{-1} vs. $[\text{NBD}]^{-1}$ plot. The analysis with diphenylamine and Michler's ketone as sensitizers is shown in Table I along with a summary of the phosphine complexes.

The deviation from a linear Φ^{-1} vs. $[\text{NBD}]^{-1}$ analysis for the more dilute concentration of (MePh₂P)₃CuCl (Figure 3) was also accompanied by an observed perturbation of its absorption spectrum. For example, 1.0×10^{-4} M (MePh₂P)₃CuCl in benzene shows a slight decrease in absorbance from 350 to 290 nm when

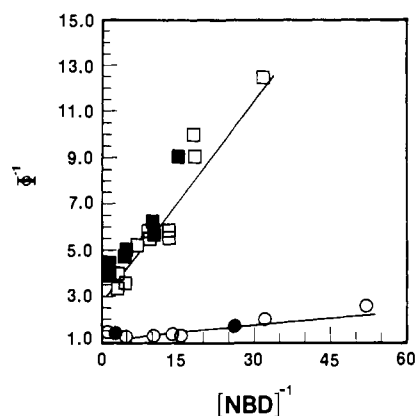


Figure 4. Quantum yield dependence for the isomerization of norbornadiene (NBD) sensitized by (MePh₂P)CuCl and (MePh₂P)₂CuCl: 3.0×10^{-4} M (MePh₂P)CuCl (□); 1.1×10^{-4} M (MePh₂P)CuCl (■); 1.3×10^{-3} M (MePh₂P)₂CuCl (●); 3.9×10^{-3} M (MePh₂P)₂CuCl (○). The (MePh₂P)CuCl and (MePh₂P)₂CuCl formulas are not meant to imply a sensitizer form but rather the ratio of MePh₂P to CuCl in solution. (The solid lines are for the model using Scheme I and values from Table II.)

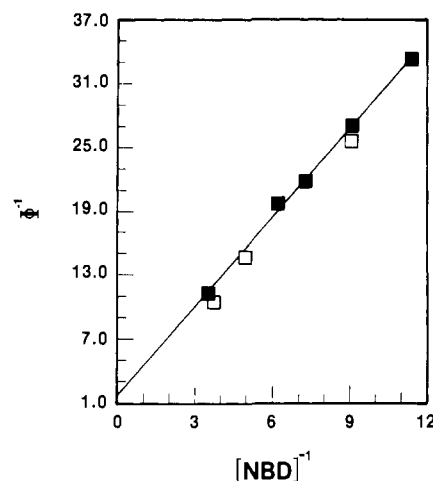


Figure 5. Quantum yield dependence for the isomerization of norbornadiene sensitized by 5×10^{-4} M (Ph₂PCH₂CH₂PPh₂)CuCl: anaerobic (■), aerobic (□). (The solid line is the least-squares fit of the anaerobic data.)

the solution contains 0.10 M NBD. When (MePh₂P)CuCl (1:1 ratio MePh₂P to CuCl) was used as a sensitizer, the irradiation light band centered at 313 nm was not completely absorbed; therefore, the amount of light passing through the solution was

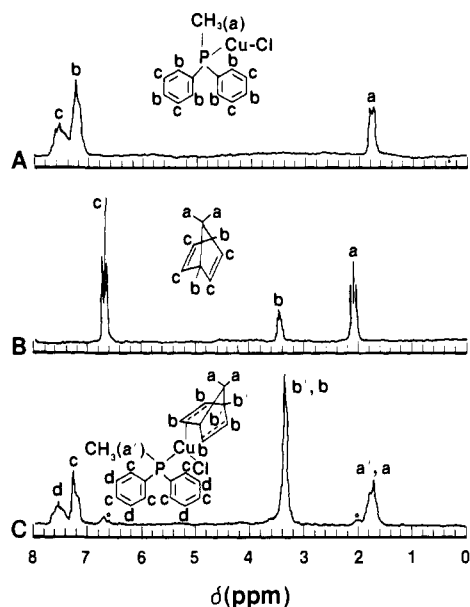


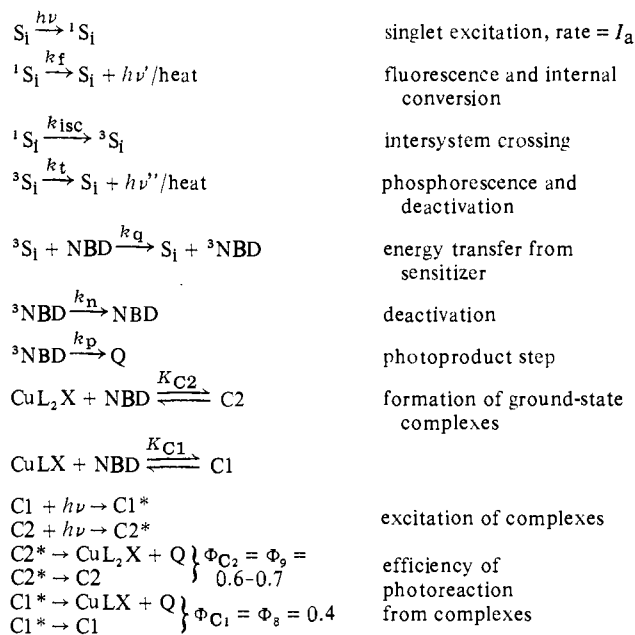
Figure 6. 90-MHz proton NMR spectra in CDCl_3 indicating the complexation of NBD with $(\text{MePh}_2\text{P})\text{CuCl}$.

monitored by a radiometer detector placed behind the sample cell. The absorbance of the $(\text{MePh}_2\text{P})\text{CuCl}$ solutions was observed to increase slightly as the NBD concentration of the solutions increased. A study of the absorbance at 313 nm as a function of the $(\text{MePh}_2\text{P})\text{CuCl}$ concentration and the NBD concentration indicated that a 1:1 complex, $(\text{NBD}):(\text{MePh}_2\text{P})\text{CuCl}$, forms with an extinction coefficient of 2×10^3 and a formation constant of 50. NBD appears to form a ground-state complex when the copper is not coordinately saturated and when a large excess of NBD is present. A $(\text{NBD})(\text{MePh}_2\text{P})\text{CuCl}$ complex has been isolated by mixing a 1:1 ratio of MePh_2P to CuCl with an excess of NBD in a minimum volume of methylene chloride. The same procedures as described in the preparation of $[(\text{MePh}_2\text{P})\text{CuCl}]_4$ were followed.¹⁵ To the warm solution of the 1:1 ratio of MePh_2P to CuCl a large excess (approximately 8 times the amount of MePh_2P) of NBD was added and the solution cooled. A light yellow precipitate formed upon cooling. The precipitate was air dried for only a few minutes. The crystals gave off the characteristic NBD odor; however, the NMR spectrum of a saturated CDCl_3 solution of the complex showed the diene protons being shifted upfield (Figure 6C). This upfield shift suggests exo coordination of NBD by Cu(I) based on studies of cationic olefin complexes of Cu(I) .¹⁷ The effect the phosphine has on the olefin coordination, if any, is unknown. A dimer, trimer, or higher n -mer of $(\text{NBD})(\text{MePh}_2\text{P})\text{CuCl}$ in which NBD is bound in an exo fashion to two different Cu atoms is not precluded by the data. Equivalency of the six hexadiene ring protons may be rationalized by a rapid equilibrium between complex and the free olefin. On the basis of the assignments made, the calculated area ratios of $(a' + a):(b' + b):(c + d)$ should be 1:1.2:2.0. The integrated ratios are in good agreement being 1:1.3:1.9, respectively. A GC/MS analysis of the solution showed only NBD, MePh_2P , and the solvent. Attempts to make a $(\text{NBD})(\text{MePh}_2\text{P})_2\text{CuCl}$ complex were not successful.

Discussion

The (diphenylmethylphosphine)copper chloride sensitizer system was explored the most thoroughly because of its interesting behavior in the photoisomerization of NBD and the potentially high limiting quantum yields. The photoisomerizations were performed with three different ratios of diphenylmethylphosphine (L) to copper chloride; 1:1, 2:1, and 3:1. From our studies on the solution equilibria of this system¹⁵ it is clear that five or more species of the form $\text{L}_n(\text{CuCl})_m$ can coexist in solution. To adequately explain

Scheme I. Mechanism of Energy Transfer by a Sensitizer Coupled with a Ground-State Complex^a



(sensitizers) (complexes)

$$\Phi = \sum_{i=1}^7 \frac{\Phi_e^{(i)} K_s^{(i)} [\text{NBD}] A_i}{(1 + K_s^{(i)} [\text{NBD}]) A_T} + \sum_{j=8}^9 \frac{(\Phi_j A_j)}{A_T} \quad (1)$$

(i and j values represent species present; see Table II)

^a S_1 is the sensitizer $(\text{MePh}_2\text{P})_n\text{Cu}_m\text{Cl}_m$ where $1 \leq n \leq 4$, $1 \leq m \leq 2$. NBD is norbornadiene and Q is quadricyclane. A_i is the absorbance for component (L) and $A_T = \sum_{i=1}^9 A_i$; $K_s = k_q/k_t$; $\Phi_e^{(i)} = \Phi_{isc}^{(i)} k_p / (k_n + k_p)$; limiting quantum yield for each component (i).

the experimental observations a model has to be formulated which incorporates the photochemical properties of the major species into a general mechanism (Scheme I). With use of the solution equilibrium constants¹⁵ it is possible to have concentrations of CuCl and ligand where one species dominates. For example, at 10^{-2} M CuCl with the L to CuCl ratio 3:1 the major species is L_3CuCl and it traps 95% of the light absorbed at 313 nm. The quantum yield dependence for this sensitizer is shown in Figure 2. The copper atom is fully coordinately saturated with ligand and the results are readily explained by a conventional triplet energy transfer mechanism as shown in the first 7 steps of Scheme I. Where one species is the overwhelming light absorber, eq 1 reduces to a one-term expression which upon inversion becomes the classic photochemical eq 2. Equation 2 can be used for L_3CuCl species

$$\Phi^{-1} = \Phi_e^{-1} (1 + K_s^{-1} [\text{NBD}]^{-1}) \quad (2)$$

to obtain the kinetic parameters from the slope-intercept data shown in Table I. By use of the competitive oxygen quenching data and assuming a quenching constant for O_2 of $3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, k_q is calculated to be $8 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ and k_t is equal to $3 \times 10^5 \text{ s}^{-1}$ for the L_3CuCl species.

For the L to CuCl ratio of 2:1 shown in Figure 4, eq 1 must be used to extract the kinetic parameters for L_2CuCl . Now it is necessary to use the data on equilibrium constants and extinction coefficients of the major species. These data are summarized in Table II. We have evidence that species 5 and 6 have properties similar to L_2CuCl , species 3.^{15a} The contributions of species 5-7 to the photochemical model are small for all cases we have treated. Even though the L_2CuCl and species 5 and 6 account for over 80% of the copper concentration, they only absorb approximately 61% of the light whereas the L_3CuCl species still absorbs approximately 36% of the light. Knowing K_s and Φ_e for the L_3CuCl species, the linear portion of Figure 4 for the 2:1 ratio (see Table

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Table II. Values Used in the Photochemical Model for Norbornadiene to Quadricyclane Conversion

no.	species	equilibria for Formation	equilibrium constant	313×10^{-3}	Φ_e	$K_s = k_q/k_t$
0	NBD			0.00036 ^d		
1	L = Ph ₂ MeP			0.065 ^a		
2	L ₃ CuCl			11.0 ^a	1.0 ^b	230 ^b
3	L ₂ CuCl	L ₃ CuCl \rightleftharpoons L ₂ CuCl + L	2×10^{-4} ^a	3.9 ^a	1.0 ^b	20 ^b
4	L ₁ CuCl	L ₂ CuCl \rightleftharpoons L ₁ CuCl + L	1×10^{-6} ^a	1.0 ^a		
5	L ₄ Cu ₂ Cl ₂	2L ₂ CuCl \rightleftharpoons L ₄ Cu ₂ Cl ₂	$6 \times 10^{+2}$ ^a	7.8 ^a	1.0 ^c	20 ^c
6	L ₃ Cu ₂ Cl ₂	L ₂ CuCl + LCuCl \rightleftharpoons L ₃ Cu ₂ Cl ₂	$8 \times 10^{+4}$ ^a	4.9 ^{a,d}	1.0 ^c	20 ^c
7	L ₂ Cu ₂ Cl ₂	2LCuCl \rightleftharpoons L ₂ Cu ₂ Cl ₂	$1 \times 10^{+5}$ ^a	2.0 ^a		
8	L ₁ CuCl-NBD	L ₁ CuCl + NBD \rightleftharpoons complex	50 ^d	2.0 ^d	0.4 ^b	
9	L ₂ CuCl-NBD	L ₂ CuCl + NBD \rightleftharpoons complex 2	5-10 ^b	3.9 ^d	0.6-0.7 ^b	

^a Reference 15a. ^b Values derived from best fit of the experimental data using modeling with Scheme I. ^c Values assumed to be the same as for L₂CuCl. ^d Values obtained experimentally.

I) was used to evaluate K_s and Φ_e for the L₂CuCl species as an energy donor.

We have chosen to treat the L to CuCl ratio of 1:1 by a different mechanism for the following reasons. First, as was discussed earlier, a complex between NBD and LCuCl was isolated and spectral characterization obtained. Second, the limiting quantum yield is less than 1.0 (Figure 4) which is different from the sensitizers L₃CuCl and L₂CuCl. Evaluation of the 1:1 ratio of the L to CuCl data shown in Figure 4 using the ground-state complex C1 (see Scheme I) gives $K_{C1} = 50$ and $\Phi_{C1} = 0.4$. We had found from spectrophotometric measurements that the complex C1 had an extinction coefficient of 2×10^3 if $K_{C1} = 50$, so the results from both types of experiments match.

At high NBD concentrations many of the data sets have a reversal in the linear trend for Φ^{-1} vs. [NBD]⁻¹. In Figure 7, the data are shown as Φ^{-1} dependence vs. [NBD]. If NBD were becoming an excited singlet state quencher, then there should be a linear relationship on this graph. This has been observed where EDTA was an electron donor for the triplet state of riboflavin but a quencher of the excited singlet state.¹⁸ After reaching the maximum quantum yield of 0.5 with 0.01 M EDTA, the photo-reduction of riboflavin was quenched by additional EDTA as predicted by a Stern-Volmer relationship. In the present situation, at high NBD concentrations, the Φ^{-1} are approaching a plateau. To adequately model this behavior, we have invoked a second complex using L₂CuCl and NBD. The justification for this complex is based on the kinetic evidence and the coordinately unsaturated nature of the L₂CuCl species. Also as was reported in the results there was an accompanying perturbation of the absorbance at 313 nm with very high NBD concentrations. This would be expected if the extinction coefficient of the complex were different from the extinction coefficient of the major species, L₃CuCl. Scheme I and Table II contain the full mechanistic aspects of the model along with the required parameters to adequately fit the experimental data. For each concentration of NBD, 7 nonlinear simultaneous equations and 2 concentration conservation constraints are used to solve for the 9 species including the 2 NBD-(arylphosphine)copper chloride complexes. We used the Newton-Raphson method and Gaussian elimination with partial pivot strategy.¹⁹ All concentrations, extinction coefficients, and kinetic parameters were introduced into eq 1.

The data in Figures 2, 3, and 4, where Φ^{-1} is graphed as a function of [NBD]⁻¹, were used to generate initial values for parameters in eq 1. They are summarized in Table I. Table II contains the remaining parameters which are required to perform the modeling. The only important parameters not generated by other experiments are those for the NBD-L₂CuCl complex C2. To adequately describe all the data, some adjustments of the parameters in Table I were made. The solid lines in Figures 2, 3, and 4 are the final predictions made by the model with use of the data in Table II. These data points are fairly insensitive to the value range for C2 parameters. However, the effect of the C2 complex is more pronounced for data points in Figure 7 which

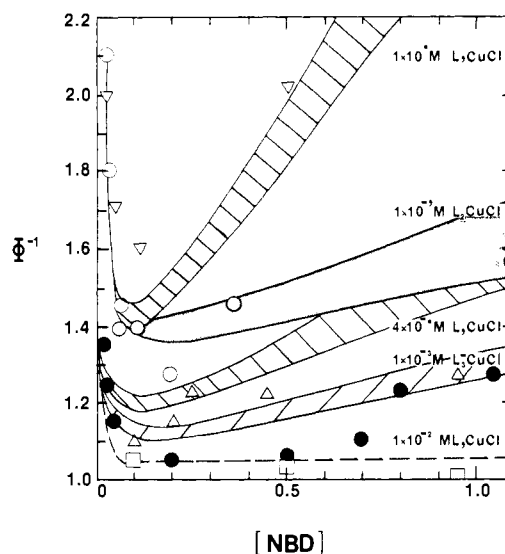


Figure 7. Prediction of the modeling of the diphenylmethylphosphine/copper chloride/NBD system using Scheme I and the values from Table II. (The shaded areas show the effect of changing Φ_{C2} from 0.6 to 0.7 holding $K_{C2} = 10$.) 1×10^{-2} M L₃CuCl (□), 1×10^{-3} M L₃CuCl (●); 4×10^{-4} M L₃CuCl (Δ); 1×10^{-3} M L₂CuCl (○); 1×10^{-4} M L₃CuCl (▽). Formulas are not meant to imply a sensitizer form but rather the ratio of MePh₂P to CuCl in solution.

shows the sensitivity of the model to variation in the quantum yield of C2. Similar results could be shown by varying the equilibrium constant K_{C2} . With $K_{C2} = 10$, all data points in Figure 7 fall close to the model range. The value $\Phi_{C2} = 0.7$ generates the lower boundary and the value $\Phi_{C2} = 0.6$ generates the upper boundary. The data for a copper-to-ligand ratio of 1:3 has a concentration range from 1×10^{-4} to 1×10^{-2} M. At the lower concentrations (10^{-4} - 10^{-3} M) there are a variety of the species present from Table II, but the dominant species are L₃CuCl, L₂CuCl, and C2 (L₂CuCl-NBD). At 10^{-2} M the only dominant species is L₃CuCl. The shaded area is different from the other four curves since it represents a copper-to-ligand ratio of 1:2 at 1×10^{-3} M. The L₂CuCl-NBD complex (C2) is dominant at higher NBD concentrations.

We have presented a complicated photochemical mechanism involving both conventional energy transfer and the excitation of ground-state complexes. We feel this is the simplest scheme which will explain all the data we have obtained.

The reason for the striking contrast between the efficiency of NBD to Q conversion with use of the (triphenylphosphine)copper halide system, L₃CuX, and the methyl-diphenylphosphine system described becomes clear when the solution equilibria data are considered. The solution equilibria predict that (Ph₃P)₂CuX and not (Ph₃P)₃CuX would be the dominant species in solution at 1×10^{-3} M CuX.^{15a} In fact, it is not possible with a 3 to 1 ratio of Ph₃P to CuX to produce a benzene solution where (PPh₃)₃CuX dominates. Therefore, the kinetic data shown in Figure 1 are not for (Ph₃P)₃CuI. This probably accounts for the low quantum yields obtained with Ph₃P as the ligand since the L₃CuX species

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was the most efficient sensitizer when Ph_2MeP was the ligand. The somewhat puzzling part of this analysis is that the L_3CuX species is a much better energy donor than the L_2CuX species. The various forms of the phosphine Cu(I) sensitizers were all determined to have approximately the same triplet energy, $E_T = 76.0$ kcal/mol.^{15c} Since the sensitizers have the same energy available for triplet sensitization, the quenching constant, k_q , for the sensitizers should be approximately the same. If k_q for L_3CuCl and L_2CuCl are the same, then the large difference in efficiency of the two sensitizers as shown by data in Table II must be a consequence of very different triplet excited state lifetimes with the coordinately saturated (arylophosphine)copper halides appearing to have longer excited-state lifetimes in solution and therefore a higher probability of transferring energy to the NBD molecule than the L_2CuX . The conclusion that the triplet lifetimes in solution at room temperature of L_3CuX and L_2CuX are considerably different finds some confirmation in the (DIPHOS)CuCl results (Figure 5). The triplet lifetime of (DIPHOS)CuCl is very short as indicated by oxygen not being able to quench the photoisomerization process.

There are two plausible explanations for a much longer solution triplet lifetime of the phosphine-saturated complex that comes from the description given to the nature of the lowest electronic transition of the (phosphine)copper(I) halide complexes. The electronic transitions of the complexes have been shown to be a perturbation of the excited states of the ligand.¹⁵ The molecular orbital description ($\sigma, d \rightarrow a_g$) was assigned, indicating that the electronic transition involved both the bond of the phosphorus lone electron pair to the metal and the d-d orbital bonding of the metal and phosphorus. The electron transition was described as an electron excitation of a phosphorus electron from the σ bond to an antibonding phenyl π -system (a_g) with a concerted flow of electron density from the metal to the phosphorus via the d-d orbital bonding. With this description, the primary relaxation and energy-transfer processes of the triplet state of the (arylophosphine)copper(I) halide complexes would be controlled by the metal. The extra arylophosphines coordinated to the metal in the L_3CuCl form could help increase the excited-state lifetime by stabilizing the excited state with a donation of electron density to the metal.

The idea of a metal-controlled excited state is substantiated by the calculated rate constant of energy transfer for $(\text{MePh}_2\text{P})_3\text{CuCl}$, $k_q = 8 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$, to NBD. The rate is considerably less than the diffusion-controlled rate of $7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ in benzene. Since k_q was calculated by using a diffusion-controlled rate of $3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for oxygen, $k_q = 8 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ becomes an upper limit. If oxygen quenching of the $(\text{MePh}_2\text{P})_3\text{CuCl}$ complex is actually less than $3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, then k_q will be less than $8 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ by the same factor. Little is known about the excited-state interactions of metal complexes and oxygen. Because d-d and charge-transfer excited states of metal complexes have no direct organic counterpart and since spin-orbit coupling is much greater than in organics, different rules may well apply. However, what work has been reported indicates that oxygen quenching is still diffusion controlled for even metal-centered excited states.^{20,21} In contrast, experimental data indicate that energy transfer from organic triplets to metal-centered excited states are usually lower than diffusion controlled even though the energy transfer is highly exoergic.^{20,21} Lower rates for exoergic energy transfer by a factor of 10 to 100 are common for metal-centered excited states.^{20,22} The most recent reason proposed for this observation is given in terms of orbital overlap between the metal-centered orbitals and the orbitals of the organic donor molecule.²⁰ An electron-exchange energy-transfer mechanism is assumed and thus orbital overlap has to occur between the metal-centered orbitals and the orbitals of the

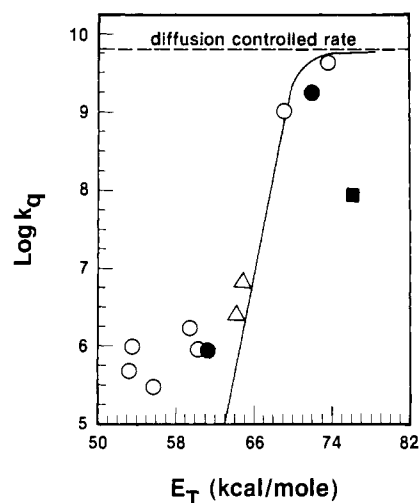


Figure 8. Variation of the rate constants for quenching, k_q , of sensitizers by norbornadiene in comparison to sensitizer triplet energy, E_T . Darkened points were determined by this study. Organic sensitizers: (O) flash photolysis data from ref 11c; (Δ) ref 3h; k_q not reported in reference, k_q estimated by using the data given and by assuming the lifetime of the sensitizer triplet was controlled by oxygen quenching since the data were taken without deaeration; (\bullet) at 72 kcal/mol Ph_2NH and at 61 kcal/mol Michler's ketone. Inorganic sensitizer: (\blacksquare) at 76 kcal/mol $(\text{MePh}_2\text{P})_3\text{CuCl}$. Solid line is the predicted energy quenching constant for the conventional energy-transfer mechanism calculated by using $E_T = 70$ kcal/mol for norbornadiene and $k_d = 6.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (diffusion controlled rate)—see ref 21, 23, and 25.

organic molecule. A much smaller or hindered orbital overlap is expected for metal-centered excited states because of the shielding effect of the ligands toward the interaction between the metal orbitals and the orbitals of the organic donor molecule.²⁰ Oxygen, being a much smaller molecule than most organic molecules used as donors, apparently can penetrate to the metal center more effectively. These ideas follow the pattern observed for the energy-transfer rate observed for $(\text{MePh}_2\text{P})_3\text{CuCl}$ and $(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)\text{CuCl}$. Figure 8 shows the energy-transfer rates previously determined for sensitizers of the NBD/Q system in comparison to those determined in this study. The rate constant, k_q , for Ph_2NH was determined in the same manner as described for $(\text{MePh}_2\text{P})_3\text{CuCl}$ with competitive oxygen quenching. For Michler's ketone, the k_q/k_t value reported in Table I along with the relaxation rate, $k_t = 4 \times 10^5$, reported in the literature²³ were used to calculate k_q . The triplet energies of Ph_2NH and Michler's ketone were also confirmed with the literature values by use of the instrumentation previously described.¹⁵ The energy transfer rate of $(\text{MePh}_2\text{P})_3\text{CuCl}$ is clearly much lower than expected for an exoergic energy transfer (Figure 8). This observation along with the suggested shortened lifetime of $(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)\text{CuCl}$ and $(\text{MePh}_2\text{P})_2\text{CuCl}$ in comparison to $(\text{MePh}_2\text{P})_3\text{CuCl}$ indicates that energy transfer takes place through a metal-controlled energy-transfer process.

The copper(I) metal center also stabilizes the photodecomposition and reactivity of the electronically excited phosphine. The free phosphine has sufficient energy ($E_T = 74\text{--}76$ kcal/mol)^{15b,24} to sensitize the isomerization of NBD to Q. However, the arylophosphines are extremely poor sensitizers; Ph_3P and MePh_2P have quantum yields reported as 0.01 and 0.04 respectively at 0.1 M NBD.^{3f} More recently Ph_3P was reported to have a quantum yield equal to 0.003 at 0.2 M NBD.^{3j} Initial experiments performed in this study are in agreement with these values. Apparently, the photodecomposition for the arylophosphines is very competitive with any energy-transfer process. The fact that

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(21) Demas, J. M.; Diemente, D.; Harris, E. W. *J. Am. Chem. Soc.* **1973**, *95*, 6864.

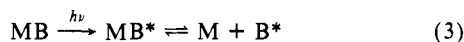
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(24) Fife, D. J.; Morse, K. W.; Moore, W. M. *J. Photochem.* **1984**, *24*, 249.

(MePh₂P)₃CuCl gives very efficient energy transfer with a maximum quantum yield of 1.0 shows that photodecomposition of the arylphosphine has been eliminated or drastically reduced. This stabilization or protection to decomposition during photolysis would be the result of the electron density which the copper is able to donate to the phosphorus during the excitation process.

The low efficiencies and discoloration observed in the (MePh₂P)₂ZnCl₂ sensitization of the NBD/Q system fit nicely with this line of reasoning. Zinc, because of its high promotion energy, would not be expected to donate any appreciable electron density back to the phosphorus during excitation. Thus (MePh₂P)₂ZnCl₂ might be expected to show the same sensitization ability as MePh₂P. In fact, both (MePh₂P)₂ZnCl₂ and (MePh₂P)HCl showed essentially the same sensitization in the NBD/Q system as MePh₂P. A generalized Lewis acid-base equilibrium between an excited complex, MB*, and its excited conjugate base, B*, adequately explains the results.



The implication is that the arylphosphines are much stronger bases in their ground state than the excited state. In fact, the arylphosphines would become electrophilic instead of nucleophilic in the electronically excited state.^{15b,24} If the conjugate acid [(MePh₂P)HCl, (MePh₂P)₂ZnCl₂, (MePh₂P)₃CuCl] is less able to donate electron density in the excitation process, then the dissociation equilibrium shown in eq 9 [M = HCl, (MePh₂P)-ZnCl₂, (MePh₂P)₂CuCl; B = MePh₂P] could become significant. In the limiting case the observed quantum yield for the photoisomerization of the NBD/Q system would be the same as the free arylphosphine.

There is one other observation worthy of discussion that comes as a byproduct of determining the quenching rate, k_q , of (MePh₂P)₃CuCl by competitive oxygen quenching. The observation that the maximum quantum yield of 1.0 with (MePh₂P)₃CuCl as a sensitizer did not change with the addition of molecular oxygen has two important consequences. First, the excited singlet lifetime of (MePh₂P)₃CuCl would be assumed to be very short (1 ns) since no singlet quenching by oxygen is observed. If the singlet lifetime of the sensitizer is sufficiently long that oxygen can quench the singlet excited state, the Φ_{isc} would decrease since less excited singlet is available for intersystem crossing. In the reciprocal plot of Φ^{-1} vs. [NBD]⁻¹ the intercept would increase, indicating that the Φ_{isc} has decreased due to singlet quenching. The Ph₂NH results show an increase in the intercept of the reciprocal plot with the addition of 1.9×10^{-3} M oxygen (Table I). The change in the intercept is exactly the same factor as the fluorescent quenching observed by 1.9×10^{-3} M oxygen. The second consequence of no observable intercept change with oxygen quenching is found in the branching ratio of the NBD

triplet ($P_i = k_p/(k_n + k_p)$). All of the NBD triplets produced by energy transfer are still converting to Q since both Φ_{isc} and P_i have to equal 1.0. With oxygen present to quench the ³NBD produced in the energy-transfer process, a competitive decay of ³NBD → ³Q and ³NBD + O₂ → NBD + ¹O₂ is established. Since no observable change in P_i resulted with oxygen quenching, the conversion of NBD triplets to Q triplets must be extremely fast ($\gg 5.7 \times 10^6$ s⁻¹). This would suggest that ³Q would have a lower energy than ³NBD or, as some authors¹² have suggested through other observations, there is a lower energy intermediate diradical triplet conformation on the triplet surfaces connecting ³NBD and ³Q which preferentially decays to Q.

Conclusions

(1) This research has shown that (phosphine)copper(I) halide complexes can be extremely efficient sensitizers of the NBD/Q system. However, the coordination number of Cu(I) is extremely important in controlling the mechanism and efficiency of sensitization.

(2) The most efficient sensitization process observed by the (phosphine)copper(I) complexes is that of conventional bimolecular energy transfer from the triplet excited state of the (phosphine)copper(I) sensitizer to NBD. The sensitization ability of (MePh₂P)₃CuCl is unprecedented by other inorganic sensitizers of the NBD/Q system reported to date. (MePh₂P)₃CuCl shows a maximum quantum yield of 1.0 with a 100% yield of Q. No adduct products or singlet quenching by Q or NBD were observed. (MePh₂P)₃CuCl also has a strong absorbance maxima at 300 nm which extends as far as 365 nm. The principle disadvantage of (MePh₂P)₃CuCl as a sensitizer is that the complex exhibits extensive ligand dissociation in dilute solutions.

(3) The bimolecular energy-transfer mechanism proposed is described as a metal-controlled process. The metal-controlled process fits the assigned $\sigma_d \rightarrow a_g$ orbital classification of the electronic transitions of the (phosphine)copper(I) complexes. The copper(I) metal is able to stabilize the triplet state of the phosphine by donation of electron density to the phosphorus via d,d orbital bonding during the excitation process. The triplet lifetimes of the (phosphine)copper(I) complexes in solution are increased considerably as the ratio of ligand to metal is increased to 3:1.

(4) A (NBD)(MePh₂P)CuCl complex was isolated. Its photochemical behavior differs from the olefin-free (arylphosphine)copper(I) halides. Even though a (NBD)-(MePh₂P)₂CuCl complex was not isolated, the quantum yield dependence of the L₂CuCl solutions with NBD concentration suggested its existence.

(5) The analysis performed in considering the equilibrium of dissociation of the (phosphine)copper(I) sensitizers and the formation of NBD ground-state complexes shows that the principal difference in the sensitization behavior of MePh₂P and Ph₃P copper(I) halide complexes is attributed to the differences in the dissociation of the complexes in solution rather than differences in electronic structure.

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