

It is interesting to compare the results obtained for the low-temperature protonation reaction described in Scheme III with reaction 9 which normally was performed at room temperature. From NMR spectroscopic data described above, it has been demonstrated that complex 4 exists in solution primarily as a capped Fe_4 tetrahedron (Figure 1). However, in order to form the carbide cluster $\text{HFe}_4(\text{CO})_{12}(\text{C}\cdot\text{AuPPh}_3)$ in reaction 9, conversion of the tetrahedral isomer to the butterfly isomer must presumably occur prior to C-O bond cleavage.

Conclusion

Formation and stabilization of the butterfly cluster $[\text{Fe}_4(\text{A})(\text{CO})_{13}]^-$ is promoted by the presence of a Lewis acid ligand bridging the hinge of the butterfly. All examples of $[\text{Fe}_4(\text{A})(\text{CO})_{13}]^-$ molecules exhibit two isomeric forms in solution (Fe_4 butterfly and Fe_4 tetrahedron) and it was possible to demonstrate that strong acceptors favor the butterfly form. The butterfly form can be further stabilized by the addition of an electrophile to the II-CO oxygen. In this instance the butterfly form is the only cluster species in solution.

The low-temperature protonation reactions suggest that the II-CO ligand possesses a more basic oxygen than even a face-capping CO ligand. The subsequent C-O bond cleavage of these II-CO ligands to form a cluster carbide species clearly indicates the importance of II-CO ligands in the activation of CO.

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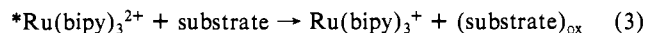
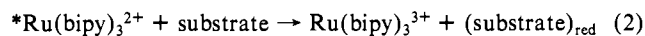
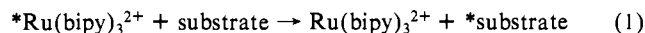
Study of Intramolecular Sensitization and Other Excited-State Pathways in Orthometallated Azobenzene Complexes of Palladium(II)

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Abstract: Reported are structural, spectral, and photochemical studies of several complexes of the type $(\text{Azb}')\text{PdBr}(\text{L})$ and $(\text{Azb}'')\text{PdBr}(\text{L})$, where Azb' is orthometallated 4-nitro-4'-(dimethylamino)azobenzene, Azb'' is orthometallated 4-methoxyazobenzene, and L is *cis*- or *trans*-4-stilbazole, pyridine, or 3-methylpyridine. In room-temperature solutions containing an equimolar amount of free L, these square-planar complexes undergo both rapid exchange of free and coordinated L and *cis*-*trans* isomerization at the Pd center. The low-energy region in the absorption spectra of the complexes is dominated by transitions that are localized largely on the orthometallated azobenzene chromophore. Neither free 4-nitro-4'-(dimethylamino)azobenzene nor 4-methoxyazobenzene luminesce in room-temperature fluid solution; upon metallation by Pd, however, intraligand fluorescence is observed. Irradiation of the complexes at a wavelength that populates an azobenzene-localized excited state causes isomerization of the 4-stilbazole ligand. Although this result demonstrates that low-energy photons absorbed by the azobenzene chromophore can be used to sensitize a photochemical reaction of a remotely located nonabsorbing ligand, the quantum yields are disappointingly low ($<10^{-3}$). The mechanism of this intramolecular sensitization and possible reasons for its inefficiency are considered.

During the past 15 years, numerous coordination compounds have been investigated as photosensitizers for organic and inorganic reactions.¹ Much of the recent impetus in this area has arisen from the desire to convert sunlight into stored chemical energy and the attendant need to extend the threshold of photoreactivity to wavelengths above 500 nm. Metal complexes containing conjugated ligands such as 2,2'-bipyridine (bipy), 1,10-phenanthroline, and various porphyrins are potentially attractive in this regard, since they absorb well into the visible spectral region owing to the presence of low-lying electronic excited states of charge-transfer or intraligand character. Moreover, many of these complexes can activate suitable substrates via pathways that involve intermolecular energy transfer and/or electron transfer.² These types of interactions are outlined for the specific case of $\text{Ru}(\text{bipy})_3^{2+}$ in eq 1-3, where the subscripts red and ox denote



the reduced and oxidized forms, respectively, of some generic substrate and the asterisk signifies an electronically excited species.

An alternative, though less-explored approach to sensitization involves the intramolecular transfer of energy from a strongly absorbing, unreactive chromophore ("antenna fragment") situated in one part of a complex to a reactive substrate located some

(1) For a review of basic principles and much of the early work in this area, see: Balzani, V.; Moggi, L.; Manfrin, M. F.; Bolletta, F.; Laurence, G. S. *Coord. Chem. Rev.* **1975**, *15*, 32.

(2) Sutin, N.; Creutz, C. *Pure Appl. Chem.* **1980**, *52*, 2717. Kalyanasundaram, K. *Coord. Chem. Rev.* **1982**, *46*, 159. Darwent, J. R.; Douglas, P.; Harriman, A.; Porter, G.; Richoux, M.-C. *Coord. Chem. Rev.* **1982**, *44*, 83.

[†] The Institute of Physical and Chemical Research.

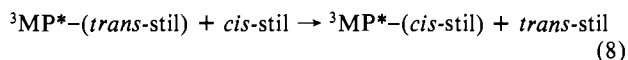
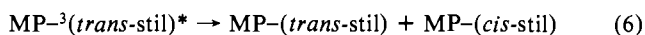
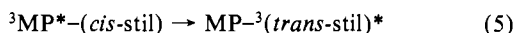
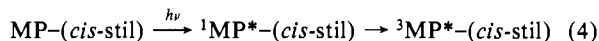
[‡] University of Georgia.

Table I. Analytical and Physical Data for (Az b')PdBr(L) (1–4) and (Az b'')PdBr(L) (5, 6) Complexes

complex	yield, %	color	mp dec, °C	anal. (calcd), %
(1) L = <i>cis</i> -4-stilbazole	23	dark green	200	C 50.83 (50.92) H 3.75 (3.80) N 10.98 (11.00)
(2) L = <i>trans</i> -4-stilbazole	56	dark purple	240–242	C 50.89 (50.92) H 3.77 (3.80) N 10.92 (11.00)
(3) L = pyridine ^a	63	golden-brown	127–130	C 40.51 (40.58) H 3.25 (3.32) N 12.17 (12.13)
(4) L = 3-methylpyridine	90	dark green	165–170	C 44.10 (44.78) H 3.62 (3.67) N 12.65 (12.76)
(5) L = <i>cis</i> -4-stilbazole ^b	86	yellow-brown	143–145	C 52.62 (52.54) H 3.77 (3.78) N 7.02 (7.00)
(6) L = <i>trans</i> -4-stilbazole	95	brown	203–205	C 53.78 (53.95) H 3.85 (3.86) N 7.20 (7.26)

^a Contains 1/2CH₂Cl₂ as solvent of crystallization. ^b Contains 1/4CH₂Cl₂ as solvent of crystallization.

distance away but still bound to the metal.³ Since the chromophore and substrate are in close proximity at a single metal center, diffusional effects are minimized and excited states that are too short-lived to participate in intermolecular energy transfer may become important in the intramolecular process. An elegant example of such behavior was reported by Whitten et al.,⁴ who investigated porphyrin complexes of zinc and magnesium containing an extraplanar, isomerizable azastilbene ligand such as *cis*- or *trans*-4-stilbazole. Light absorbed by the long-wavelength transitions of the metalloporphyrin chromophore was found to promote efficient geometrical isomerization of the coordinated azastilbene. The high quantum yields (>1 in some cases) for this transformation were attributed to a quantum chain process that arose from reversible intramolecular energy transfer between the triplet states of the porphyrin and the azastilbene ligand. The key features of the proposed mechanism are summarized in eq 4–8, where MP represents the metalloporphyrin, *cis*-stil and



trans-stil denote the isomeric 4-stilbazoles, and the numeric superscripts designate the spin multiplicities of the excited states involved. Reverse energy transfer in eq 7 coupled with rapid ligand exchange in eq 8 account for the high quantum yields observed.

In this article, we describe our recent studies of a series of palladium(II) complexes containing both an orthometallated azobenzene derivative and a substitutionally labile 4-stilbazole ligand (see Figure 1). Our interest in these complexes arose from several considerations: (1) little information currently exists concerning the excited-state properties of orthometallated complexes, (2) the complexes absorb strongly in the visible region and thus are of potential use as photosensitizers, and (3) the presence within the same complex of the azobenzene chromophore and a labile, isomerizable ligand may facilitate the type of intramolecular energy-transfer process described above (eq 4–8). Reported herein

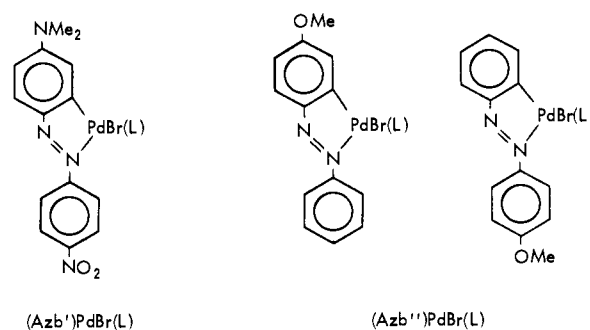


Figure 1. Pd(II) complexes examined in this study.

are structural, spectral, and photochemical data that bear directly on these and related points of interest.

Experimental Section

Literature procedures⁴ were followed in the preparations of *trans*- and *cis*-4-stilbazole. *trans*- and *cis*-stilbene were purchased from Aldrich Chemical Co. Samples of 4-nitro-4'-(dimethylamino)azobenzene and 4-methoxyazobenzene were obtained from Tokyo Chemical Industry Co., Ltd.

Preparation of [(Az b')PdBr]₂ and [(Az b'')PdBr]₂. 4-Nitro-4'-(dimethylamino)azobenzene (2.6 g, 9.6 mmol) was dissolved in tetrahydrofuran (THF), and a small amount of insoluble material was removed by filtration. Palladium acetate (1.8 g, 8 mmol) in THF (200 mL) was added to the filtrate, and over a period of 3 days, golden-green crystals of [(Az b')Pd(OAc)]₂·THF precipitated (2.8 g, 2.9 mmol), mp >300 °C dec. Anal. Calcd for C₃₆H₄₀N₈O₉Pd₂: C, 45.92; H, 4.28; N, 11.90. Found: C, 45.84; H, 4.29; N, 11.73. A portion of this material (420 mg) was dissolved in dichloromethane (200 mL), a methanol (30 mL) solution of lithium bromide (5 g) was added, and the resulting mixture was shaken for 5 h. Following removal of the solvent under reduced pressure, the dark-brown residue was shaken with water. Filtration yielded [(Az b')PdBr]₂ as a powder which was then washed several times with water and finally with a small portion of methanol. The yield was nearly quantitative, mp >300 °C dec. Anal. Calcd for C₂₈H₂₆Br₂N₈O₄Pd₂: C, 36.91; H, 2.88; Br, 17.54; N, 12.30. Found: C, 35.78; H, 2.88; Br, 17.63; N, 11.77. By a similar procedure, [(Az b'')PdBr]₂ (2.16 g) was obtained as an orange powder from palladium acetate (1.8 g) and 4-methoxyazobenzene (2.6 g), mp 238–241 °C dec. Anal. Calcd for C₂₆H₂₂N₂Br₂O₂Pd₂: C, 39.28; H, 2.79; N, 7.05. Found: C, 38.81, H, 2.75, N, 6.99.

Preparation of (Az b')PdBr(L) and (Az b'')PdBr(L) (1–6). These complexes were prepared by adding the stoichiometric amount of L (L = *cis*- or *trans*-4-stilbazole, pyridine, or 3-methylpyridine) to the corresponding bromo-bridged Pd dimer suspended in dichloromethane. After filtration, hexane was added slowly to afford crystals of the desired monomeric complex. Analytical and physical data are summarized in Table I.

Preparation of [(Az b')Pd(PPh₂CH₂CH₂Ph₂P)]Br (7). 1,2-Bis(diphenylphosphino)ethane (diphos) (25 mg, 0.063 mmol) was added to a suspension of [(Az b')PdBr]₂ (40 mg, 0.063 mmol) in dichloromethane

(3) For recent examples of this general strategy in binuclear transition metal complexes, see: Moore, K. J.; Lee, L.; Figard, J. E.; Gelroth, J. A.; Stinson, A. J.; Wohlers, H. D.; Petersen, J. D. *J. Am. Chem. Soc.* **1983**, *105*, 2274; Kane-Maguire, N. A. P.; Allen, M. M.; Vaught, J. M.; Hallock, J. S.; Heatherington, A. L. *Inorg. Chem.* **1983**, *22*, 3851.

(4) Whitten, D. P.; Wildes, P. D.; DeRosier, C. A. *J. Am. Chem. Soc.* **1972**, *94*, 7811.

(15 mL) and the mixture stirred overnight. After removal of insoluble material by filtration, the solution was concentrated to ca. 3 mL. Ether (2 mL) was added to precipitate dark-brown crystals of **7** (29 mg, 0.034 mmol), mp 173–175 °C. Anal. Calcd for $C_{40}H_{37}BrN_4O_2P_2Pd$: C, 56.26; H, 4.37; N, 6.56. Found: C, 56.34; H, 4.35; N, 6.45.

Preparation of (Azb'')Pd(η^5 -C₅H₅) (8). A solution of [(Azb'')PdBr]₂ (100 mg, 0.135 mmol) in benzene (10 mL) was added to a THF solution of NaC₅H₅ (0.4 mmol). After 30 min, the dark-brown solution was concentrated and chromatographed on alumina. A dark-brown band was eluted with benzene/dichloromethane (3/1). After removal of the solvent under reduced pressure, hexane was added to the residue and the mixture was allowed to stand overnight whereupon dark-red crystals of **8** formed (32 mg, 0.084 mmol), mp 95–96 °C. Anal. Calcd for C₁₈H₁₆N₂OPd: C, 56.49; H, 4.21; N, 7.32. Found: C, 56.39; H, 4.27; N, 7.32. ¹H NMR (CDCl₃), δ 3.89, 3.91 (OMe, ca. 1:1), 5.86, 5.88 (C₅H₅, ca. 1:1), 6.7–8.3 (aromatics).

Photodecomposition of 2 and 3. Complex **2** (83 mg, 0.14 mmol) and *trans*-4-stilbazole (5 mg) were dissolved in dichloromethane (50 mL) and irradiated with a 100-W high-pressure mercury lamp in a Pyrex vessel. After 4 days, the darkened reaction mixture was concentrated and poured onto a silica gel column. An orange-red band was eluted with dichloromethane and a purple band was eluted with dichloromethane/THF (20/1). Unreacted **2** (46 mg) was recovered from the second fraction. Concentration of the first fraction and addition of hexane yielded fine, purple crystals of 4-nitro-2'-bromo-4'-(dimethylamino)azobenzene (31 mg, 0.089 mmol), mp 193–195 °C dec. Anal. Calcd for C₁₈H₁₆BrN₂O₂: C, 48.16; H, 3.75; N, 16.05. Found: C, 48.99; H, 3.75; N, 16.03. ¹H NMR (CDCl₃) δ 3.13 (s, 6, N-CH₃), 6.68 (br d, 1, *J* = 9.3 Hz), 7.02 (br s, 1), 7.84 (d, 1, *J* = 9.3 Hz), 7.99 (d, 1, *J* = 8.8 Hz), 8.34 (d, 1, *J* = 8.8 Hz). The structure of this compound was assigned by comparison of its NMR spectrum to those of 4-nitro-4'-(dimethylamino)azobenzene and 4-(dimethylamino)azobenzene.

Photodecomposition of **3** gave the same brominated azobenzene in good yield.

Physical Measurements. Electronic absorption spectra were recorded on a Cary 219 spectrophotometer. Luminescence spectra were taken with a Perkin-Elmer MPF-44B spectrofluorimeter and, unless indicated otherwise, are uncorrected for photomultiplier response. Picosecond lifetime measurements were obtained with an apparatus described elsewhere.⁵ Proton NMR spectra were run on a JEOL JNM-GX400 spectrometer; chemical shifts are reported in parts per million (ppm) relative to TMS as an internal standard. Solution conductivities were measured with a Yellow Springs Instrument Model 31 conductivity bridge and calibrated cell.

Quantum Yield Measurements. Photolyses were conducted with a 200-W high-pressure mercury-arc lamp (Illumination Industries) in conjunction with suitable interference and blocking filters to isolate the 436-nm or 546-nm emission line. Incident light intensity was determined by Reineckate actinometry.⁶ In a typical photochemical experiment, a nitrogen-purged dichloromethane solution containing 1×10^{-4} M Pd complex and excess *cis*- or *trans*-4-stilbazole was irradiated with stirring in a 1-cm rectangular quartz cell fitted with a ground-glass stopper. The temperature during photolysis was maintained at 25 ± 0.5 °C by a thermostated cell holder. Two methods were used to determine the extent of photoinduced isomerization of 4-stilbazole.

Method A. The change in the absorption spectrum upon photolysis was used to evaluate the isomeric composition of solutions originally charged with equimolar amounts (1×10^{-4} M) of Pd(II) complex and free 4-stilbazole. For example, 308 nm is a convenient wavelength for monitoring the decrease in absorbance, ΔA , that occurs upon irradiating **2** and *trans*-4-stilbazole. Knowing the extinction coefficients of the photoproducts (**1** and *cis*-4-stilbazole) at this wavelength, we can calculate the absorbance, A_{tot} , that would result from total conversion. The actual percent conversion is then determined from eq 9, where A_{in} is the initial absorbance (i.e., before photolysis) at 308 nm.

$$\% \text{ conversion} = \frac{\Delta A}{A_{in} - A_{tot}} \times 100 \quad (9)$$

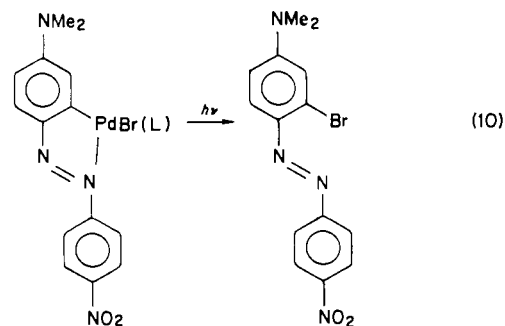
Method B. Irradiated and dark solutions containing the Pd(II) complex and a large excess (0.1 M) of 4-stilbazole were analyzed for isomeric composition by gas chromatography. The apparatus consisted of a Varian 2700 chromatograph equipped with a flame ionization detector and containing a 12 ft \times 1/8 in. stainless steel column packed with 5% OV-101 on Chromosorb G-HP (80–100 mesh). Operating temperatures were as follows: injector, 243 °C; column, 225 °C; detector, 275 °C. The

straight-chain hydrocarbon, C₁₇H₃₆, was used as an internal standard. Gas chromatographic peak areas were integrated by a Perkin-Elmer Sigma 10 data system.

Results and Discussion

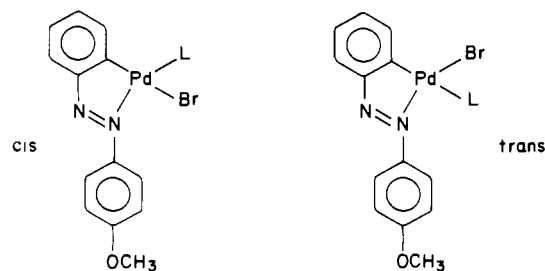
(a) Structures and Solution Properties. The bromo-bridged dimer, [(Azb')PdBr]₂, is sparingly soluble in chloroform, dichloromethane, and THF, while [(Azb'')PdBr]₂ and the monomeric species **1–6** dissolve to a greater extent in these polar solvents. Solutions of **1–4** in CH₂Cl₂ form a small amount of solid [(Azb')PdBr]₂ on standing for several hours, indicating that there is an equilibrium in solution between the bridged complex and (Azb')PdBr(L). This problem was minimized by the addition of at least an equimolar amount of L to the solution; presumably the excess ligand drives the equilibrium toward the more soluble monomeric complex (however, see below).

Orthopalladation of an unsymmetrically substituted azobenzene compound (e.g., XC₆H₄N=NC₆H₄Y) can occur in either ring, thus raising the possibility that the product will exist as an isomeric mixture. From a systematic study of product distributions, Bruce et al.⁷ concluded that palladation occurs preferentially in the ring containing the most electron density. This preference is clearly evident in the case of 4-nitro-4'-(dimethylamino)azobenzene. Thus, both **3** and **4** contain only one ¹H NMR resonance attributable to the NMe₂ group, indicating that metallation occurs specifically on one phenyl ring. Since the ring bearing the electron-releasing NMe₂ group should be the favored site of attack, complexes **1–4** are assigned the structure (with respect to the azobenzene ligand) shown in Figure 1. This structure is also consistent with the stereochemistry of the brominated azobenzene isolated after prolonged photolysis of **2** and **3** (eq 10).



In contrast to the behavior of the strongly polarized 4-nitro-4'-(dimethylamino)azobenzene molecule, palladation of 4-methoxyazobenzene occurs almost equally on both rings (Figure 1). This conclusion follows straightforwardly from the ¹H NMR spectrum of **8**, which contains two resonances of equal intensities for both the OCH₃ and C₅H₅ groups.

Another important structural question concerns the position of ligand L in relation to the coordinated phenyl ring in **1–6**. As depicted below, *cis* and *trans* isomers are possible in these nominally square-planar complexes.⁸ Information bearing on this point



(7) Bruce, M. I.; Goodall, B. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1978**, 687.

(8) In the bridge-splitting reaction between [(Azb)PdX]₂ (Azb is orthometallated azobenzene) and pyridine, for example, the solid product isolated exists as the *trans* isomer when X is Br and as a mixture of *cis* and *trans* isomers when X is Cl. Crociani, B.; Boschi, T.; Pietropaolo, R.; Belluco, U. *J. Chem. Soc. A* **1970**, 531.

(5) Tamai, N.; Yamazaki, I.; Masuhara, H.; Mataga, N. *Chem. Phys. Lett.* **1984**, *104*, 485.

(6) Wegner, E.; Adamson, A. W. *J. Am. Chem. Soc.* **1966**, *88*, 394.

Table II. Electronic Absorption Spectra of Pd(II) Complexes Containing an Orthometallated Azobenzene Derivative

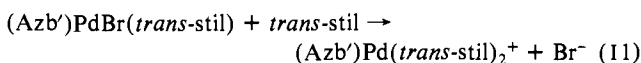
complex ^a	λ_{\max} (ϵ) ^b
1	560 (3.7×10^4), 400 sh (7×10^3), 300 (2.5×10^4)
2	560 (3.9×10^4), 400 sh (8×10^3), 320 (5.1×10^4)
(Az ^b)Pd(diphos) ⁺	554 (3.3×10^4), 380 sh (6×10^3)
5	455 (6.9×10^3), 380 sh (9×10^3), 295 (2.4×10^4)
6	454 (6.5×10^3), 380 sh (1×10^4), 330 (3.9×10^4)

^aSee Table I for formulas of numbered complexes. ^bAbsorption maxima in nm; ϵ in $M^{-1} \text{ cm}^{-1}$. Spectra measured in CH_2Cl_2 .

was obtained in a variable-temperature NMR study of a CD_2Cl_2 solution containing $4.4 \times 10^{-2} \text{ M}$ **4** and $3.2 \times 10^{-2} \text{ M}$ free 3-methylpyridine. At room temperature, the ^1H spectrum contains a single peak at 2.30 ppm due to the methyl protons of 3-methylpyridine and another peak at 3.15 ppm attributable to the methyl protons of the substituted azobenzene ligand. On lowering the temperature to -80°C , the former singlet splits into three peaks at 2.27, 2.32, and 2.43 ppm. The 2.32 ppm resonance is assigned to the methyl protons of free 3-methylpyridine, while the remaining two peaks correspond to the coordinated ligand occupying positions *cis* and *trans* to the metallated phenyl group. The peak arising from the methyl protons of the substituted azobenzene splits into two pairs of doublets, one at 2.88 and 3.21 ppm and the other at 3.25 and 3.33 ppm, with the peak heights within each pair being equal. This splitting pattern reflects the presence of *cis* and *trans* isomers coupled with restricted rotation of the NMe_2 group at low temperature.

The NMR data indicate that exchange of free and coordinated 3-methylpyridine and *cis*-*trans* interconversion at the Pd center both occur rapidly on the NMR time scale at room temperature. The calculated room-temperature lifetimes of the *cis* and *trans* species in solution are $<3.5 \times 10^{-3} \text{ s}$. When the spectrum of **4** without added 3-methylpyridine was measured immediately after dissolution, broad peaks attributable to *cis* and *trans* isomers could be detected. This finding indicates that isomerization occurs more slowly in the absence of free ligand and suggests that rearrangement and (presumably) ligand exchange proceed, at least in part, via an associative pathway. While **4** is the only complex for which detailed NMR data are available, we feel that its behavior in room-temperature solution is representative of the other, closely related systems listed in Table I. Thus, it will be assumed that exchange of ligand L and *cis*-*trans* isomerization at the Pd atom are occurring under the conditions normally employed in the spectral and photochemical studies described below.

Complexes **1**-**6** are formulated in Table I as nonelectrolytes, and in accord with this representation, the room-temperature molar conductance of a CH_2Cl_2 solution containing $1 \times 10^{-4} \text{ M}$ **2** and an equivalent amount of *trans*-4-stilbazole is very small ($<0.4 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$). Upon addition of a 1000-fold excess of the free *trans* ligand, however, the conductance increases appreciably ($3.5 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$).⁹ This result indicates that at sufficiently high concentrations, 4-stilbazole can displace bromide from the first coordination sphere of the orthometallated Pd(II) complex (eq 11). Similar behavior has been reported previously by Crociani et al.⁸



(b) Absorption Spectra. Table II summarizes the electronic absorption spectra of several Pd(II) complexes containing an orthometallated azobenzene derivative. The data have been corrected for the absorbance of excess 4-stilbazole¹⁰ present in

(9) For comparison, a CH_2Cl_2 solution containing $6 \times 10^{-4} \text{ M}$ tetraethylammonium chloride has a molar conductance of $15.2 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ at room temperature.

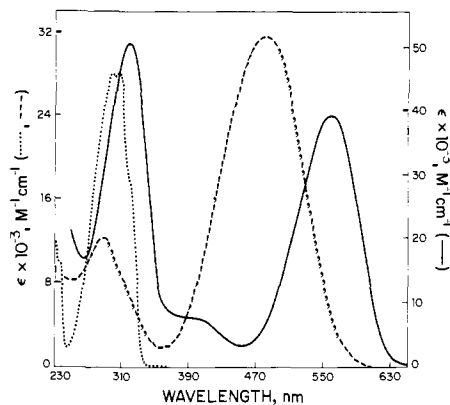


Figure 2. Electronic absorption spectra of **2** (—), 4-nitro-4'-(dimethylamino)azobenzene (---), and *trans*-4-stilbazole (···) in CH_2Cl_2 .

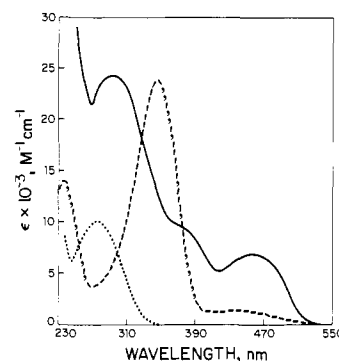


Figure 3. Electronic absorption spectra of **5** (—), 4-methoxyazobenzene (---), and *cis*-4-stilbazole (···) in CH_2Cl_2 .

the system to repress dimerization (*vide supra*). This correction only becomes significant below $\sim 360 \text{ nm}$, and thus the peak positions and extinction coefficients are subject to greater experimental uncertainty in this wavelength region.

The detailed spectra of **2** and **5** are shown in Figures 2 and 3, respectively, accompanied in each case by the spectra of the corresponding uncomplexed azobenzene derivative and 4-stilbazole. Spectral assignments for the free ligands will be considered first, since they provide a basis for interpreting the transitions in the Pd(II) complexes. The broad, relatively weak band at 432 nm in the spectrum of 4-methoxyazobenzene (Figure 3) arises from a spin-allowed $n\text{-}\pi^*$ transition.¹¹ The two more intense peaks at 346 and 239 nm are assigned as spin-allowed $\pi\text{-}\pi^*$ transitions.^{11,12} The presence of both electron-withdrawing (NO_2) and electron-donating (NMe_2) substituents in 4-nitro-4'-(dimethylamino)azobenzene introduces substantial charge-transfer character into the lowest spin-allowed $\pi\text{-}\pi^*$ transition which now occurs at 480 nm (Figure 2); this band obscures the lowest spin-allowed $n\text{-}\pi^*$ transition whose energy is less sensitive to substituent effects.¹¹ A second $\pi\text{-}\pi^*$ transition is responsible for the band at 286 nm. Lastly, the spectra of the isomeric 4-stilbazoles contain spin-allowed $\pi\text{-}\pi^*$ transitions¹³ at 308 nm (*trans*-stil, Figure 2) and 276 nm (*cis*-stil, Figure 3). These intense bands presumably mask the weak, spin-allowed $n\text{-}\pi^*$ transition expected to lie in the same wavelength region.

Turning now to the Pd(II) complexes, we propose that the band at 560 nm in the spectrum of **2** (Figure 2) corresponds to a $\pi\text{-}\pi^*$

(10) For example, spectra were recorded of $1 \times 10^{-4} \text{ M}$ solutions of **2** containing different concentrations ($1\text{--}7 \times 10^{-4} \text{ M}$) of free *trans*-4-stilbazole. Each spectrum was then corrected by subtracting the calculated absorbance due to the free ligand. The extinction coefficients of the resulting spectra agreed to within $\pm 4\%$.

(11) Bisle, H.; Römer, M.; Rau, H. *Ber. Bunsenges. Phys. Chem.* **1976**, *80*, 301.

(12) Mustroph, H.; Epperlein, H. *J. Prakt. Chem.* **1980**, *322*, 305.

(13) Bartocci, G.; Bortolus, P.; Mazzucato, U. *J. Phys. Chem.* **1973**, *77*, 605.

Table III. Emission Spectra and Lifetimes of Pd(II) Complexes Containing an Orthometallated Azobenzene Derivative

complex ^a	excitation λ , nm	λ_{\max} , nm ^b	lifetime, ps
1	540	639	<i>c</i>
2	560	638	63 ^d
(Az ^{b'})Pd(diphos) ⁺	560	632	64 ^d
6	400, 500	550	<i>e</i>

^aSee Table I for formulas of numbered complexes. ^bEmission maximum in CH₂Cl₂ at 25 °C. Typically, the solution contained 1×10^{-4} M complex and, in the cases of **1**, **2**, and **6**, an equimolar amount of the corresponding free 4-stilbazole. ^cNot determined. ^dSample excited at 585 nm; emission monitored at 630 nm. ^eEmission intensity remained unchanged after bubbling sample solution with O₂.

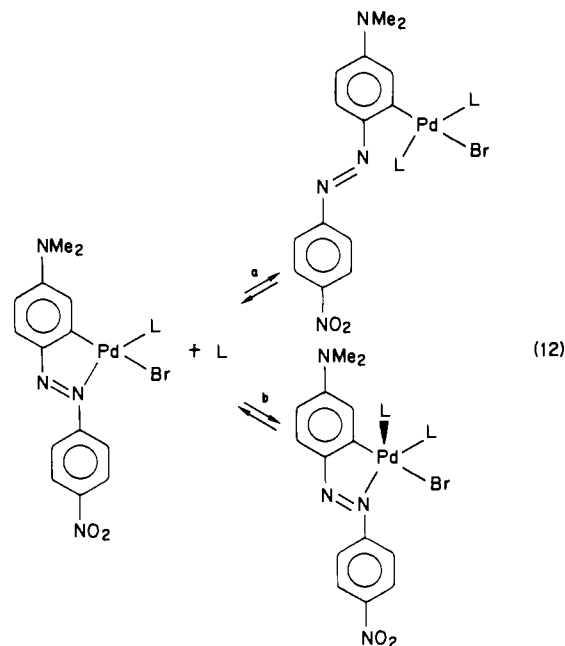
transition localized on the orthometallated 4-nitro-4'-(dimethylamino)azobenzene ligand. Support for this intraligand assignment is provided by the insensitivity of the transition energy to changes in the coordination environment about the metal center; thus, a comparable band appears at 554 nm ($\epsilon = 3.3 \times 10^4$ M⁻¹ cm⁻¹) in the spectrum of (Az^{b'})Pd(diphos)⁺.¹⁴ The other prominent band in the spectrum of **2** occurs at 320 nm and probably contains contributions from two different intraligand transitions. One can be assigned as the $\pi-\pi^*$ transition of coordinated *trans*-4-stilbazole,¹⁵ while the other is the second $\pi-\pi^*$ transition of the orthometallated azobenzene. The shoulder at ~ 400 nm is tentatively assigned as a ligand-field transition lying on the tail of the intense ligand-localized transitions. In PdBr₂(py)₂, for example, a ligand field band occurs at 415 nm with $\epsilon = 3 \times 10^2$ M⁻¹ cm⁻¹.¹⁶

Several overlapping bands are evident in the absorption spectrum of **5**, and this situation complicates the task of assigning the transitions involved. The peak at 295 nm appears to be composed of at least two transitions, one of which is the $\pi-\pi^*$ transition localized on the coordinated *cis*-4-stilbazole. The other contributor may be the lowest $\pi-\pi^*$ transition localized on the orthometallated 4-methoxyazobenzene, but this assignment is rather speculative. The shoulder at ~ 380 nm can be attributed to a ligand-field transition superimposed upon the tail of the 295-nm band. While the band at 455 nm possesses an energy comparable to that of the $n-\pi^*$ transition of free 4-methoxyazobenzene, it is considerably more intense. For lack of a better description, we tentatively assign this band as a metal-perturbed $n-\pi^*$ transition.¹⁷

The near superimposability of the absorption spectra of **1** and **2** above 350 nm suggests that the spectral assignments proposed for the latter complex in this wavelength region apply equally well to the former. The disparity at shorter wavelengths arises from differences in the $\pi-\pi^*$ transitions of the coordinated *cis*- and *trans*-4-stilbazole molecules. A similar relationship exists between the spectra of **5** and **6**.

It was noted earlier that **2**, and presumably the other complexes in Table I, is susceptible to ligand substitution processes (e.g., eq 11) in the presence of an enormous excess (e.g., 1000:1) of L. Additional evidence for changes in the coordination environment of Pd is provided by the following experiment. One side of a two-compartment spectrophotometer cell was filled with a 2×10^{-4} M solution of **2** in CH₂Cl₂, while the other side contained a 0.2 M solution of free *trans*-4-stilbazole. Comparison of the absorption spectra taken before and after mixing the two solutions reveals some important differences; thus, an isosbestic point occurs at 630 nm and the intensity of the peak at 560 nm increases by

$\sim 9\%$ upon mixing. While these spectral changes may solely reflect the substitution of bromide (eq 11), two other possibilities should be mentioned. One involves the dechelation of the orthometallated azobenzene ligand (eq 12a),⁷ while the other is the formation of a five-coordinate Pd(II) complex (eq 12b). At present, we have no firm basis for assessing the importance of these latter pathways.



(c) Emission Spectra and Lifetimes. Neither 4-nitro-4'-(dimethylamino)azobenzene nor 4-methoxyazobenzene luminesce in room-temperature CH₂Cl₂ solution. The former compound, however, exhibits a weak emission with λ_{\max} at 610 nm in a frozen (90 K) hydrocarbon matrix. This emission was assigned originally as a fluorescence from the lowest $n-\pi^*$ singlet excited state.¹¹ More recent work by Schulte-Frohlinde et al.¹⁸ places the singlet $\pi-\pi^*$ excited state below this $n-\pi^*$ state, and for this reason (also see ref 19a), we favor the alternative assignment of the weak emission from 4-nitro-4'-(dimethylamino)azobenzene as a $\pi-\pi^*$ fluorescence. While *cis*-4-stilbazole is nonemissive in room-temperature solution, the *trans* isomer emits weakly with λ_{\max} at 356 nm. This luminescence is short-lived (<1 ns) and has been characterized as fluorescence from the first $\pi-\pi^*$ singlet excited state.¹³

Several of the Pd(II) complexes investigated in this study luminesce in room-temperature solution. Table III contains a compilation of emission maxima along with some excited-state lifetimes measured under comparable conditions. Complexes containing orthometallated 4-nitro-4'-(dimethylamino)azobenzene emit at similar wavelengths, suggesting that the same emissive excited state is involved in each case. Given the short lifetime and modest shift from the position of the $\pi-\pi^*$ fluorescence of the free ligand, we assign the luminescence of **1**, **2**, and (Az^{b'})Pd(diphos)⁺ as ligand-localized $\pi-\pi^*$ fluorescence. The excitation spectrum measured for **2** closely matches its absorption spectrum in the region 500–600 nm. Based upon the crossing point of the excitation and corrected emission spectra, we estimate a 0–0 energy of 47–48 kcal for the emissive excited state in **2**.

Less information is available concerning the luminescence properties of 4-methoxyazobenzene and its Pd(II) complexes. Excitation of **6** at either 400 or 500 nm results in a very weak emission that overlaps the $n-\pi^*$ absorption band. Based upon its position and the absence of significant quenching in an O₂-saturated solution, we tentatively assign this emission as a ligand-localized $n-\pi^*$ fluorescence.¹⁹

(14) The intraligand $\pi-\pi^*$ transition that occurs at 554–560 nm in the spectra of Pd(II) complexes containing orthometallated 4-nitro-4'-(dimethylamino)azobenzene is considerably red-shifted from the corresponding transition (480 nm) in the free ligand. This shift reflects the high sensitivity of the first $\pi-\pi^*$ transition in azobenzenes to substituent effects.¹¹

(15) This assignment is in accord with the spectral changes (described in a later section) that occur upon photolysis of **5**.

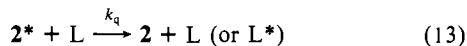
(16) Replacement of a pyridine ligand by a C-bonded phenyl group should enhance the strength of the ligand field about the Pd atom. Consequently, the ligand-field transition responsible for the 415-nm band in the spectrum of PdBr₂(py)₂ would be expected to occur at higher energies in **2**.

(17) The nonbonding electron pair involved in this type of transition is located on the azo nitrogen atom that remains uncoordinated (see Figure 1).

(18) Görner, H.; Gruen, H.; Schulte-Frohlinde, D. *J. Phys. Chem.* **1980**, *84*, 3031.

The observation that azobenzene derivatives luminesce more efficiently when bound to a metal has precedent in the studies of Rau et al.^{11,20} These workers noted that luminescence intensities of azo compounds can be increased by minimizing the degree of distortion in the excited state. For example, fluorescence has been observed from cyclic compounds containing a *cis*-azo linkage, acyclic azo compounds containing bulky substituents, and several azo compounds embedded in low-temperature rigid matrices. In each of these cases, large-scale molecular distortions that can facilitate radiationless deactivation of the excited state are inhibited and radiative decay thereby becomes more probable. Since 4-nitro-4'-(dimethylamino)azobenzene and 4-methoxyazobenzene are not subject to such inhibition in room-temperature fluid solution, neither of these molecules emits. Upon metallation by Pd, however, rigidity is imparted to the azo linkage and the efficiency of emission increases significantly.

The effect of excess ligand on the emission spectra of the Pd(II) complexes listed in Table III was investigated. Addition of 0.1 M *trans*-4-stilbazole to a CH₂Cl₂ solution originally containing 1 × 10⁻⁴ M **2** and 1 × 10⁻⁴ M *trans* ligand results in a reduction of the emission intensity by 50% without causing a discernible shift in the band maximum. Similarly, **1** experiences a 40% reduction in luminescence intensity in the presence of 0.1 M *cis*-4-stilbazole. We have considered two alternative causes for this behavior: (1) collisional excited-state quenching²¹ by the free ligand (e.g., eq 13); (2) formation of a new Pd(II) complex having luminescence characteristics different from those of its parent.



Alternative (1) seem unlikely on grounds that k_q ²² in eq 13 would need to be 4 × 10¹⁰ M⁻¹ s⁻¹ to accommodate the observed quenching of the short-lived emissive state of **2**. This value is uncomfortably larger than the diffusion-controlled limit of ~1 × 10¹⁰ M⁻¹ s⁻¹. Moreover, no quenching of **2** occurs in the presence of 0.1 M *trans*-stilbene, a molecule having electronic properties (e.g., energy of ³(π-π*) excited state) very similar to those of *trans*-4-stilbazole but lacking the nitrogen atom needed for coordination to the metal. This latter finding is clearly consistent with alternative (2), which we favor for a number of additional reasons. Recall that conductivity and absorption data reported earlier clearly indicate the occurrence of a chemical reaction between **2** and added *trans*-4-stilbazole (eq 11). Further evidence for this type of process is provided by the unusual luminescence behavior of (Az^{b'})Pd(diphos)⁺ and **6** in the presence of excess ligand. In the former case, addition of 0.1 M *trans*-4-stilbazole causes a 50% increase in emission intensity with no shift in peak position. An even more dramatic effect of added ligand occurs for **6**; the emission undergoes a substantial blue-shift and a several-fold increase in intensity. Such results again suggest that the original Pd(II) complex has been modified by interaction with the free ligand.

The luminescence behavior of **6** is rather complex and deserves further comment. A freshly prepared solution containing 1 × 10⁻⁴ M **6** and an equal amount of *trans*-4-stilbazole emits at ~550 nm as noted in Table III. After 24 h, however, the emission band has undergone a blue-shift and an increase in intensity. These

(19) (a) Chelation of an azobenzene derivative to Pd (e.g., Figure 1) destroys the interaction between the two lone pairs of electrons situated on the adjacent nitrogen atoms,^{19b} and as a result, the lowest n-π* excited state moves to higher energy. If this effect is sufficiently large in the case of **6**, this n-π* state may lie above the π-π* state, in which case the observed fluorescence could be π-π* in character. Low-temperature emission studies presently under way (personal communication from R. J. Watts) may help to clarify this question of orbital parentage. (b) Robin, M. B. In "The Chemistry of the Hydrazo, Azo, and Azoxy Groups"; Patai, S., Ed.; Wiley: London, 1975; Part 1, Chapter 1.

(20) Rau, H. *J. Luminesc.* **1970**, *1,2*, 191. Bisle, H.; Rau, H. *Chem. Phys. Lett.* **1975**, *31*, 264.

(21) Long-range, Coulombic energy transfer is unlikely owing to the absence of overlap between the emission spectra of the Pd(II) complexes and the absorption spectra of the isomeric 4-stilbazoles. Turro, N. J. "Modern Molecular Photochemistry"; Benjamin/Cummings: Menlo Park, CA, 1978; Chapter 9.

(22) The usual Stern-Volmer kinetic scheme was used to evaluate k_q .

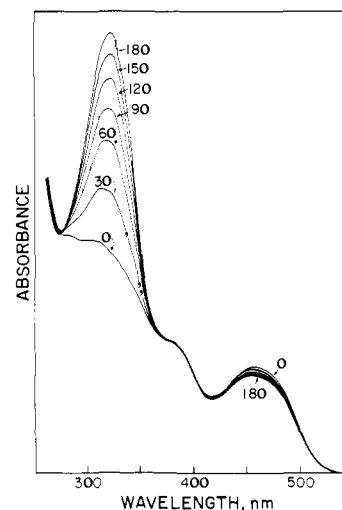


Figure 4. Effect of irradiation (>360 nm) upon the absorption spectrum of **5** in CH₂Cl₂; indicated times are in minutes.

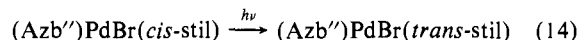
Table IV. Quantum Yields for Photoisomerization of 4-Stilbazole and Stilbene in the Presence of Pd(II) Complexes

expt	sample ^a	excitation λ, nm	φ _{isom} ^b
1	1 + 1.3 × 10 ⁻⁵ M <i>cis</i> -stil ^c	546	2 × 10 ⁻⁴
2	2 + 1 × 10 ⁻⁴ M <i>trans</i> -stil	546	3 × 10 ⁻⁴
3	2 + 0.1 M <i>trans</i> -stil	546	5 × 10 ⁻⁵
4	6 + 0.1 M <i>trans</i> -stil	436	9 × 10 ⁻⁴
5	(Az ^{b'})Pd(diphos) ⁺ + 1 × 10 ⁻⁴ M <i>trans</i> -stil	546	<3 × 10 ^{-5d}
6	2 + 0.1 M <i>trans</i> -stilbene	546	<1 × 10 ^{-5d,e}

^a Unless noted otherwise, complex concentration was 1 × 10⁻⁴ M and solvent was CH₂Cl₂. ^b φ_{isom} represents the quantum yield for *cis* to *trans* (or *trans* to *cis*) isomerization in a sample originally containing excess 4-stilbazole or stilbene. ^c Complex concentration was 1 × 10⁻⁵ M. ^d No isomerization detected after irradiation for 8 h; the φ_{isom} value is based upon our estimated limit of detection. ^e Method B described in the Experimental Section was used for the analysis of *trans*- and *cis*-stilbene.

changes are accelerated by increasing the concentration of free ligand. Although the nature of the ground-state reaction between **6** and *trans*-4-stilbazole that causes such behavior has not been established, it clearly results in a substantial perturbation of the orthometallated 4-methoxyazobenzene chromophore.²³

(d) **Photochemical Behavior.** Figure 4 illustrates the spectral changes that result upon irradiating a CH₂Cl₂ solution of **5** with polychromatic light (>360 nm). The long-wavelength transition in the complex undergoes a modest decrease in intensity, while the shoulder at ~380 nm is essentially unperturbed. The most striking change occurs in the region around 320 nm where a new band characteristic of coordinated *trans*-4-stilbazole appears (refer to Figure 2). We attribute this behavior to the occurrence of the photoisomerization process described by eq 14.

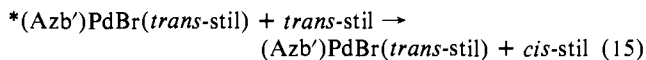


Photoisomerization quantum yields (φ_{isom}) are listed in Table IV for a number of Pd(II) complexes in the presence of excess 4-stilbazole. It should be emphasized that in these experiments, the complexes were excited with narrow bandwidth radiation that was absorbed solely by the long-wavelength transition(s) localized on the orthometallated azobenzene ligand. Thus, the occurrence of isomerization under these conditions establishes that selective activation of the azobenzene chromophore can sensitize the reaction of a nonabsorbing 4-stilbazole molecule. Two important questions then come to mind: (1) What is the mechanism by which

(23) In contrast, the absence of a detectable wavelength shift in the emission spectra of **1**, **2**, and (Az^{b'})Pd(diphos)⁺ in the presence of excess 4-stilbazole suggests that the orthometallated 4-nitro-4'-(dimethylamino)-azobenzene moiety is affected to a much smaller extent.

excitation energy is transmitted from the light-absorbing site to the reaction center? (2) What factors contribute to the disappointingly low quantum yields?

Since both coordinated and free 4-stilbazole are present in the systems listed in Table IV, we begin the discussion of mechanism by considering whether photoisomerization is an intramolecular or intermolecular process. In the former case, the azobenzene chromophore and isomerizable substrate residue within the same complex as in eq 14. This should be contrasted to the intermolecular pathway outlined in eq 15; here the photoexcited complex undergoes a bimolecular interaction with free 4-stilbazole that results in isomerization of the latter. Several lines of evidence



are available to discount the latter type of process. There is, for example, no correlation between ϕ_{isom} and the concentration of added 4-stilbazole (compare experiments 2 and 3 in Table IV). Such behavior seems incompatible with an intermolecular pathway that features quenching of the photoexcited complex by free ligand. Moreover, *trans*-stilbene, which does not coordinate to the Pd atom, undergoes no measurable isomerization when irradiated in the presence of **2** (Table IV, compare experiments 3 and 6). Finally, the disparity in the photoisomerization yields of **2** and $(\text{Azb}')\text{Pd}(\text{diphos})^+$ (compare experiments 2 and 5 in Table IV) is difficult to rationalize in terms of an intermolecular mechanism, since the two complexes possess very similar excited-state energies and lifetimes (Table III). Only **2** can bind 4-stilbazole, however, and thus we conclude that such binding is an integral part of the overall mechanism of photoinduced isomerization.

Our results do not establish the nature of the intramolecular interaction between the initially excited azobenzene chromophore and the isomerizable 4-stilbazole molecule. It seems reasonable, however, to assume that intramolecular energy transfer can occur in these Pd(II) complexes and we proceed from this premise in the following discussion.²⁴ Furthermore, since 4-stilbazole undergoes efficient triplet-sensitized isomerization via its $^3(\pi-\pi^*)$ state,²⁵ we shall restrict our attention to the process of triplet-triplet energy transfer.

The lowest $\pi-\pi^*$ triplet states of the isomeric 4-stilbazoles lie ~ 50 kcal (*trans* compound) and ~ 57 kcal (*cis* compound) above the ground state.⁴ These energies refer to Franck-Condon²⁶ (FC) triplet states having geometries identical with those of the corresponding planar ground-state molecules. Considerable evidence suggests, however, that the potential surface connecting these FC triplets contains a minimum at a geometry that is twisted about the C=C bond.²⁷ Moreover, the energy of this twisted configuration is thought to be considerably below that of the FC *cis* triplet but comparable to that of the FC *trans* triplet. Since none of the Pd(II) complexes examined in this study undergo detectable

phosphorescence in room-temperature fluid solution, the energies of their low-lying triplet states are unknown. For purposes of this discussion, the energy of the fluorescent state in **2** (~ 47 kcal) will be taken as an upper limit to the energy of the lowest triplet state of the orthometallated 4-nitro-4'-(dimethylamino)azobenzene chromophore. On this basis, we estimate that intramolecular energy transfer from this triplet state to the FC triplet state of *trans*-4-stilbazole is endothermic by at least 3 kcal. This energy deficit constitutes an activation barrier to energy transfer and likely contributes to the low overall quantum yields observed for **2**. Energy transfer to the FC triplet of *cis*-4-stilbazole should be even less favorable with an estimated endothermicity of at least 10 kcal. The finding that photoisomerization of *cis*- and *trans*-4-stilbazole occurs with comparable quantum yields (compare experiments 1 and 2 in Table IV) therefore suggests that energy transfer to the *cis* isomer does not result in population of the FC triplet but instead leads directly to the production of a twisted excited state of considerably lower energy. Such behavior is commonly termed "nonvertical energy transfer" and has been observed in several systems containing stilbene or closely related analogues.²⁷

While endothermicity in the energy-transfer process is one probable cause of the low ϕ_{isom} values found for **1** and **2**, it may not be the only factor involved. Thus, inefficient photoisomerization also occurs for **6**, even though the azobenzene-localized excited states in this complex are appreciably higher in energy than those in **1** and **2**. Apparently, the flow of energy from the initially excited chromophore in **6** (and perhaps in **1** and **2**) to the reactive 4-stilbazole ligand does not compete effectively with other excited-state decay channels. The nature of these competing deactivation processes and the influence of the metal on them are interesting topics²⁸ that deserve further study.

Concluding Remarks

This study has yielded a number of interesting findings about complexes of the type $(\text{Azb}')\text{PdBr}(\text{L})$ and $(\text{Azb}'')\text{PdBr}(\text{L})$ (Figure 1). The absorption spectra of these compounds contain intense bands that appear to be predominantly intraligand in character. While the uncoordinated azobenzene derivatives do not emit in room-temperature fluid solution, the rigidity imparted to the azo linkage upon metallation by Pd enhances the efficiency of radiative decay, and intraligand fluorescence can be observed. It was hoped that the combination of the strongly absorbing azobenzene chromophore and the labile, isomerizable 4-stilbazole ligand within the same complex would be conducive to intramolecular sensitization. Although the results indicate that this process does occur in at least some of the complexes investigated (e.g., **1** and **2**), the quantum yields are much too low for these systems to be of practical interest. Extension of the present study to orthometallated azobenzene complexes of other transition metals should prove to be of value in delineating more precisely the factors that control the efficiency of intramolecular sensitization.

Acknowledgment. We are grateful to Drs. N. Tamai and I. Yamazaki for performing the picosecond lifetime measurements and to Prof. H. Rau for thought-provoking discussions concerning spectral assignments in azobenzenes. We thank the Science and Technology Agency, Japan, and the U.S. National Science Foundation (Grants CHE-8210558 and INT-8309942) for financial assistance.

(24) Another possibility is intramolecular electron transfer between the photoexcited azobenzene chromophore and the 4-stilbazole ligand. It should be noted that Whitten et al.⁴ were able to discount this type of pathway in the metalloporphyrin-azastilbene systems they investigated.

(25) Whitten, D. G.; Lee, Y. J. *J. Am. Chem. Soc.* **1972**, *94*, 9142. Wrighton, M. S.; Morse, D. L.; Pdungsap, L. *Ibid.* **1975**, *97*, 2073.

(26) That is, states that are formed by a "vertical" or Franck-Condon transition.

(27) For an excellent discussion of excited-state energetics and energy-transfer processes in stilbene and related systems, see: Lamola, A. A. In "Energy Transfer and Organic Photochemistry"; Lamola, A. A., Turro, N. J., Eds.; Interscience: New York, 1969; p 17.

(28) For example, see: Fisher, D. P.; Piermattie, V.; Dabrowiak, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 2811.