Photophysics and Photochemistry of Stilbene-Containing Platinum Acetylides

Ksenija Haskins-Glusac, Ion Ghiviriga, Khalil A. Abboud, and Kirk S. Schanze*

Department of Chemistry, University of Florida, P.O. Box, 117200, Gainesville, Florida 32611-7200

Received: January 22, 2004

A series of four platinum acetylide complexes that contain 4-ethynylstilbene (4-ES) ligands have been subjected to a detailed photochemical and photophysical investigation. The objective of the work is to understand the structure and reactivity of the lowest excited states in π -conjugated Pt-acetylides. The 4-ES ligand was chosen for this work because the excited-state properties of the stilbene chromophore are well understood. In particular, stilbene features fluorescence and phosphorescence, and also undergoes trans-cis photoisomerization from the triplet excited state. Two of the complexes investigated contain phosphine ligands and have the structures trans-Pt(PBu₃)₂(4-ES)₂ and cis-Pt(dppe)(4-ES)₂ (2 and 3, respectively, where PBu₃ = tributylphosphine and dppe = bis-1,2-diphosphinoethane). The other two complexes contain substituted 2,2'-bipyridine ligands and have the structures $Pt(t-Bu-bpy)(4-ES)_2$ and $Pt(4,4'-CO_2Et-bpy)(4-ES)_2$ (3 and 4, respectively, where t-Bubpy = 4,4'-di-*tert*-butyl-2,2'-bipyridine and 4,4'-CO₂Et-bpy = 4,4'-bis(carboethoxy)-2,2'-bipyridine). The crystal structure of 2 is reported. The complex features a square planar PtP_2C_2 geometry and the planes of the phenyl groups in the 4-ES ligands are twisted approximately 60° relative to the plane defined by the PtP₂C₂ core. The series of complexes was examined by using absorption, variable-temperature photoluminescence, and transient absorption spectroscopy. In addition, the photochemical reactivity of the complexes was explored by UV-visible absorption and NMR spectroscopy. The available experimental data indicate that in all of the complexes excitation leads to high-yield production of a ${}^{3}\pi,\pi^{*}$ excited state that is localized on one of the 4-ES ligands. At low temperatures, the ${}^{3}\pi,\pi^{*}$ state exhibits strong phosphorescence that is very similar to the phosphorescence of *trans*-stilbene. At temperatures above the glass-to-fluid temperature of the solvent medium, the ${}^{3}\pi,\pi^{*}$ state decays rapidly ($\tau \approx 40$ ns). The decay pathway is believed to involve rotation around the C=C bond of one of the 4-ES moieties. This model is supported by the photochemical results, which show that steady-state photolysis leads to trans-cis isomerization of one of the 4-ES ligands with a quantum efficiency of 0.4.

Introduction

 π -Conjugated materials exhibit a variety of useful optical properties for applications such as organic light-emitting diodes (OLEDs), photovoltaic devices, and nonlinear optical effects.¹⁻⁵ Although the focus of most work in the field has been on allorganic materials, there is increasing interest in the properties and applications of organometallic systems that feature transition metals which interact strongly with the π -conjugated electronic system.⁶ Metals such as Re, Ru, Os, Ir, Pt, and Au exert a strong influence on the optical properties of a conjugated system via several mechanisms, including spin-orbit coupling induced singlet-triplet mixing and introduction of low-energy charge transfer states into the excited-state manifold. One area that has received considerable recent attention is the use of organometallic materials in OLEDs to increase the electron-to-photon quantum efficiency of the devices.^{7,8} The heavy metals are thought to increase the quantum efficiency by increasing the efficiency of light emission from triplet excitons created by electron-hole pair recombination. The effect of the heavy metal is believed to result from its large spin-orbit coupling constant which increases the rates of intersystem crossing and triplet radiative decay (phosphorescence).

Although much is known about the properties of singlet states in π -conjugated systems, less is known regarding the corresponding triplets.^{9–15} One reason for the lack of information regarding the triplet state is that the singlet—triplet optical transitions (absorption and light emission) are spin-forbidden, which makes it difficult to apply optical spectroscopy to probe the triplet states. Issues that are of interest with respect to the triplet manifold include the effect of conjugation length on triplet energy and electron—phonon coupling, and the dependence of the singlet—triplet splitting on molecular structure and conjugation length.

We have an ongoing interest in the photophysical properties of π -conjugated systems that contain transition metals which interact strongly with the π -electron system.^{16–18} One area of particular interest in our work involves platinum acetylides.^{19,20} This class of materials exhibits optical properties that are similar to oligo- and poly(phenylene ethynylene)s,²¹ which can be thought of as the all-organic analogues of platinum acetylide oligomers and polymers. Because of the heavy-atom effect arising from the platinum center, the excited-state properties of Pt-acetylides are dominated by the triplet manifold because the materials feature high singlet—triplet intersystem crossing yields and efficient radiative decay from the triplet state.^{12,15,22}

The present investigation examines a series of π -conjugated Pt-acetylide oligomers toward the objective of understanding the photophysics and photochemistry of the triplet state in this class of materials. Some important questions that are addressed by this work include the following. (1) What is the extent of

^{*} Author to whom correspondence should be addressed. Tel: 352-392-9133. Fax: 352-392-2395. E-mail: kschanze@chem.ufl.edu.



Figure 1. Structures of the Pt-acetylide complexes.

 π -delocalization in the singlet and triplet manifolds of Ptacetylides? (2) How does the coordination geometry at the platinum center influence π -delocalization? (3) How do lowenergy charge-transfer excited states influence the photophysics and photochemistry of the systems? To meet the project objectives, we selected stilbene as a model π -conjugated "ligand" at the platinum center. Stilbene was selected for this investigation because it has been studied for more than 50 years and consequently a great deal is known regarding its excitedstate properties and those of its substituted derivatives.²³⁻²⁶ Stilbene is of interest not only because it features interesting singlet- and triplet-state photophysics, but also because it undergoes efficient trans-cis photoisomerization.²³ This rich excited-state behavior affords the opportunity to use both photophysical and photochemical methods to characterize the excited states of π -conjugated Pt-acetylides.

In the present contribution we probe the photophysics and trans-cis olefin photoisomerization of platinum acetylide complexes 2-5, each of which contains two 4-ethynylstilbene (4-ES) chromophores attached to the platinum center via acetylide linkages (Figure 1). In phosphine complexes 2 and 3, the coordination geometry is varied with the goal to probe how geometry influences π -conjugation through the metal center. In complex 1, the stilbene units are replaced by diphenylacetylene ligands.^{27,28} Due to the presence of the triple bond, complex **1** is unable to undergo twisting in the excited state leading to photoisomerization, and thus it serves as a "model compound" for comparison with the 4-ES complexes. The 2,2'-bipyridine ligand in complexes 4 and 5 introduces an energetically lowlying $d\pi$ (Pt) $\rightarrow \pi^*$ (bpy) metal-to-ligand charge transfer (MLCT) excited state. Previous work by Eisenberg and coworkers²⁹ and our group³⁰ on complexes of the type (diimine)Pt($-C \equiv C - Ar$)₂ demonstrates that the energy of the MLCT state can be tuned by varying the substituents on the diimine ligand. Electron donor substitutents, such as the tertbutyl group used in compound 4, increase the energy of the MLCT state, while electron-withdrawing substituents, such as the carboxy ester groups in compound 5, reduce the energy of MLCT. In the present investigation, we sought to determine how the MLCT manifold influences the photophysics and photochemistry of the stilbene complexes. In particular, we

TABLE 1: Selected Bond Lengths (Å) and Angles (deg) for Complex 2 $% \left({{{\rm{Complex}}} \right)$

Pt-C1	2.002(3)	C2-C3	1.436(4)
Pt-P	2.3099(7)	C7-C8	1.396(5)
P-C21	1.821(3)	C9-C10	1.335(5)
C1-C2	1.201(5)	C10-C11	1.466(5)
C1-Pt-C1	180.00(15)	C10-C9-C6	127.2(3)
C1-Pt-P	86.66(9)	C9-C10-C11	124.9(3)
C2-C3-C4	120.5(3)	C16-C11-C10	118.6(3)
C5-C6-C9	118.6(3)	C12-C11-C10	123.4(3)

expected that in **4** the energy of the MLCT state would be higher than that of the 4-ES localized ${}^{3}\pi,\pi^{*}$ state, while in **5** the converse would be true. Thus, we anticipated that the photophysics and photochemistry of these two complexes would differ.

Although Pt-acetylide oligomers and polymers have been the focus of a number of previous photophysical investigations, $^{10,12,15,22,27,28,31-34}$ the present work is unique in that it uses a combined photochemical and photophysical approach to provide clear insight into the structure, properties, and reactivity of the triplet excited-state manifold in a set of π -conjugated Pt-acetylides.

Results and Discussion

Crystal Structure of Complex 2. The molecular structure of **2** is shown in Figure 2a, while the important bond lengths and angles are shown in Table 1. The geometry of this complex is slightly distorted from square planar, with a P–Pt–C angle of 86.6°. The Pt–P and Pt–C bond lengths are 2.31 Å and 2.00 Å, respectively, in good agreement with the lengths in analogous Pt-acetylide systems.^{35,36} The phenyl rings are rotated at an angle of 62.7° with respect to the P₂PtC₂ plane, even though the conformation in which the aromatic rings lie in the same plane as the P₂PtC₂ plane is expected to be more stable.¹⁰ This geometric distortion is believed to be due to the bulky butyl groups on phosphine ligands forcing the phenyl ligands to twist. Similar out-of-plane phenyl orientations were observed in the crystal structures of Pt(bpy)(–C≡C–C₆H₄–CH₃)₂ and **1**.^{37–39}

The crystal packing diagram for **2** is shown in Figure 2b. The organization of the molecules into the crystal appears to be driven by the bulky PBu₃ groups and has little similarity to the crystal packing of oligo(*p*-phenylene vinylene)s, which have similar long axis dimensions compared to complex **2**.⁴⁰ The molecules are aligned in a zigzag configuration, and there is no evidence for π -stacking between aromatic rings on adjacent complexes. The shortest distance between adjacent Pt atoms in the crystal is 12.8 Å. This is significant because it indicates that there is no interaction between Pt-centers in the solid.

UV–Visible Absorption Spectroscopy. The absorption spectra of complexes 2–5 are shown in Figure 3a along with the spectrum of (E)-4-ethynylstilbene (the free ligand, 4-ES). The absorption of 4-ES appears as a broad band with three well-resolved vibronic bands that are due to C=C stretching modes of the ethylene unit and the aromatic rings. The absorption maximum of 4-ES ($\lambda = 324$ nm) is red-shifted in comparison with the absorption of *trans*-stilbene ($\lambda = 293$ nm),⁴¹ but the spectra of the two compounds have a similar band shape and vibronic structure. The red-shifted absorption of 4-ES is due to conjugation of the ethynyl group with the stilbene chromophore.

The spectra of the platinum complexes are dominated by an intense band in the near-UV region that is clearly derived from the stilbene chromophore. First, in complex **2**, where the 4-ES ligands are in a trans geometry, the band is relatively featureless



Figure 2. (a) Molecular structure of 2 with atomic numbering scheme, and (b) crystal packing diagram for 2.



Figure 3. (a) UV-visible absorption spectra of 4-ethynylstilbene and complexes 2-5 in THF solution: (-) 4-ethynylstilbene; (---) 2; (···) 3; (-·-) 4; (-··-) 5. (b) Fluorescence (inset, F) and phosphorescence (P) spectra of complexes 2-5: (---) 2; (···) 3; (-·-) 4; (-) 5. Fluorescence measurements were conducted at room temperature in THF solution, while the phosphorescence spectra were recorded at 80 K in 2-MTHF glass.

with $\lambda_{max} = 370$ nm. Note that the absorption is red-shifted significantly from that of 4-ES, a fact which implies that there is delocalization of the stilbene localized molecular orbitals mediated by the Pt $d\pi$ orbitals. In addition, the lack of vibronic structure in the absorption band indicates that electron–vibronic coupling is weak, which is also consistent with a delocalized excited state.

The 4-ES ligands in 3-5 are in a cis geometry at the Pt center. In these complexes, the absorption band is blue-shifted relative to its position in 2. In addition, the bands display a more pronounced vibrational structure, which indicates that electronvibrational coupling is stronger. Taken together, these observations imply that there is weaker interaction between the 4-ES ligands in the complexes 3-5 and as a result the singlet excited state is more localized on a single stilbene ligand.

The absorption spectra of **4** and **5** exhibit an additional lowenergy absorption band ($\lambda \approx 400-450$ nm). This band is similar to that observed in other complexes of the type (diimine)Pt^{II}L₂, and it is clearly due to the d π (Pt) $\rightarrow \pi^*$ (bpy) MLCT transition.

Photoluminescence Spectroscopy. The emission spectra of complexes 2-5 are presented in Figure 3b. At room temperature, all of the complexes exhibit a short-lived, weak emission ($\tau <$ 300 ps, $\Phi < 0.01$) with $\lambda_{max} \approx 410$ nm (Figure 3b, inset). At low temperature in a solvent glass (T < 120 K), an additional structured emission band is observed with $\lambda_{max}\,\approx\,630$ nm (Figure 3b, main panel). By analogy with trans-stilbene, we attribute the 410 nm emission to fluorescence from the ${}^{1}\pi,\pi^{*}$ excited state,²⁶ and the 630 nm emission to phosphorescence from the ${}^{3}\pi,\pi^{*}$ state.^{25,42} These assignments are supported by the emission lifetimes, as the fluorescence has $\tau < 1$ ns and the low-temperature phosphorescence lifetimes are greater than 100 μ s. An interesting feature is that the phosphorescence band maxima are nearly identical in the four complexes. This observation implies that the ${}^{3}\pi,\pi^{*}$ state is localized on a single 4-ES ligand, regardless of the coordination geometry (i.e, cis or trans). This finding is consistent with a number of recent studies of π -conjugated systems which show that the triplet excited state is localized.^{10,12,15,20} Another interesting finding is that we observe no evidence for MLCT emission in complexes 4 and 5 (MLCT emission would appear as a broad, structureless emission band).^{29,30} This finding contrasts with studies of related complexes of the type (diimine)Pt(C=C-Ar)₂,which feature moderately efficient MLCT emission in fluid solution at ambient



Figure 4. Variable temperature emission spectra, 2-MTHF solvent: (a) complex 2; (b) complex 1. In order of decreasing intensity: 80, 120, 130, and 140 K. (c) Phosphorescence decay lifetimes as a function of temperature, 2-MTHF solvent. (■): complex 1; (▲): complex 2.

temperatures and in low-temperature glasses.^{29,30} We elaborate on the significance of this finding in the discussion section.

Figure 4a illustrates the variable temperature emission spectra (range $80 \rightarrow 140$ K) for complex 2, while Figure 4c shows the dependence of the phosphorescence lifetime on temperature. As the temperature is raised, both the phosphorescence intensity and lifetime of complex 2 decrease dramatically to the point where the phosphorescence can barely be observed at 140 K. In the temperature range from 80 to 130 K, the solvent (2-Me-THF) undergoes a glass-to-fluid transition, suggesting that the change in phosphorescence intensity of 2 is correlated with the change in the solvent viscosity. Similar behavior was also observed for complexes 3-5.

Extensive work on the stilbene triplet excited state has demonstrated that the phosphorescence quantum efficiency and lifetime increase with increased solvent viscosity.^{24,25} This effect has been attributed to the influence of viscosity on the rate of triplet state nonradiative decay via twisting around the C=C bond. In effect, the rate of twisting is slowed in viscous or glassy solvents, and consequently the triplet state radiative decay (phosphorescence) efficiency increases. In accord with this, it has also been shown that the quantum efficiency for trans \rightarrow cis photoisomerization of stilbene via the triplet state decreases with increasing solvent viscosity.²⁴ By analogy to the observations on stilbene,²⁵ we believe that the precipitous decline of the phosphorescence intensity at the 2-Me-THF glass to fluid transition for complexes 2–5 arises due to an increase in the



Figure 5. Transient absorption difference spectrum of **2** in argondeoxygenated THF solution at 298 K following 355 nm pulsed excitation. Inset shows transient absorption decay at 420 nm.

rate of C=C bond rotation in the triplet excited state above the glass to fluid transition. In effect, triplet state nonradiative decay via C=C bond rotation is prohibited in the frozen matrix, and consequently phosphorescence is observed.

To confirm that the decrease in the phosphorescence intensity of complexes 2-5 above the solvent glass to fluid transition originates from twisting of the olefinic bond in the stilbene moiety, the phosphorescence intensities and lifetimes of complexes 1 and 2 as a function of temperature were compared. In contrast to stilbene chromophore in complex 2, the acetylene linkage in complex 1 does not undergo twisting in the excited state, thereby enhancing the probability for radiative decay. Figures 4b and 4c show the variable temperature emission of complex 1 and the corresponding changes in the phosphorescence decay lifetime. In contrast to the properties of complex 2, the emission intensity and lifetime of 1 varies weakly over the 80-140 K range. Indeed, even at ambient temperature 1 exhibits efficient phosphorescence from the diphenylacetylene localized ${}^{3}\pi,\pi^{*}$ state ($\Phi = 0.15, \tau = 42 \ \mu s$).²⁸ These results support the hypothesis that the rapid nonradiative decay pathway operative in 2-4 above the solvent glass-to-fluid temperature is rotation of the 4-ES C=C bond.

Transient Absorption Spectroscopy. Laser flash photolysis investigations have been carried out on a variety of Pt-acetylide complexes and polymers, both in solution and as solid films.^{22,27,28,43} These systems typically exhibit excited-state absorption in the visible region due to the ${}^{3}\pi,\pi^{*}$ excited state. For example, the transient absorption spectrum of **1** features a broad excited-state absorption with $\lambda_{max} \approx 580$ nm and a lifetime of 42 μ s.²⁸ The transient absorption is believed to arise from the ${}^{3}\pi,\pi^{*}$ excited-state localized on the diphenylacetylene ligand.

In an attempt to observe excited states present following nanosecond excitation of the Pt-stilbene complexes, laser flash photolysis experiments were carried out on 2-5. In each case, degassed solutions of the complexes were excited by using 10 ns, 355 nm pulses from a Nd:YAG laser. Relatively short-lived (i.e., sub- μ s lifetime) transient absorptions were observed following pulsed excitation of 2-4. The transient absorption spectrum of complex 2 is illustrated in Figure 5. The spectrum is characterized by bleaching of the ground-state absorption in the 300-400 nm region, combined with a broad excited-state absorption feature extending from 400 to 600 nm. The transient which gives rise to the absorption decays with a lifetime of 40 ns. Virtually identical transient absorption spectra and decay lifetimes were observed for complexes 3 and 4, so these data are not presented herein. An interesting feature is that no

Stilbene-Containing Platinum Acetylides

transient absorption could be observed for complex **5**, even at very small delay times after the laser pulse. This result indicates that for this complex the excited state decays too rapidly to be detected in the nanosecond time regime.

Görner and Schulte-Frohlinde (G/SF) published a detailed study of the transient absorption spectroscopy of stilbene triplet excited states.⁴⁴ These authors reported that in solution at ambient temperature the triplet excited state of *trans*-stilbene features a broad excited state absorption that extends from below 350 nm to approximately 400 nm. The transient decays with a lifetime of ≈ 60 ns at ambient temperature. A detailed analysis of the solvent, sensitizer, and quenching effects on the transient led G/SF to assign the transient absorption to a mixture of the trans and twisted triplet excited states (³t* and ³p*, respectively) that are in equilibrium.

A comparison of our observations with the results reported by G/SF on trans-stilbene lead us to assign the short-lived transient absorption observed for 2–4 to a ${}^{3}\pi,\pi^{*}$ state that is localized on a single 4-ES ligand. In particular, we believe that the transient is likely a stilbene localized triplet, in which the olefin is in the trans geometry (i.e., ${}^{3}t^{*}$). The short lifetime likely arises due to rapid nonradiative decay of the triplet via twisting around the C=C bond in the 4-ES moiety. Importantly, the behavior of the stilbene acetylide complexes 2-5 in solution differs significantly from that of other Pt-acetylide oligomers and polymers, where long-lived ${}^{3}\pi,\pi^{*}$ states are observed by transient absorption and phosphorescence.²⁸ We attribute the different properties of the 4-ES complexes to rapid excitedstate decay via C=C bond rotation in the stilbene chromophore. The premise that twisting around the olefinic bond is an important nonradiative decay channel in 2-5 is supported by the results of photochemical studies outlined in the following section. The significance of the lack of a transient absorption for 5 will be discussed below.

Photochemical Measurements. In the photophysical study described above, it was found that the triplet excited state in complexes 2-5 decays rapidly via a nonradiative pathway. To confirm that this rapid nonradiative decay pathway involves twisting of the stilbene C=C bond in the triplet excited state, steady-state photochemical investigations were carried out to produce evidence for trans \rightarrow cis photoisomerization. In initial experiments, solutions of the complexes were irradiated with 366 nm light and the changes in the absorption spectra as a function of irradiation time were recorded. The changes in the absorption spectrum induced by photolysis of 2 are shown in Figure 6, and similar spectra were observed for 3-5. In all cases, irradiation induces bleaching of the π,π^* absorption band in the 300-400 nm region, while there is a concomitant appearance of a weaker absorption band in the 250–300 nm region. The changes observed in the UV absorption spectra are very similar to those that accompany the trans \rightarrow cis photoisomerization of stilbene.45,46 This finding strongly suggests that UV photolysis of 2-5 leads to trans \rightarrow cis photoisomerization of one (or both) of the 4-ES ligands. Another interesting finding is that photolysis of 4 and 5 with 436 nm light induces the same changes in the UV absorption as observed when the compounds are subjected to UV photolysis. This result shows that excitation into the $d\pi$ (Pt) $\rightarrow \pi^*$ (bpy) MLCT manifold leads to trans \rightarrow cis isomerization of the 4-ES ligand. This photochemical result is consistent with the transient absorption studies of 4 and 5, which suggest that the MLCT state is very short-lived.

To fully characterize the products formed by steady-state photolysis of the Pt-stilbene complexes, ¹H NMR spectroscopy was used to monitor the photochemical reaction. Figure 7a



Figure 6. The changes in the absorption spectrum of 2 upon irradiation at 366 nm in 10 min intervals. Top: absorption spectra at different photolysis times; bottom: absorption difference spectra relative to the spectrum at t = 0.



Figure 7. (a) Aromatic region ¹H NMR spectrum of **2** in $CDCl_3/C_6D_6$ (2:1 mixture); (b) Aromatic region ¹H NMR of the same sample after it was irradiated at 366 nm for 10 min. Insets: ¹H NMR spectrum of olefinic hydrogen atoms (spectrum obtained with sample in pure C_6D_6 as a solvent).

illustrates the aromatic region of the ¹H NMR spectrum of complex 2 (CDCl₃/ C_6D_6 mixture solvent) prior to photolysis. A complete assignment of the ¹H resonances was achieved by 2D NMR techniques (see Supporting Information). The resonances in the region between 6.9 and 7.30 ppm correspond to protons on the 4-ES phenyl rings. The two alkene protons appear in the spectrum as a closely spaced pair of doublets at $\delta =$ 6.79 and 6.83 ppm with coupling constant J = 16.4 Hz. Figure 7b shows the ¹H NMR spectrum after the sample of 2 was irradiated at 366 nm for several minutes. There are clearly a number of new peaks that arise in the aromatic region as a result of the photolysis, but of most significance is the new set of resonances that appear at $\delta \approx 6.3$ ppm. As can be seen in the Figure 7b inset (right side), this resonance is due to a closely spaced pair of doublets at $\delta = 6.27$ and 6.30 ppm with coupling constant J = 12.5 Hz. On the basis of the chemical shift and



Figure 8. Jablonski diagrams for (a) complexes 2 and 3, (b) complex 4, and (c) complex 5; solid arrows represent radiative processes, and dashed arrows represent nonradiative decays. Horizontal dashed lines in Figures 8b and 8c represent the ³MLCT state at 80 K. Note that in all figures, the energy of ${}^{1}\pi,\pi^{*}$ is taken from the fluorescence maximum (i.e., the relaxed state energy) while that of ¹MLCT is taken from the absorption maximum (i.e., an unrelaxed state energy).

coupling constant, this signal is attributed to the olefinic protons on a cis-stilbene unit produced by photoisomerization. The left inset in Figure 7b shows an expansion of the resonances due the olefinic protons in the trans-stilbene unit(s) in the photolyzed sample (this expansion is for a sample that was run in pure C_6D_6 as a solvent). Interestingly, it is evident in this expansion that there is a set of two chemically distinct pairs of olefinic protons that appear to belong to trans-stilbene (i.e., they have similar chemical shifts and coupling constants). One pair is due to the olefinic hydrogens in the starting complex, 2. We attribute the extra set of resonances ($\delta = 6.78$ and 6.82 ppm, J = 16.4Hz) to the olefinic protons in the *trans*-stilbene moiety of the photoproduct. This result strongly suggests that the primary photoproduct arises from isomerization of one stilbene moiety, producing a complex that has a *trans*- and a *cis*-stilbene unit, i.e.,

$$(Bu_{3}P)_{2}Pt(-C \equiv C - t - St)_{2} + h\nu \rightarrow$$

$$(Bu_{3}P)_{2}Pt(-C \equiv C - t - St)(-C \equiv C - c - St) (1)$$

Similar ¹H NMR spectra were observed as a result of photolysis of complexes **3**-**5**, suggesting that the same process occurs in all of the complexes. The quantum efficiency for photoisomerization of complex **2** via eq 1 was determined by integrating the NMR peak that corresponds to *cis*-stilbene olefinic protons and the value was found to be $\phi_{t-c} = 0.42$.

Photophysical Model: $Pt(P)_2(-C \equiv C-St)_2$ Complexes. In view of their photophysical properties, complexes 2-5 can be classified into two subgroups, and their behavior will be discussed separately in the sections that follow. The first group consists of phosphine-containing complexes 2 and 3, in which the absorption, emission, and transient absorption arise solely from π,π^* transitions. The second group consists of the 2,2'-bipyridine-containing complexes which feature a manifold of energetically low-lying MLCT states in addition to the π,π^* states.

Figure 8a presents a Jablonski diagram that is consistent with the photophysical behavior of phosphine complexes 2 and 3. Light absorption gives rise to the ${}^{1}\pi,\pi^{*}$ excited state (path 1 in Figure 8a), with energy of 3.3 eV in complex 2 and 3.5 eV in complex 3. For both complexes the π,π^{*} absorption is redshifted relative to its position in the 4-ES free ligand which suggests that the Pt center promotes delocalization of the 4-ES based π and π^{*} orbitals that are involved in the optical transition. Such delocalization is consistent with the results of molecular orbital calculations on square planar, bis-acetylide complexes of d⁸ metals, which imply that mixing of the metal-centered d π (and p) orbitals with the π and π^* MOs of the acetylide ligands leads to π -type conjugation through the metal center.¹⁰ Thus, in effect, the lowest energy absorption in 2 and 3 arises from a transition between HOMO and LUMO levels that are substantially delocalized over the entire molecules. The fact that the π,π^* transition is blue-shifted in 3, in which the two 4-ES units are coordinated cis at the Pt center implies that the degree of interaction between the two 4-ES ligands is lower.⁴⁷ This finding is in agreement with the results of an investigation by Ziessel and co-workers which demonstrated that the rate of triplet energy transfer between chromophores linked via a cis-Pt acetylide is lower than in the corresponding trans-linked system.⁴⁸ These authors concluded that the difference in energy transfer rate results from a lower electronic interaction between chromophores that are linked by the cis-Pt acetylide unit.

Once the ${}^{1}\pi,\pi^{*}$ excited state is produced by light absorption, it relaxes predominantly via intersystem crossing (path 3, Figure 8b) to produce the ${}^{3}\pi,\pi^{*}$ state (although some fluorescence is observed, it has a low quantum efficiency). Time-resolved photoacoustic calorimetry indicates that the intersystem crossing quantum efficiency (ϕ_{isc}) in **2** is 0.75 \pm 0.05.⁴⁹ Phosphorescence from the ${}^{3}\pi,\pi^{*}$ excited state (path 4) occurs only at low temperatures, where the solvent is a rigid glass. The phosphorescence energy in complexes 2 and 3 is 1.95 eV, which is very similar to the phosphorescence energy of trans-stilbene (2.10 eV),^{25,42} implying that the triplet excited state is "confined" on a single 4-ES moiety. It is interesting that the phosphorescence spectra of complexes 2 and 3 are almost identical, even though their molecular structures and absorption spectra are different. A similar trend was observed in the transient absorption measurements, where spectra of complexes 2 and 3 are almost identical. In addition, the phosphorescence band shape and vibronic structure observed for 2 and 3 are very similar to those of *trans*-stilbene.^{25,42} Taken together, these results strongly suggest that the ${}^{3}\pi,\pi^{*}$ state in 2 and 3 is *localized* on a single 4-ES chromophore. Interestingly, the presence of the Pt center appears to have little effect on the electronic structure of the triplet; the metal simply acts as a "heavy-atom substitutent" which increases the spin-orbit coupling which enhances intersystem crossing and radiative decay. The finding that the triplet is be localized on a single 4-ES unit in 2 and 3 (rather than delocalized over the entire complex) is consistent with theory and recent experimental work which demonstrates that triplet excited states are less spatially delocalized compared to the singlet states of the same orbital parentage.^{10,12,15,20,50} Although the triplet state appears to be localized on a single 4-ES unit, during the lifetime of the triplet it seems likely the that the triplet transfers from one chromophore to another via an energetically degenerate triplet energy transfer process.

Above the glass-to-fluid temperature of the solvent, the phosphorescence of 2 and 3 disappears, signaling that the triplet excited state decays rapidly via twisting around the C=C bond (path 6). By analogy with the photophysics and photochemistry of other substituted stilbenes,²³⁻²⁶ it is believed that this process leads to the twisted triplet state (³p) in which the dihedral angle between the phenyl rings is $\approx 90^{\circ}$. The rate of the C=C bond rotation corresponds to the rate of triplet excited-state decay, which was found from transient absorption measurements to be $k = 1.6 \times 10^7 \text{ s}^{-1}$. This value is in excellent agreement with the triplet decay rate of trans-stilbene, which is also believed to decay via C=C bond rotation.⁴⁴ Furthermore, there is good correspondence between the photoisomerization quantum yield of complex 2 and that for *trans*-stilbene under triplet sensitized conditions. In particular, the overall yield for photoisomerization of complex 2 is ϕ_{t-c} 0.42, while $\phi_{isc} = 0.75$ (photoacoustic calorimetry, see above). The product, $\phi_{t-c} \propto \phi_{isc}$ affords the efficiency of isomerization from the triplet state, $\phi_{T^*,t-c} = 0.53$. By comparison, under triplet sensitized conditions the photoisomerization yield of *trans*-stilbene is $\phi_{T^*,t-c} = 0.55$.⁵¹ These results confirm the hypothesis outlined above that the ${}^{3}\pi,\pi^{*}$ state is localized on a 4-ES chromophore.

Photophysical Model: Pt(bpy)(−C≡C−Ar)₂ Complexes. Complexes 4 and 5 each contain a 2,2'-bipyridine ligand which introduces a manifold of low-lying MLCT states based on the $d\pi$ (Pt) $\rightarrow \pi^*$ (bpy) transition. In a previous study,³⁰ we analyzed the photophysical properties of a series of complexes of the type $(4,4'-X_2-bpy)$ Pt(C=C-tol)₂ (where $4,4'-X_2-bpy$ is a 2,2bipyridine that is substituted in the 4,4'-positions, and C=Ctol is p-ethynyltoluene). In this series the $d\pi$ (Pt) $\rightarrow \pi^*$ (bpy) MLCT state is the lowest excited state, and MLCT photoluminescence is observed at 298 and 80 K.^{29,30} The emission energies of the tert-butyl- and diester-substituted bpy complexes afford values for the energy of the relaxed MLCT state at 298 K in fluid solution, $E_{\text{MLCT}} = 2.12$ and 1.84 eV, respectively.³⁰ Due to the rigidochromic effect, the energy of the MLCT state is increased in a glass at 80 K, and for the same two complexes in the glass $E_{\text{MLCT}} = 2.42$ and 2.14 eV, respectively.³⁰

In the analysis of the photophysics and photochemistry of 4 and 5, we assume that E_{MLCT} is the same as in the corresponding $(4,4'-X_2-bpy)Pt(C \equiv C-tol)_2$ complexes. Thus, given that the energy of the 4-ES localized ${}^{3}\pi,\pi^{*}$ state is ≈ 1.97 eV, it was anticipated that for 4 in fluid solution the energetic ordering of the excited states would be ${}^{3}MLCT > {}^{3}\pi,\pi^{*}$, and for 5 in fluid solution the ordering would be reversed (i.e., ³MLCT < ${}^{3}\pi,\pi^{*}$). On the other hand, due to the rigidochromic effect, it was anticipated that in a low-temperature glass the state ordering would be ³MLCT > ${}^{3}\pi,\pi^{*}$ for 4 and 5. Consequently, in fluid solution it was expected that the properties of 4 and 5 would be different. Specifically, we anticipated that MLCT emission would be observed from 5, and that that trans-cis photoisomerization would be observed in 4, but not in 5. By contrast, in a low-temperature glass, the photophysics of both complexes was expected to be the same, with phosphorescence from the 4-ES based ${}^{3}\pi,\pi^{*}$ being observed.

The observations on **4** and **5** in the frozen glass show that the expectations based on this analysis are borne out by experiment. Thus, both complexes feature strong phosphorescence from the 4-ES ${}^{3}\pi,\pi^{*}$ state, as expected if the state ordering is ${}^{3}\text{MLCT} > {}^{3}\pi,\pi^{*}$. Moreover, in fluid solution complex **4** behaves as expected if the state ordering is ${}^{3}\text{MLCT} > {}^{3}\pi,\pi^{*}$: trans—cis photoisomerization is observed, even for irradiation into the MLCT absorption, and ${}^{3}\text{MLCT}$ emission is not observed. On the other hand, the properties of **5** in fluid solution are opposite to what is expected if the state ordering is ${}^{3}\text{MLCT} < {}^{3}\pi,\pi^{*}$ —this complex behaves the same as **4**!

Jablonski diagrams that are used to explain the observed properties of 4 and 5 are shown in Figures 8b and 8c, respectively. The energies for ${}^{1}\pi,\pi^{*}$ and ${}^{1}MLCT$ transition are estimated from the fluorescence and absorption spectra, respectively, while the energies of the ³MLCT states are taken to be the same as in the corresponding $(4,4'-X_2-bpy)Pt(C=C-tol)_2$ complexes.³⁰ (In these diagrams the ³MLCT levels in fluid and glassy media are shown as solid and dashed lines, respectively.) Since the energetic ordering is ${}^{3}MLCT > {}^{3}\pi, \pi^{*}$ in solution and in the glass for 4, the photophysics of this complex are very similar to that of 2 and 3. Thus, excitation of 4 in the near-UV (path 1) produces the ${}^{1}\pi,\pi^{*}$ state, which undergoes rapid intersystem crossing (path 3) to ${}^{3}\pi,\pi^{*}$. Alternatively, visible excitation (path 7) affords ¹MLCT which rapidly intersystem crosses to ³MLCT (path 8).⁵² Since no emission is observed from ³MLCT, we conclude that intramolecular energy transfer from ³MLCT to ³ π , π^* (path 9) is very rapid, i.e., $k \ge 10^9$ s⁻¹. Rapid energy transfer is consistent with the fact that the process is exothermic ($\Delta G \leq -0.1$ eV), and there is strong coupling between the ³MLCT and ³ π,π^* manifolds. Finally, once it is formed ${}^{3}\pi,\pi^{*}$ state relaxes either by C=C bond twisting (path 6, fluid solution) or by phosphorescence (path 4, solvent glass).

In a solvent glass, the photophysics of 5 are identical to those of 4. Excitation into either the π,π^* or MLCT manifolds (paths 1 and 7, Figure 8c) is followed by relaxation into the ${}^{3}\pi,\pi^{*}$ state (via path 3 or path 8 followed by 9), which then relaxes by phosphoresecence or nonradiative decay. The unique feature with respect to 5 is that in fluid solution ${}^{3}MLCT$ is more than 0.1 eV below the spectroscopic energy of the ${}^{3}\pi,\pi^{*}$ state. In view of this, one would expect that: (1) ³MLCT to ${}^{3}\pi,\pi^{*}$ energy transfer is slow (if it occurs at all), (2) the ³MLCT state is "longlived" (i.e., $\tau > 20$ ns),³⁰ and (3) ³MLCT emission is observed. A possible explanation for the anomalous behavior of 5 is that ³MLCT is rapidly deactivated by intramolecular "nonvertical" energy transfer⁵³⁻⁵⁵ to directly afford the 4-ES localized twisted triplet state, ³p (path 9a, Figure 8c). Because the energy of ³p lies below that of the (spectroscopic) trans-triplet, nonvertical energy transfer is exothermic and consequently quite rapid. In addition, ³p is likely to be very short-lived, and thus, the twostep process (³MLCT \rightarrow ³p \rightarrow ground state) provides a rapid pathway for excited-state decay. This explains why no transient is observed by laser flash photolysis for 5 and that trans-cisphotoisomerization is observed even for irradiation into the lowenergy MLCT absorption band. Note that nonvertical energy transfer has been the subject of extensive investigation in bimolecular systems, and it is well-established that photoisomerization of trans-stilbene is efficiently sensitized by triplet energy donors with energies 0.3-0.4 eV below the spectroscopic energy of trans-stilbene.53,54,56 The present investigation may provide the first example of a system in which intramolecular nonvertical energy transfer plays an important role in determining the photochemical and photophysical properties of a molecular system.

Summary and Conclusions

This study was carried out with the objective of providing experimental information concerning the properties of singlet and triplet excited states in π -conjugated Pt acetylide systems. To address these objectives, a family of Pt-acetylides that contain the *trans*-stilbene chromophore were synthesized and fully characterized. Stilbene was chosen for the investigation because it contains an extended π -conjugated electronic system, and because its photochemical and photophysical properties have been thoroughly investigated.

The absorption spectra of the family of complexes reveals that the singlet excited state is delocalized over the entire π -conjugated system. The extent of delocalization appears to be greatest in complex 2, in which the two 4-ES ligands are trans at the Pt center. This result indicates that π -conjugation through Pt is most efficient when the acetylide ligands are coordinated trans. The photophysical and photochemical investigations designed to probe the long-lived excited states demonstrate that in all of the complexes the properties are dominated by the ${}^{3}\pi,\pi^{*}$ excited-state localized in the 4-ES chromophore. Interestingly, the properties of the ${}^{3}\pi,\pi^{*}$ state in the Pt-acetylide complexes are remarkably similar to those of trans-stilbene. From this we conclude that in the Pt-acetylide complexes the ${}^{3}\pi,\pi^{*}$ state is *localized* on a single 4-ES unit (i.e., in the triplet, there is not significant delocalization of the excitation energy through Pt into the other 4-ES ligand). This finding is consistent with a mounting body of evidence which demonstrates that in organic and organometallic π -conjugated systems singlet excitations are delocalized, while the triplet states of the same electronic configuration are spatially confined.^{12,15,20}

Another component of the project examined how introduction of a manifold of MLCT states influences the photophysical properties of Pt-acetylide complexes. Two molecular systems were examined that contained 2,2-bipyridine ligands having different electron-acceptor properties. The bpy-substituted complexes exhibit low-energy absorption bands arising from the $d\pi$ (Pt) $\rightarrow \pi^*$ (bpy) transition. However, the remarkable finding is that the photophysics and photochemistry of the complexes are hardly affected by the MLCT state. This finding was unexpected in complex **5**, where the spectroscopic energy of ³MLCT is below that of the 4-ES localized ${}^3\pi,\pi^*$ state. It is believed that the unusual properties of this complex arise as a result of rapid nonvertical energy transfer from ³MLCT to ${}^3\pi,\pi^*$.

Experimental Section

Synthesis. (E)-4-Bromostilbene and the substituted 2,2'bipyridine ligands were prepared according to literature procedures.^{57,58} The (2,2'-bipyridine)PtCl₂ complexes were prepared by reaction of K₂PtCl₄ with the bipyridine ligand in refluxing aqueous HCl solution.²⁹ *trans*-Pt(PBu₃)₂Cl₂ and Pt(dppe)Cl₂ were prepared as reported in the literature.^{59,60} A sample of **1** was provided by Dr. Thomas Cooper of the Air Force Research Laboratory.

(E)-4-(Trimethylsilylethynyl)stilbene. A mixture of 100 mg $(3.8 \times 10^{-4} \text{ mol})$ of (E)-4-bromostilbene, 16 mg $(2.28 \times 10^{-5} \text{ mol})$ of Pt(PPh₃)₂Cl₂, 8 mg $(4.56 \times 10^{-5} \text{ mol})$ of CuI, 3 mL of diisopropylamine, and 5 mL of THF was prepared in a round-bottomed flask. The solution was degassed for 15 min under argon, whereupon 90 mg $(9.6 \times 10^{-4} \text{ mol})$ of trimethylsilyl-acetylene was added and the solution was heated overnight at 80–90 °C. The solvent was evaporated under reduced pressure and the crude product was purified by silica column chromatography, using a 1:1 mixture of hexanes/CH₂Cl₂ as an eluant. The product was obtained in 85% yield (90 mg). ¹H NMR

(CDCl₃, 300 MHz) δ 7.50 (d, 6H), 7.33 (t, 2H), 7.22 (t, 1H), 7.08 (dd, 2H), 0.12 (s, 9H) ppm.

(E)-4-Ethynylstilbene. A solution of 100 mg (3.6×10^{-4} mol) of (E)-4-(trimethylsilylethynyl)stilbene in 4 mL of methanol was placed in a round-bottomed flask. Then a solution of 200 mg of KOH in 2 mL of water was added to the flask. The reaction mixture was stirred at room temperature for 3 h. After extraction with CH₂Cl₂ and removal of the solvent, the crude product was purified by silica column chromatography by using hexanes/methylene-chloride mixture in a 3:1 ratio as eluant. The product was obtained in 95% yield (70 mg). ¹H NMR (CDCl₃, 300 MHz) δ 7.55 (m, 6H), 7.38 (t, 2H), 7.25 (t, 1H), 7.10 (dd, 2H), 3.15 (s, 1H) ppm. HRMS: Calcd for C₁₆H₁₂, 204.0971; Found, 204.0943.

Syntheses of Complexes 2–5. Complexes 2–5 were synthesized by reaction of the corresponding L_2PtCl_2 complex with (E)-4-ethynylstilbene, according to the method described by James and co-workers.³² The crude complexes were purified by chromatography on alumina using CH_2Cl_2 as the eluant. Further purification was achieved by crystallization from acetone (compound 2) or a CH_2Cl_2 /hexanes mixture (compounds 3–5). The purified complexes were fully characterized by ¹H NMR and high-resolution mass spectrometry. Spectral data for the new compounds are listed below.

Complex 2. ¹H NMR (CDCl₃/C₆D₆ = 3:1, 500 MHz) δ 7.50 (d, 4H), 7.36 (t, 4H), 7.34 (d, 4H), 7.20 (d, 4H), 7.10 (t, 2H), 7.01 (d, *J* = 16.4 Hz, 2H), 6.97 (d, *J* = 16.4 Hz, 2H), 2.18 (m, 12H), 1.70 (m, 12H), 1.46 (sextet, 12H), 0.96 (t, 18H) ppm. HRMS (LSIMS): Calcd for C₅₆H₇₆P₂Pt, 1005.512; Found, 1005.512.

Complex 3. ¹H NMR (CDCl₃, 300 MHz) δ 7.94 (t, 4H), 7.18–7.51 (m, 30H), 7.11 (d, 4H), 7.02 (d, J = 18 Hz, 2H), 6.96 (d, J = 18 Hz, 2H), 2.41 (t, 4H) ppm. HRMS (LSIMS): Calcd for C₅₈H₄₆P₂Pt, 1000.280; Found, 1000.281.

Complex 4. ¹H NMR (CDCl₃, 300 MHz) δ 7.99 (s, 2H), 7.73 (d, 4H), 7.60 (d, 4H), 7.50 (d, 4H), 7.44 (d, 4H), 7.35 (t, 4H), 7.20 (t, 2H), 7.09 (d, J = 14.1 Hz, 2H), 7.04 (d, J = 14.1 Hz, 2H), 1.41 (s, 18H) ppm. HRMS (LSIMS): Calcd for C₅₀H₄₆N₂Pt, 870.339; Found, 870.338.

Complex 5. ¹H NMR (CDCl₃, 300 MHz) δ 9.95 (d, 2H), 8.60 (s, 2H), 8.05 (d, 2H), 7.53 (d, 4H), 7.32–7.48 (m, 12H), 7.25 (t, 2H), 7.09 (d, *J* = 15 Hz, 2H), 7.06 (d, *J* = 15 Hz, 2H), 4.40 (q, 4H), 1.42 (t, 6H) ppm. HRMS (LSIMS): Calcd for C₄₈H₃₈N₂O₄Pt, 902.256; Found, 902.260.

X-ray Diffraction Analysis. Data were collected at 173 K on a Siemens SMART PLATFORM equipped with A CCD area detector and a graphite monochromator utilizing Mo K α radiation ($\lambda = 0.71073$ Å). Cell parameters were refined using up to 8192 reflections. A full sphere of data (1850 frames) was collected using the ω -scan method (0.3° frame width). The first 50 frames were remeasured at the end of data collection to monitor instrument and crystal stability (maximum correction on I was <1%). Absorption corrections by integration were applied based on measured indexed crystal faces.

The structure was solved by the Direct Methods in *SHELX-TL5*, and refined using full-matrix least squares. The non-H atoms were treated anisotropically, whereas the hydrogen atoms were calculated in ideal positions and were riding on their respective carbon atoms. Crystal, data collection, and refinement parameters are summarized in Table 2. The asymmetric unit consists of a half Pt complex. A total of 268 parameters were refined in the final cycle of refinement using 8529 reflections with $I > 2\sigma(I)$ to yield R₁ and wR₂ of 3.27% and 8.52%, respectively. Refinement was done using F^2 .

BLE 2: Crystallographic Data for Complex 2				
empirical formula	$C_{56}H_{76}P_2Pt$	crystal size	$0.21 \times 0.17 \times 0.11 \text{ mm}^3$	
formula weight	1006.20	θ range for data collection	1.97 to 28.91°	
temperature	173(2) K	index ranges	$-13 \le h \le 13$	
wavelength	0.71073 Å	0	$-14 \le k \le 12$	
crystal system	Triclinic		$-12 \le l \le 17$	
space group	$P\overline{1}$	reflections collected	8529	
unit cell dimensions	a = 10.0075(5) Å	independent reflections	5704 [R(int) = 0.0661]	
	b = 10.7197(6) Å	completeness to $\theta = 28.91^{\circ}$	86.8%	
	c = 12.8122(7) Å	absorption correction	integration	
	$\alpha = 101.670(1)^{\circ}$	max and min transmission	0.7729 and 0.5162	
	$\beta = 109.882(1)^{\circ}$	refinement method	Full-matrix least squares on F^2	
	$\gamma = 95.533(1)^{\circ}$	data/restraints/parameters	5704/0/268	
volume	1245.3(1) Å ³	Goodness-of-fit on F^2	1.082	
Z	1	final R indices $[I > 2\theta(I)]$	R1 = 0.0327, $wR2 = 0.0852$ [5704]	
density (calcd)	1.342 Mg/m^3	R indices (all data)	R1 = 0.0327, wR2 = 0.0852	
absorption coefficient	2.916 mm^{-1}	largest diff. peak and hole	1.383 and -0.731e•Å ⁻³	
F(000)	520	U I		

TAB

Photophysical Measurements. Spectroscopic experiments were carried out either in CH₂Cl₂ or 2-methyltetrahydrofuran (2-MTHF), and these solvents were purified by distillation from CaH₂ and Na/benzophenone, respectively. Spectroscopy carried out at room temperature was performed using samples that were degassed by argon purging for 20 min. Low-temperature spectroscopic experiments were carried out on samples that were degassed by four repeated freeze-pump-thaw cycles on a high vacuum line. UV-visible absorption spectra were obtained on a Cary 100 instrument. All photophysical experiments were carried out with sample concentrations in the range of 2-20 μ M. At these low concentrations, the lifetimes were not concentration dependent.

Steady-state photoluminescence spectroscopy was carried out on a SPEX Fluorolog instrument. Emission spectra were corrected by using correction factors generated in-house with a standard calibration lamp. Sample concentrations were sufficiently low such that the absorbance at all wavelengths was <0.2 (typical concentration = 5 \times 10⁻⁶ M). Low-temperature photoluminescence experiments were carried out with samples contained in an LN2 cooled optical cryostat (Oxford Instruments, DN-1704) connected to an Omega CYC3200 temperature controller.

Transient absorption spectroscopy was carried out on an instrument that has been described previously.⁶¹ Samples were contained in a cell that holds a total volume of 10 mL, and the contents were continuously recirculated through the pumpprobe region of the cell. Samples were degassed by argon purging for 30 min. Excitation was provided by the 3rd harmonic output of a Nd:YAG laser (355 nm, Spectra Physics, GCR-14). Typical pulse energies were 5 mJ/pulse which corresponded to an irradiance in the pump-probe region of 20 mJ/cm.

Photoisomerization Studies. Steady-state photochemical experiments were carried out by using the 375 nm (compound 2) and 350 nm (compounds 3-5) output from a 75 W highpressure Xe lamp. The photolysis beam was passed through a grating monochromator and focused onto a 1×1 cm quartz cell that contained 3 mL of an argon degassed sample solution. Samples were exposed to light in 10 min intervals and the change in the UV-visible absorption spectrum was monitored.

The trans-cis photoisomerization reaction was monitored by ¹H NMR spectroscopy. Compound **2** was dissolved in CDCl₃ and placed in an NMR tube with a vacuum valve. The solution was degassed by four repeated freeze-pump-thaw cycles on a high vacuum line. The NMR tube was placed in a housing (an aluminum box with an opening on the top to place the NMR tube and another 2 in. \times 2 in. opening with a LG350 and a UG-11 filter which allows for light to reach the sample). The sample was irradiated by a 450 W medium-pressure mercury lamp, which was placed ~ 15 in. from the housing. The lamp was held in a quartz immersion well which allowed for water cooling. The sample was irradiated in 1 min intervals, and the changes were monitored by NMR spectroscopy (300 MHz Gemini). The concentration of the cis isomer produced after photolysis was determined by integrating the olefinic peaks in the NMR spectra.

The photoisomerization quantum yield for compound 2 was determined using Aberchrome 540 as an actinometer.⁶² Aberchrome is known to undergo a photocyclization process with a quantum efficiency of 0.20. The solution was prepared by dissolving 11.92 mg of Aberchrome in 10 mL of toluene. A volume of 1 mL of the actinometer solution was placed in an NMR tube and photolyzed for 1 min, upon which time the sample was diluted to 5 mL and the absorbance at 494 nm was measured. The procedure was repeated for different photolysis times (2, 3, 4 and 5 min). The results were plotted as the change of absorption at 494 nm per time, which gave a slope S = A/t. The intensity of the incident light was calculated from the slope according to following equation:

$$I = \frac{S \times V \times N}{\Phi \times \epsilon} \tag{2}$$

where V is the volume of the sample, Φ is the quantum yield for the Aberchrome cyclization ($\Phi = 0.20$), N is Avogadro's number, and ϵ is the molar extinction coefficient of the cyclic product at 494 nm ($\epsilon = 8200 \text{ M}^{-1} \text{ cm}^{-1}$).

Acknowledgment. We gratefully acknowledge the National Science Foundation (CHE-0211252) for support of this work.

Supporting Information Available: Two-dimensional NMR spectra and detailed ¹H and ¹³C assignments for complex 2. Crystallographic data for complex 2 in CIF format. This information is available free of charge via the Internet at http:// pubs.acs.org.

References and Notes

(1) Handbook of Conducting Polymers, 2nd ed.; Skotheim, T. A., Elsenbaumer, R. L., Reynolds, J. R., Eds.; Marcel Dekker: New York, 1998

(2) McGehee, M. D.; Miller, E. K.; Moses, D.; Heeger, A. J. In Advances in Synthetic Metals. Twenty Years of Progress in Science and Technology; Bernier, P., Lefrant, S., Bidan, G., Eds.; Elsevier: Amsterdam, 1999; pp 98-205.

- (4) Gunder, P. Nonlinear Optical Effects and Materials; Springer: New York, 2000.
- (5) Brabec, C. J.; Sariciftci, N. S.; Hummelen, J. C. Adv. Funct. Mater. 2001, 11, 15–26.
- (6) Kingsborough, R. P.; Swager, T. M. Prog. Inorg. Chem. 1999, 48, 123–231.
- (7) Baldo, M. A.; O'Brien, D. F.; You, Y.; Shoustikov, A.; Sibley, S.; Thompson, M. E.; Forrest, S. R. *Nature* **1998**, *395*, 151–154.
- (8) Adachi, C.; Baldo, M. A.; Thompson, M. E.; Forrest, S. R. J. App. Phys. 2001, 90, 5048–5051.
- (9) Scurlock, R. D.; Wang, B. J.; Ogilby, P. R.; Sheats, J. R.; Clough, R. L. J. Am. Chem. Soc. **1995**, 117, 10194–10202.
- (10) Beljonne, D.; Wittmann, H. F.; Köhler, A.; Graham, S.; Younus,
- M.; Lewis, J.; Raithby, P. R.; Khan, M. S.; Friend, R. H.; Bredas, J. L. J. Chem. Phys. **1996**, 105, 3868–3877.
- (11) Walters, K. A.; Ley, K. D.; Schanze, K. S. J. Chem. Soc., Chem. Commun. 1998, 10, 1115–1116.
- (12) Wilson, J. S.; Köhler, A.; Friend, R. H.; Al-Suti, M. K.; Al-Mandhary, M. R. A.; Khan, M. S.; Raithby, P. R. J. Chem. Phys. 2000, 113, 7627–7634.
- (13) Monkman, A. P.; Burrows, H. D.; Hamblett, I.; Navarathnam, S.; Svensson, M.; Andersson, M. R. *J. Chem. Phys.* **2001**, *115*, 9046–9049.
- (14) Monkman, A. P.; Burrows, H. D.; Hartwell, L. J.; Horsburgh, L. E.; Hamblett, I.; Navaratnam, S. *Phys. Rev. Lett.* **2001**, *86*, 1358–1361.
- (15) Köhler, A.; Wilson, J. S.; Friend, R. H.; Al-Suti, M. K.; Khan, M. S.; Gerhard, A.; Bassler, H. J. Chem. Phys. **2002**, *116*, 9457–9463.
- (16) Walters, K. A.; Ley, K. D.; Cavalaheiro, C. S. P.; Miller, S. E.; Gosztola, D.; Wasielewski, M. R.; Bussandri, A. P.; van Willigen, H.; Schanze, K. S. J. Am. Chem. Soc. **2001**, *123*, 8329–8342.
- (17) Wang, Y.; Liu, S.; Pinto, M. R.; Dattelbaum, D. M.; Schoonover,
- J. R.; Schanze, K. S. J. Phys. Chem. A **2001**, 105, 11118–11127. (18) Liu, Y.; Li, Y.; Schanze, K. S. J. Photochem. Photobiol. C:
- *Photochem. Rev.* **2002**, *3*, 1–23. (19) Li, Y.; Whittle, C. E.; Walters, K. A.; Ley, K. D.; Schanze, K. S.
- In Electronic, Optical and Optoelectronic Polymers and Oligomers; Jabbour,
- G. E., Meijer, E. W., Sariciftci, N. S., Swager, T. M., Eds.; Materials
- Research Society: Warrendale, PA, 2002; Vol. 665, pp 61–72. (20) Liu, Y.; Jiang, S. J.; Glusac, K.; Powell, D. H.; Anderson, D. F.;
- Schanze, K. S. J. Am. Chem. Soc. 2002, 124, 12412–12413. (21) Bunz, U. H. F. Chem. Rev. 2000, 100, 1605–1644.
- (22) Chawdhury, N.; Köhler, A.; Friend, R. H.; Younus, M.; Long, N. J.; Raithby, P. R.; Lewis, J. *Macromolecules* **1998**, *31*, 722–727.
- (23) Saltiel, J.; D'Agostino, J.; Megarity, E. D.; Metts, L.; Neuberger, K. R.; Wrighton, M.; Zafiriou, O. C. In *Organic Photochemistry*; Chapman,
- O. L., Ed.; Marcel Dekker: New York, 1973; Vol. 3, p 1.
- (24) Görner, H.; Schulte-Frohlinde, D. J. Phys. Chem. 1979, 83, 3107-3118.
 - (25) Görner, H. J. Phys. Chem. 1989, 93, 1826-1832.
 - (26) Waldeck, D. H. Chem. Rev. 1991, 91, 415-436.
- (27) Cooper, T. M.; McLean, D. G.; Rogers, J. E. Chem. Phys. Lett. 2001, 349, 31-36.
- (28) Rogers, J. E.; Cooper, T. M.; Fleitz, P. A.; Glass, D. J.; McLean, D. G. J. Phys. Chem. A **2002**, 106, 10108–10115.
- (29) Hissler, M.; Connick, W. B.; Geiger, D. K.; McGarrah, J. E.; Lipa, D.; Lachicotte, R. J.; Eisenberg, R. *Inorg. Chem.* **2000**, *39*, 447–457.
- (30) Whittle, C. E.; Weinstein, J. A.; George, M. W.; Schanze, K. S. *Inorg. Chem.* **2001**, *40*, 4053–4062.
- (31) Khan, M. S.; Kakkar, A. K.; Long, N. J.; Lewis, J.; Raithby, P.; Nguyen, P.; Marder, T. B.; Wittmann, F.; Friend, R. H. J. Mater. Chem.
- **1994**, *4*, 1227–1232. (32) James, S. L.; Younus, M.; Raithby, P. R.; Lewis, J. J. Organomet. *Chem.* **1997**, *543*, 233–235.

- (33) Chawdhury, N.; Köhler, A.; Friend, R. H.; Wong, W.-Y.; Lewis, J.; Younus, M.; Raithby, P. R.; Corcoran, T. C.; Al-Mandhary, M. R. A.; Khan, M. S. *J. Chem. Phys.* **1999**, *110*, 4963–4970.
- (34) Wilson, J. S.; Chawdhury, N.; Al-Mandhary, M. R. A.; Younus, M.; Khan, M. S.; Raithby, P. R.; Köhler, A.; Friend, R. H. J. Am. Chem.
- Soc. 2001, 123, 9412–9417. (35) Baraban, J. M.; McGinnety, J. A. Inorg. Chem. 1974, 13, 2864–
- 2869. (36) Mayor, M.; von Hanisch, C.; Weber, H. B.; Reichert, J.; Beckmann,
- D. Angew. Chem.-Int. Ed. 2002, 41, 1183-1186. (37) Davy, J.; Gunter, M. E.; Tiekink, E. R. T. Zeitschrift Fur
- (37) Davy, J., Gunter, M. E., Heknik, E. K. 1. Zeuschrijt Fur Kristallographie **1998**, 213, 483–486.
- (38) Lang, H.; del Villar, A.; Rheinwald, G. J. Organomet. Chem. 1999, 587, 284–289.
- (39) Whittle, C. E. Ph.D. Dissertation, University of Florida, Gainesville, 2001.
- (40) Claes, L.; Francois, J. P.; Deleuze, M. S. Chem. Phys. Lett. 2001, 339, 216-222.
- (41) Albert, I. D. L.; Ramasesha, S. J. Phys. Chem. 1990, 94, 6540-6543.
- (42) Saltiel, J.; Khalil, G. E.; Schanze, K. Chem. Phys. Lett. 1980, 70, 233–235.
- (43) Wittmann, H. F.; Friend, R. H.; Khan, M. S.; Lewis, J. J. Chem. Phys. 1994, 101, 2693-2698.
- (44) Görner, H.; Schulte-Fröhlinde, D. J. Phys. Chem. 1981, 85, 1835–1841.
 - (45) Görner, H.; Kuhn, H. Adv. Photochem. 1995, 19, 1.
- (46) Schanze, K. S.; Lucia, L. A.; Cooper, M.; Walters, K. A.; Ji, H.-F.; Sabina, O. J. Phys. Chem. A **1998**, 102, 5577–5584.
- (47) We note that the fluorescence of 3 is red-shifted relative to its position in the other complexes. The red-shift may have its origin in a steric or electronic interaction between the ethynylstilbene and dppe ligands.
- (48) Grosshenny, V.; Harriman, A.; Hissler, M.; Ziessel, R. J. Chem. Soc., Faraday Trans. 1996, 92, 2223.
- (49) Walters, K. A.; Schanze, K. S. *The Spectrum* (Newsletter of the Center for Photochemical Sciences, Bowling Green State University, http://www.bgsu.edu/departments/photochem/Summer1998Spectrum.pdf) **1998**, *11*, 1–4.
- (50) McGlynn, S. P.; Smith, F. J.; Cilento, G. Photochem. Photobiol. 1964, 3, 269-294.
- (51) Hammond, H. A.; DeMeyer, D. E.; Williams, J. L. R. J. Am. Chem. Soc. **1969**, *91*, 5180–5181.
- (52) Damrauer, N. H.; Cerullo, G.; Yeh, A.; Boussie, T. R.; Shank, C. V.; McCusker, J. K. Science **1997**, 275, 54–57.
- (53) Hammond, G. S.; Saltiel, J. J. Am. Chem. Soc. 1963, 85, 2516-2517.
- (54) Saltiel, J.; Hammond, G. S. J. Am. Chem. Soc. 1963, 85, 2515–1516.
- (55) Saltiel, J.; Mace, J. E.; Watkins, L. P.; Gormin, D. A.; Clark, R. A.; Dmitrenko, O. J. Am. Chem. Soc. 2003, 125, 16158–16159.
- (56) Saltiel, J.; Marchand, G. R.; Kirkorkaminska, E.; Smothers, W. K.; Mueller, W. B.; Charlton, J. L. J. Am. Chem. Soc. **1984**, 106, 3144–3151.
- (57) Plevyak, J. E.; Dickerson, J. E.; Heck, R. F. J. Org. Chem. 1979, 44, 4078–4080.
- (58) Cook, M. J.; Lewis, A. P.; McAuliffe, G. S. G.; Skarda, V.; Thomson, A. J.; Glasper, J. L.; Robbins, D. J. J. Chem. Soc. – Perkin Trans. 2 **1984**, 1293–1301.
- (59) Chock, P. B.; Halpern, J.; Paulik, F. E. Inorg. Synth. 1990, 28, 349-351.
- (60) Clark, H. C.; Manzer, L. E. J. Organomet. Chem. 1973, 59, 411–428.
- (61) Wang, Y. S.; Schanze, K. S. Chem. Phys. 1993, 176, 305–319.
 (62) Heller, H. G.; Langan, J. R. J. Chem. Soc. Perkin Trans. 2 1981, 341–343.