

Preparation of Oligodiazo Compounds by Using the Suzuki Coupling Reaction and Characterization of Their Photoproducts

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Abstract: [9-[10-(4-*tert*-Butyl-2,6-dimethyl)phenyl]anthryl](4-bromo-2,6-dimethylphenyl)diazomethane was found to be stable enough to survive under Suzuki coupling conditions and underwent mono-, di-, and trisubstitution with benzene mono-, di-, and triboronic acids to afford benzene derivatives having one, two, and three diazo units, respectively. The products from irradiation of those diazo compounds were characterized by ESR and SQUID measurements, which revealed that triplet, quintet, and septet ground states were formed from mono-, bis-, and tris(diazo) compounds, respectively. The stability of those high-spin species was estimated by temperature-dependent ESR and UV/vis measurements as well as laser flash photolysis, which indicated that all three species are stable up to 160 K and have a half-life of a few seconds in solution at room temperature. The finding unequivocally shows that a precursor diazo unit can basically be handled as a building block to construct polydiazo compounds and that persistent triplet carbenes, even though they greatly lose typical reactivity as a triplet carbene, still retain electronic properties and act as a spin source when aligned properly in the π -electron frameworks to generate a high-spin molecule with remarkable thermal stability.

There has been an ever-increasing interest in molecular magnetism, in which spins of unpaired electrons in p-orbitals of light atoms such as carbon, nitrogen, and oxygen are mainly responsible; in addition, many attempts have been made to realize organic ferromagnetic materials.^{1,2} Spin sources used for such studies are mostly thermodynamically stable radicals, such as galvinoxyls,^{2j} triphenylmethyls,^{3a} and nitroxides,^{3b} mostly because of their ease of preparation and operation. Potential problems emerge for these radicals. For instance, the exchange coupling between the neighboring nitroxides is weak, and, hence, contamination of the lower-spin states in the polyradicals cannot be avoided. Triplet carbenes are regarded as one of the most effective spin sources because the magnitude of the exchange

coupling between the neighboring centers is large.^{4,5} Moreover, the photolytic production of polycarbenes is possible in solid solution at cryogenic temperatures if poly(diazo) precursors are available. Actually, Iwamura and co-workers have prepared a "starburst"-type nonadiazo compound and have demonstrated that nine diazo groups are photolyzed at low temperature to give a nonadecet ground state ($S = 9$).⁵

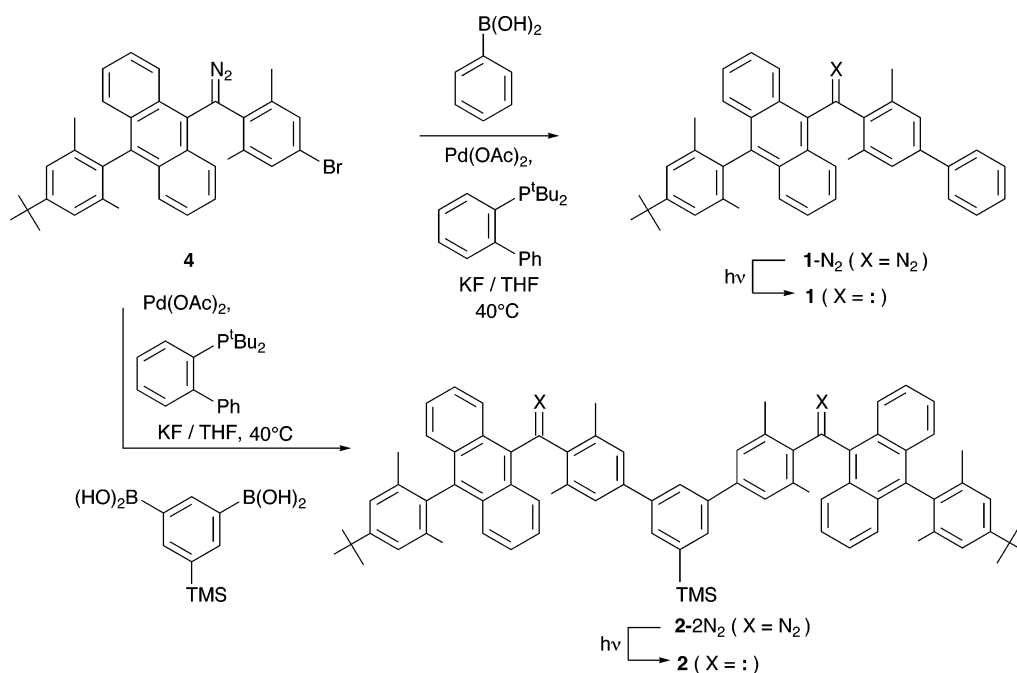
However, those systems have two disadvantages that hinder their further extension to usable magnetic materials. First, a triplet carbene unit is highly unstable and lacks the stability for practical application under ambient conditions. To overcome these difficulties, we have made great efforts to stabilize and hopefully isolate the triplet carbene and succeeded in preparing fairly stable ones surviving for minutes in solution and for years in the crystalline state at room temperature.⁶ Therefore, the next step is to explore a way to connect them while retaining a robust π -spin polarization.

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Scheme 1



The second disadvantage that arises is that diazo groups are also generally labile⁷ and, hence, are usually introduced at the last step of synthesis.⁵ In other words, the diazo compound cannot be used as a building block to prepare a more complicated polydiazo compound, and, thus, the synthesis of the precursor diazo compounds becomes more difficult and laborious as the number of diazo units increases. We found, almost accidentally, that a diphenyldiazomethane prepared to generate a persistent triplet carbene is also persistent for the diazo compound and, hence, can be further modified, with the diazo group intact, into a more complicated diazo compound. For instance, bis(2,4,6-tribromophenyl)diazomethane is found to be stable enough to survive under Sonogashira coupling reaction conditions and undergoes a coupling reaction with (trimethylsilyl)acetylene to give bis(2,6-dibromo-4-trimethylsilylphenyl)diazomethane. Three units of the diazo compound are introduced at the 1-, 3-, and 5-positions of the benzene ring through the ethynyl group by employing a similar coupling reaction to give a tris(diazo) compound, which eventually generates a fairly stable septet ground-state tris(carbene) upon irradiation.⁸

These results suggest that the diazo compound can be used as a building block to prepare a polydiazo compound, which can then generate high-spin polycarbene with considerable thermal stability. Thus, it is very important to explore the applicability of this approach, as it may open a window to a new route to organic magnetic materials. We found that diaryldiazomethane is stable enough to survive the Suzuki coupling reaction.⁹ This enables us to introduce the diazo unit to a phenyl ring directly without using the ethynyl group. This

is a report of the preparation of an oligo(diazo) compound using the Suzuki coupling reaction and the characterization of oligo(carbene) generated from those precursor oligo(diazo) compounds.

Results and Discussion

Synthesis of Precursor Oligodiazo Compounds. The diazo unit we used in this study was the one having 10-(4-*tert*-butyl-2,6-dimethylphenyl)anthryl and 4-bromo-2,6-dimethylphenyl groups, which can generate a fairly persistent triplet carbene.¹⁰ To test the stability of the diazomethane under Suzuki coupling conditions, we first treated it with phenylboronic acid in the presence of Pd(OAc)₂ as a catalyst with P(^tBu)₂(2-BP) as a ligand and KF as a base in tetrahydrofuran (THF) at 40 °C (Scheme 1). The usual workup gave the desired phenylated compound (1-N₂) as an orange solid in 88% yield with the diazo group intact. Encouraged by the finding, we reacted the diazomethane with 5-trimethylsilylbenzene-1,3-diboric acid under similar conditions. The 1,3-bis(diazo) compound (2-2N₂) was obtained as an orange solid in 51% yield in this case. Coupling with benzene-1,3,5-triboric acid did not work under similar conditions. However, trisubstitution was realized by using tetrabutylammonium bromide and K₃PO₄, in place of the phosphine and base, respectively, in dimethylformamide (DMF) at 40 °C (Scheme 2).¹¹

All of the diazo compounds were purified by TLC followed by a repeated chromatograph on a gel permeation column. Appreciable decomposition of the diazo group was not noted in all cases, at least under the conditions employed here. The diazo compounds were fairly stable and could be stored in a refrigerator for several months without any appreciable decomposition.

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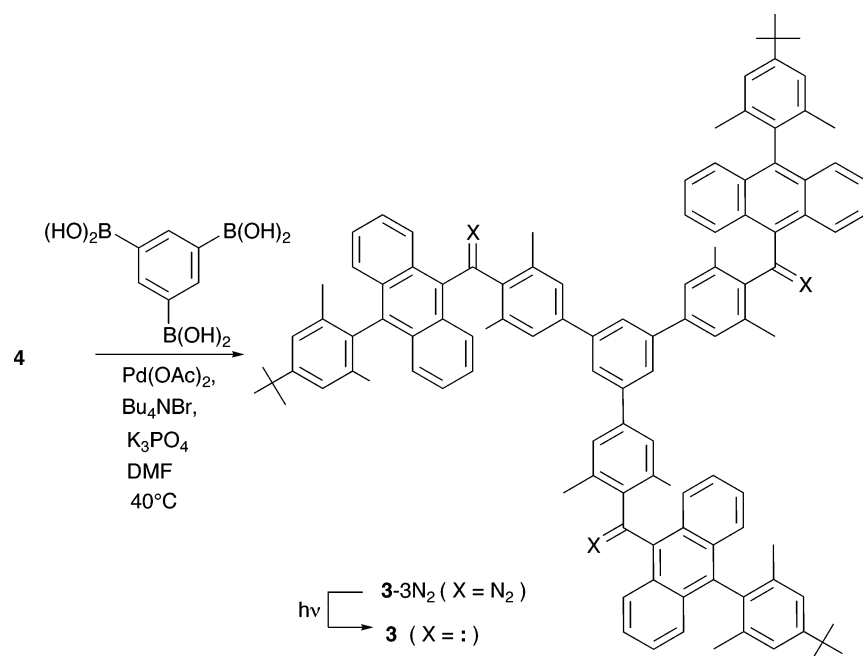
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Scheme 2



Spectroscopic Studies

ESR Studies. Irradiation ($\lambda > 350$ nm) of **1-N₂** in 2-methyltetrahydrofuran (2-MTHF) at 77 K gave rise to a paramagnetic species (Figure 1a) readily characterized from its ESR spectrum as a derivative of a triplet carbene (³**1**).¹² The ESR signals were persistent at this low temperature but disappeared irreversibly when the matrix temperature was raised to room temperature and recooled to 77 K. The EPR signals were analyzed in terms of the zero-field splitting (ZFS) parameters, which gave $D = 0.1950$ cm⁻¹ and $E = 0.0033$ cm⁻¹.

To estimate the temperature at which the triplet signals disappear, the 2-MTHF glass containing carbene ³**1** was warmed gradually in 10 K increments to a desired temperature, allowed to stand at that temperature for 5 min, and recooled to 77 K to measure the ESR. When the 2-MTHF glass was warmed to around 100 K, a new set of triplet peaks ($D = 0.1532$ cm⁻¹ and $E = 0.0008$ cm⁻¹) appeared at the expense of the original peaks (Figure 1b). These changes were not reversible; when the sample was cooled to 77 K, no change took place, except that the signal intensity increased according to the Curie law. Changes of this kind have often been observed for sterically congested triplet diarylcarbenes and are usually interpreted in terms of geometrical changes.^{12c,13} The new set of signals started to decrease at around 140 K and disappeared completely at 160 K.

Similar irradiation of the bis(diazo) compound (**2-2N₂**) in 2-MTHF at 77 K gave ESR spectra (Figure 2a) that were

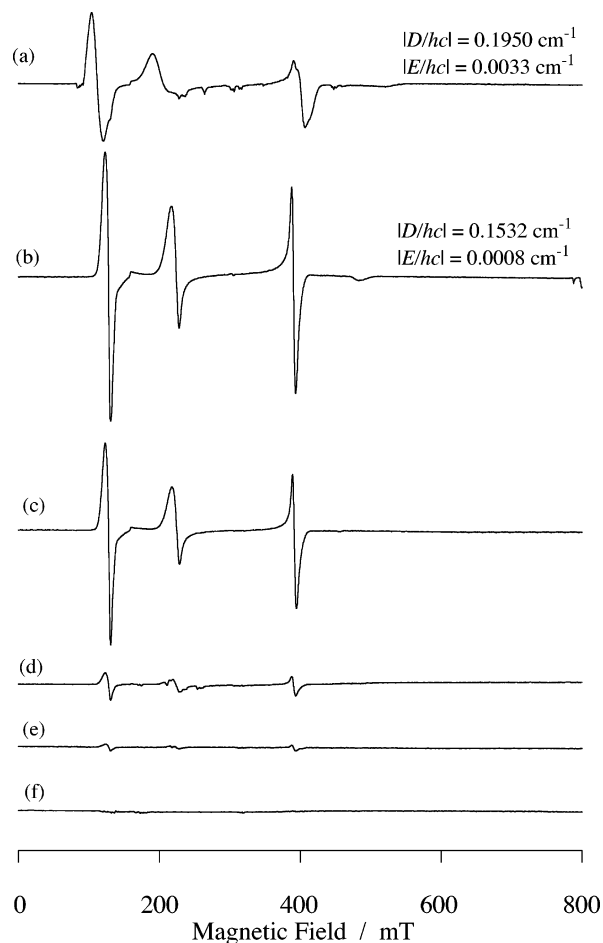


Figure 1. (a) ESR spectra obtained by irradiation of monodiazocompound **1-N₂** in 2-methyltetrahydrofuran at 77 K. (b–e) ESR spectra observed at 77 K in 2-methyltetrahydrofuran after warming the matrix containing ³**1** to (b) 100, (c) 120, (d) 140, (e) 160, and (f) 180 K.

completely different from those observed for the corresponding monocarbene ³**2**. The spectra showed rather strong signals centered at around 300 mT along with weak signals ascribable

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(13) When a carbene is generated in rigid matrices at very low temperature, it should have the geometry dictated by that of the precursor. Even if the thermodynamically most stable geometry of the carbene is different from that at birth, the rigidity of the matrices prevents the carbene from achieving its minimum-energy geometry. When matrices are softened by annealing, the carbene undergoes relaxation to the preferred geometry, probably to gain relief from steric compression.

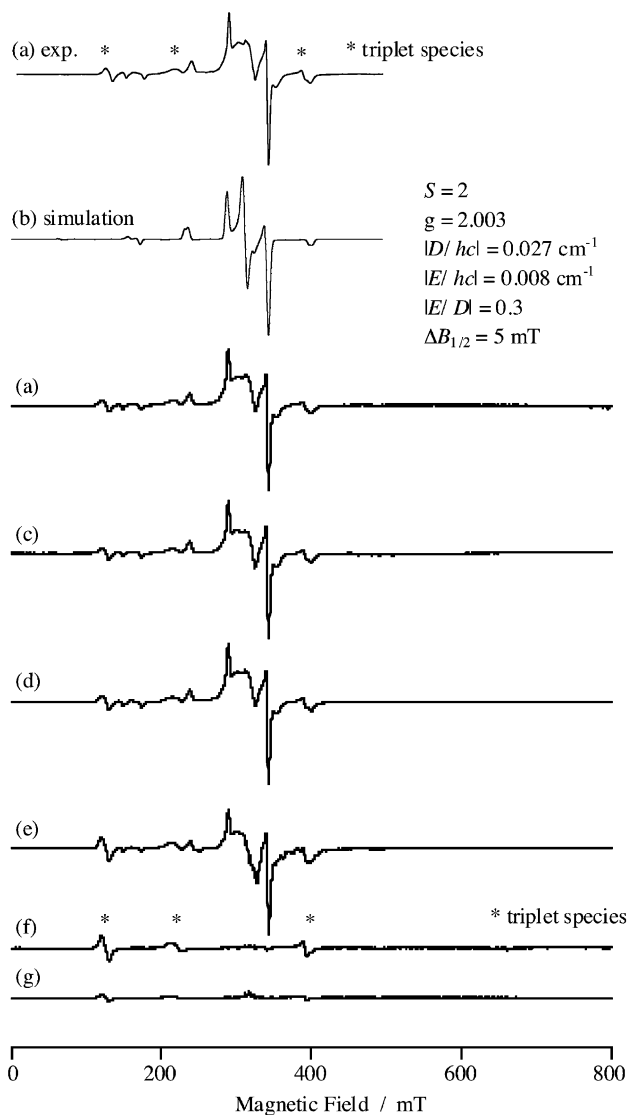


Figure 2. (a) ESR spectra obtained by irradiation of bis(diazo) compound **2-2N₂** in 2-methyltetrahydrofuran at 77 K. (b) Simulated spectra of ⁵² with $S = 2$, $g = 2.003$, $D = 0.027 \text{ cm}^{-1}$, and $E = 0.008 \text{ cm}^{-1}$. (c–g) ESR spectra observed at 77 K in 2-methyltetrahydrofuran after warming the matrix containing ⁵² to (c) 120, (d) 140, (e) 160, (f) 180, and (g) 200 K.

to a triplet species. The latter signals are assigned to triplet monocarbene (³2) probably formed as a result of incomplete decomposition of the bis(diazo) compound. The major signals are well reproduced by computer simulation,¹⁴ shown in Figure 2b, employing a quintet Hamiltonian with $S = 2$, $g = 2.003$, $D = 0.027 \text{ cm}^{-1}$, and $E = 0.008 \text{ cm}^{-1}$. We, therefore, assign the signals to quintet biscarbene **2**, ⁵2. The quintet signals do not decay appreciably up to 140 K, start to decompose at around 150 K, and disappear irreversibly above 160 K.

Irradiation of the tris(diazo) compound (**3-3N₂**) again gave ESR spectra (Figure 3a) that were completely different from those observed for either monocarbene or biscarbene. The main spectra consisted of well-resolved signals centered around ca. 335 mT; signals attributable to triplet carbene and quintet bis(carbene) were very weak, if at all detected. The smaller signal

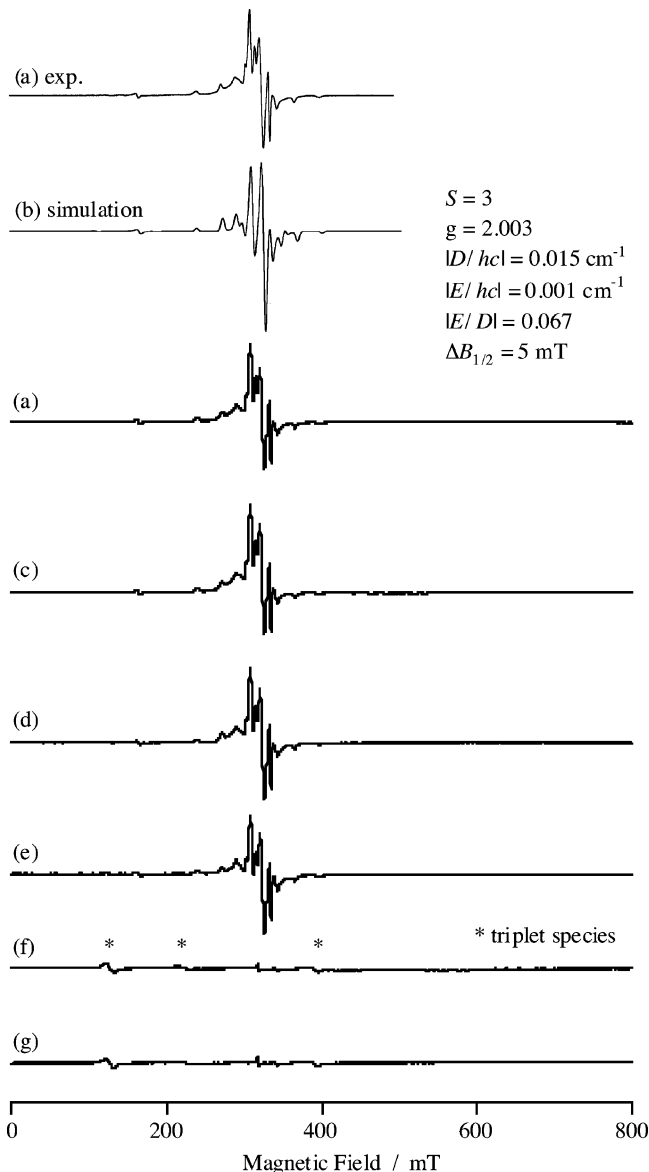


Figure 3. (a) ESR spectra obtained by irradiation of tris(diazo) compound **3-3N₂** in 2-methyltetrahydrofuran at 77 K. (b) Simulated spectra of ⁷³ with $S = 3$, $g = 2.003$, $D = 0.015 \text{ cm}^{-1}$, and $E = 0.001 \text{ cm}^{-1}$. (c–g) ESR spectra observed at 77 K in 2-methyltetrahydrofuran after warming the matrix containing ⁷³ to (c) 120, (d) 140, (e) 160, (f) 180 and, (g) 200 K.

spacing observed here, in comparison to that for the quintet biscarbene, is consistent with the tendency that as the spin multiplicity became higher, the D values became smaller. As shown by the simulation¹⁴ shown in Figure 3b, these peaks can be fitted to a septet tris(carbene) spectrum with parameters $S = 3$, $g = 2.003$, $D = 0.015 \text{ cm}^{-1}$, and $E = 0.001 \text{ cm}^{-1}$. Thus, we assign the signals to septet tri(carbene) **3**, ⁷3. The signals are also stable up to 140 K, but they decay irreversibly above 160 K.

It is interesting to note that high-spin species are likely formed as a main product at the initial stage of irradiation without the intervention of a lower-spin state. A similar observation has been reported in the photolysis of “simple” poly(diphenyldiazomethane) in a matrix at low temperature and is explained by assuming that the excess energy after removal of a nitrogen molecule in the photoexcited state can be transferred intramolecularly to other diazo groups in a matrix where the dissipation

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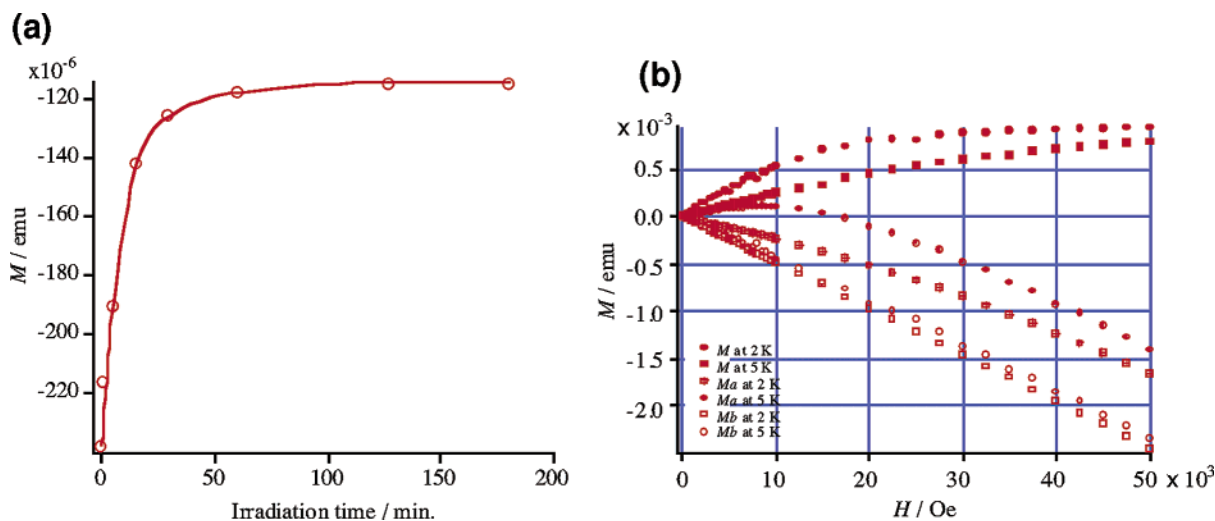


Figure 4. (a) Plot of magnetization (M in emu) as a function of irradiation time observed in the photolysis of bis(diazo) compound $2\text{-}2\text{N}_2$ in 0.10 mM 2-methyltetrahydrofuran matrix measured at 5.0 K and 5 kOe. (b) Field dependence of the magnetization of the photoproduct from bis(diazo) compound $2\text{-}2\text{N}_2$ in 0.10 mM 2-methyltetrahydrofuran matrix measured at 2.0 and 5.0 K. M_b and M_a refer to the magnetization value before and after irradiation, respectively, and $M = M_a - M_b$.

of excess energy is inefficient.^{15a} However, it is to be noted here that photodeazetation processes are sensitive to experimental conditions such as wavelength and intensities of the light and concentration of the precursor.^{15b–d} One needs more elaborated works to make the process clearer.

SQUID Measurements. To confirm whether the high-spin states observed for mono- to tricarbene are in the ground state or not, magnetic measurements were carried out.

The 2-MTHF solution of bis(diazo) compounds ($2\text{-}2\text{N}_2$) was placed inside the sample compartment of a superconducting quantum interference device (SQUID) magnet/susceptometer and was irradiated at 5–10 K with a light ($\lambda = 488$ nm) from an argon ion laser through an optical fiber. The development on magnetization (M/emu) at 5 K in a constant field of 5 kOe with the irradiation time for the bis(diazo) compound was measured in situ and is shown in Figure 4a. As the irradiation time increased, the M values gradually increased and reached a plateau after several hours. After the M values reached a plateau, the magnetization values after irradiation, M_a , were measured at 2.0 and 5.0 K in a field range of 0–50 kOe. The magnetization values of the sample before irradiation, M_b , were also measured under the same conditions. The magnetization (M) due to the species generated by photolysis was then obtained by subtracting the corresponding values obtained before and after irradiation (Figure 4b). Thus, the effect of any paramagnetic impurities could be canceled by this treatment. The plots of the magnetization normalized by the saturation magnetization (M/M_s) versus the temperature-normalized magnetic field (H/T) were analyzed in terms of the Brillouin function as follows:^{1c,5,16}

$$M = M_a - M_b = FN g J \mu_B B(\chi) \quad (1)$$

where F is the photolysis factor of diazo compound, N is the number of the molecule, J is the quantum number for the total

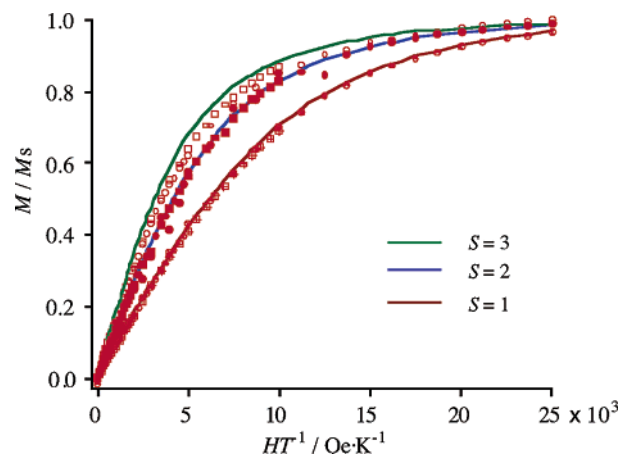


Figure 5. Plot of M/M_s versus H/T of the photoproduct from mono- (1-N_2 : \otimes , $+$), bis- ($2\text{-}2\text{N}_2$: \bullet , \blacksquare), and tris(diazo) compound ($3\text{-}3\text{N}_2$: \circ , \square) measured at 2.0 (\circ) and 5.0 (\square) K. The solid lines represent theoretical curves with $S = 1, 2,$ and 3 .

angular momentum, μ_B is the Bohr magneton, g is the Landé g -factor, and k_b is the Boltzmann constant. Because these carbene are constituted of light elements, the orbital angular momentum should be negligible, and J can be replaced with the spin quantum number S . The M/M_s versus H/T plots are shown in Figure 5 together with theoretical curves with $S = 1, 2,$ and 3 .¹⁷

The observed data for the bis(diazo) compound traced the theoretical curve with $S = 2$. The observed data were fitted with eq 1 with $S = 1.92$ and $F = 0.56$. The value is close to the theoretical value of 2, indicating that the two carbene centers interact ferromagnetically to produce a quintet ground state, as was expected. Because the magnetization data at two different temperatures were fitted to the same Brillouin function, the sample is considered to be free from ferro- or antiferromagnetic intermolecular interactions, and the quintet state is considered to be a ground state.

The data obtained for photoproducts from similar irradiation of tris- and mono(diazo) compounds were also analyzed in a

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(17) M_s values obtained from the best fitted curves were used.

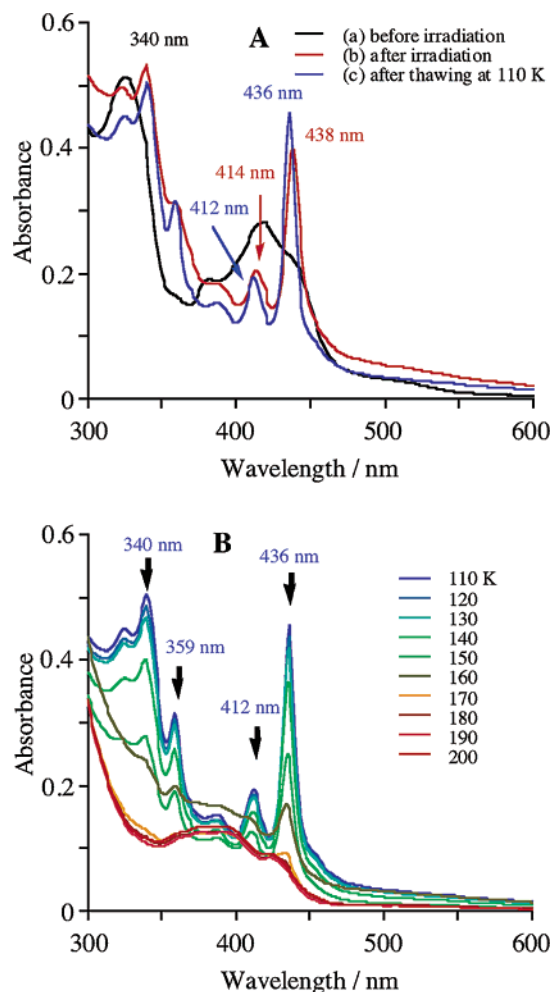


Figure 6. UV/vis spectra obtained by irradiation of monodiazo compound **1-N₂**. (A) (a) Spectra of **1-N₂** in 2-methyltetrahydrofuran at 77 K. (b) The same sample after irradiation ($\lambda > 350$ nm). (c) The same sample after thawing to 110 K. (B) UV/vis spectral change measured at 10 K increments upon thawing the same sample from 110 to 200 K.

similar manner to give $S = 2.56$ and 0.96 and $F = 0.55$ and 1.00 , respectively. Again the values are close to the theoretical values. Therefore, the result of the field dependence of M for photoproducts from **2-2N₂** and **3-3N₂** suggests that a persistent triplet diarylcarbene unit incorporated into a π -network in a ferromagnetic fashion indeed acts as a spin source to generate a high-spin ground state.

UV/Vis Spectroscopic Study in a Matrix at Low Temperature. To examine the stability of those high-spin species in solution at room temperature, it is necessary to know the UV/vis spectroscopic feature of the species, because time-resolved UV/vis spectroscopy is most conveniently employed for such a study.^{6,18}

Irradiation of **1-N₂** in a 2-MTHF matrix at 77 K resulted in rapid disappearance of the original absorption due to **1-N₂** and concurrent growth of sharp and strong absorption bands at 340,

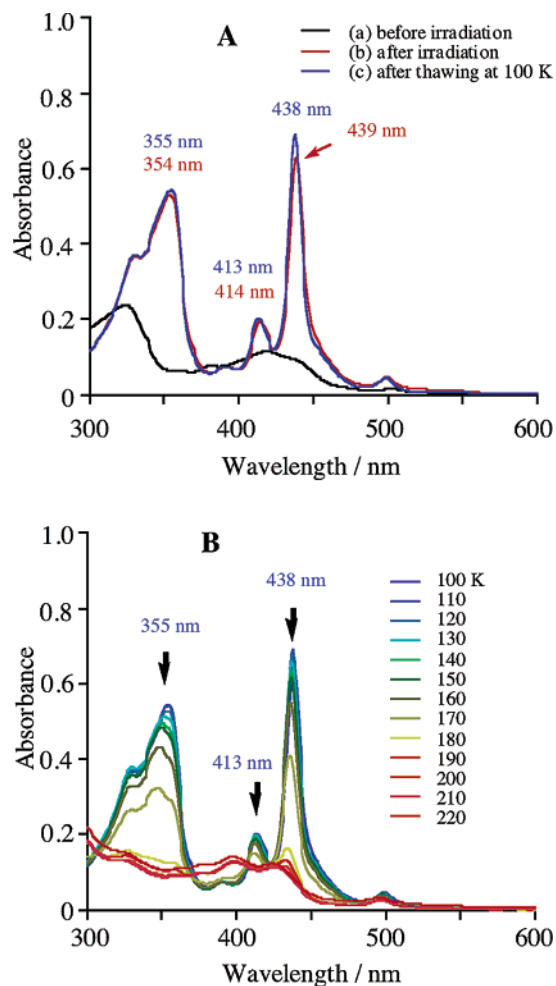


Figure 7. UV/vis spectra obtained by irradiation of bis(diazo) compound **2-2N₂**. (A) (a) Spectra of **2-2N₂** in 2-methyltetrahydrofuran at 77 K. (b) The same sample after irradiation ($\lambda > 350$ nm). (c) The same sample after thawing to 100 K. (B) UV/vis spectral change measured at 10 K increments upon thawing the same sample from 110 to 220 K.

358, 414, and 438 nm (Figure 6). Because ESR signals ascribable to triplet carbene are observed under identical conditions, the absorption spectrum can be safely assigned to triplet carbene **3¹**. When the matrix was gradually thawed, the bands become sharper, and the bands at longer wavelength, that is, 414 and 438 nm, shifted a bit to 412 and 436 nm, respectively, at around 100 K. This change can be attributed to the geometrical change of the triplet carbene associated with a change in viscosity of the matrixes upon annealing, as has been revealed in ESR experiments. Upon further thawing, the band started to disappear at around 130 K and completely vanished at around 170 K.

Similar irradiation of bis- (**2-2N₂**) and the tris(diazo) compounds (**3-3N₂**) in a 2-MTHF matrix at 77 K again resulted in rapid disappearance of the original absorption due to diazo compounds and concurrent growth of sharp and strong absorption bands at 354, 414, and 439 nm and 356, 413, and 442 nm, respectively, which are very similar to those of the triplet monocarbene **3¹** (Figures 7 and 8). Again, because ESR signals ascribable to **5²** and **7³** are observed under identical conditions, the absorption spectra can be assigned to quintet and septet states. The similarity of the spectra with those of the monocarbene also supports the assignments; diradical centers introduced

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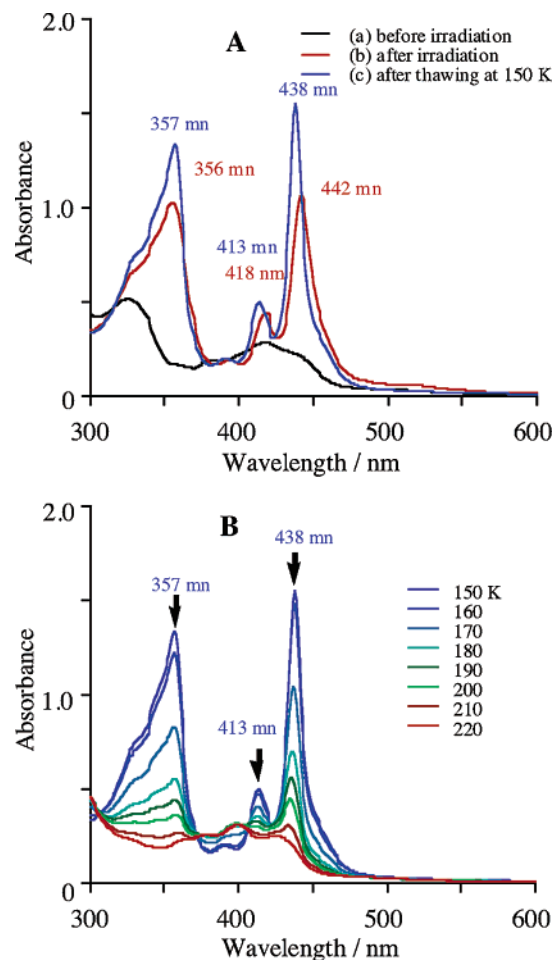


Figure 8. UV/vis spectra obtained by irradiation of tris(diazo) compound **3-3N₂**. (A) (a) Spectra of **3-3N₂** in 2-methyltetrahydrofuran at 77 K. (b) The same sample after irradiation ($\lambda > 350$ nm). (c) The same sample after thawing to 150 K. (B) UV/vis spectral change measured at 10 K increments upon thawing the same sample from 150 to 220 K.

in the conjugative manner usually show completely different spectra with strong absorption bands in the visible region as a result of extended conjugation of unpaired electrons in the π framework.¹⁹ Upon thawing the matrix, the bands become sharper, with a slight shift at around 100 K, and were observable up to 170 K. Thus, the thermal stability of bis- and tris(carbenes) is essentially identical to that of the monocarbene.

Time-Resolved UV/Vis Spectroscopic Study in Solution at Room Temperature. To determine the stability of the present carbenes more accurately, the lifetime was estimated in a degassed benzene at room temperature, in which we measured the lifetime of a series of sterically congested diarylcarbenes.⁶

Laser flash photolysis (LFP) of **1-N₂** (1×10^{-4} M) in a degassed benzene solution at room temperature with a 10 ns, 70–90 mJ, 308 nm pulse from a XeCl excimer laser produced a transient species showing a strong absorption at 340, 358, 414, and 438 nm, which appeared coincident with the pulse (Figure 9). The transient absorption bands are essentially the same as those observed in the photolysis of **1-N₂** in 2-MTHF at 77 K. Thus, we assigned the transient product to **3¹**. The

inset (a) in Figure 9 shows that the transient bands decay very slowly and that it takes 5 s before all of the bands completely disappear. The decay of **3¹** is found to be of the second order ($2k/\epsilon l = 0.65$ s⁻¹). The rough lifetime of **3¹** is estimated in the form of the half-life, $t_{1/2}$, to be 1.1 s. In accordance with the kinetic observation, the MS analysis of the spent solution indicates the presence of a peak at 1060.58 m/z , corresponding to the dimer of the carbene as a major peak.²⁰

A similar LFP of **2-2N₂** again generated transient absorption bands similar to those observed in the photolysis at 77 K (Figure 10). The fact that the molecular extinction coefficient of this species is roughly 2 times as large as that observed for **3¹** indicates that the transient bands are due to **5²** rather than to a monocarbene generated by incomplete decomposition of **2-2N₂**. This is further supported by the finding that analysis of the spent solution by IR spectroscopy indicated the absence of a characteristic band due to the diazo group. Again, the transient bands decayed very slowly in a second-order fashion ($2k/\epsilon l = 0.17$ s⁻¹), and the half-life, $t_{1/2}$, was estimated to be 2.3 s.²¹

LFP of **3-3N₂** generated transient bands similar to those obtained in the photolysis at 77 K and ascribable to **7³** based on observations similar to those in the photolysis of **2-2N₂** (Figure 11). The bands decayed in a second-order kinetic fashion ($2k/\epsilon l = 1.5$ s⁻¹) with a $t_{1/2}$ of 1.2 s.²²

Conclusion

The present investigation demonstrates that the preparation of usable high-spin organic materials employing a triplet carbene as a spin source is an achievable objective.

The finding that a precursor diazo unit can basically be handled as a building block to construct polydiazo compounds will make the project very realistic. Thus, one can introduce the building block very easily on properly designed π -topological linkers ad libitum. In other words, a polydiazo compound designed to generate a desired high-spin polycarbene can be prepared with great ease. A starburst nonadiazo compound, for instance, was prepared by trimerization of aryl ethynyl ketone, followed by oxidation, hydrazoneation of the resulting nano-ketone, and polyoxidation.⁵ The method is elegant, but it is not applicable to other more complicated systems, including sterically congested derivatives.

The study also reveals that persistent triplet carbenes, even though they greatly lose typical reactivity as a triplet carbene, still retain electronic properties and act as a spin source when aligned properly in the π -electron frameworks to generate a high-spin molecule, just as a prototypical triplet carbene does.

- (20) The main decay pathway of those sterically congested diarylcarbenes in benzene is coupling at the carbene center. However, as the carbene center is more crowded, coupling at the aromatic rings where unpaired electrons are delocalized becomes the more important process. See refs 6 and 10.
- (21) The TOF-MS analysis of the spent solution indicates the presence of peaks at 2109.16 m/z corresponding to the dimer of bis(carbene) **2** as a main peak, along with weak peaks at 3163.74, 4218.32, 5272.90, 6325.48, and 7382.06 m/z , corresponding to the trimer, tetramer, pentamer, hexamer, and heptamer of bis(carbene) **2**, respectively. The peak at 2109.16 m/z is well simulated by the dimer C₁₅₈H₁₅₆Si₂. The intensities of the peaks at higher oligomers decrease sharply with the increasing molecular weights (see Figure 2S).
- (22) The TOF-MS analysis of the spent solution indicates the presence of peaks at 2919.79 m/z corresponding to the dimer of tris(carbene) **3** as a main peak, along with weak peaks at 4385.25, 5619.18, 7254.25, and 8696.23 m/z , roughly corresponding to the trimer, tetramer, pentamer, and hexamer of tris(carbene) **3**, respectively. The intensities of the peaks at higher oligomers decrease sharply with the increasing molecular weights (see Figure 3S).

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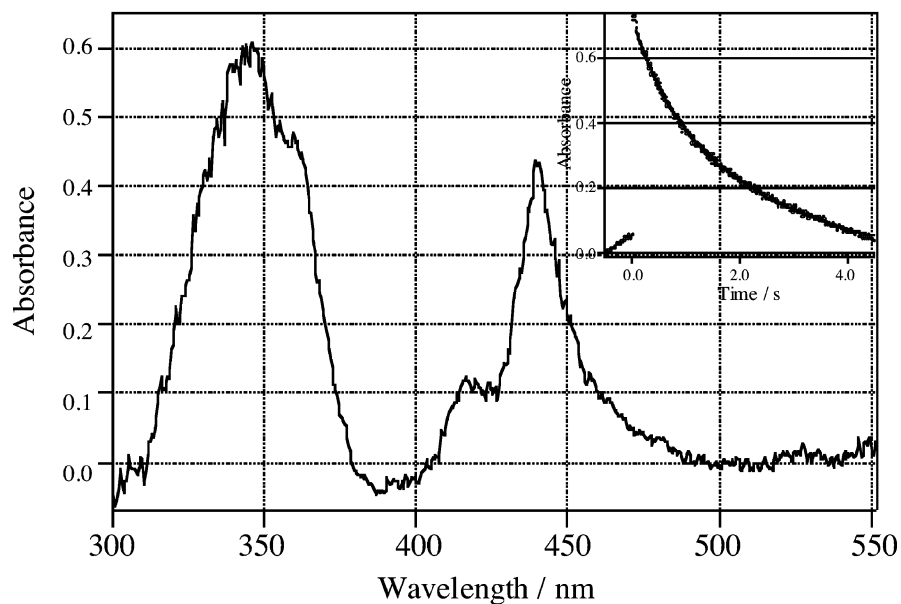


Figure 9. Absorption of transient products formed during irradiation of monodiazo compound **1-N₂** in degassed benzene at room temperature recorded 10 μ s after excitation. The inset shows the time course of the absorption at 450 nm (oscilloscope trace).

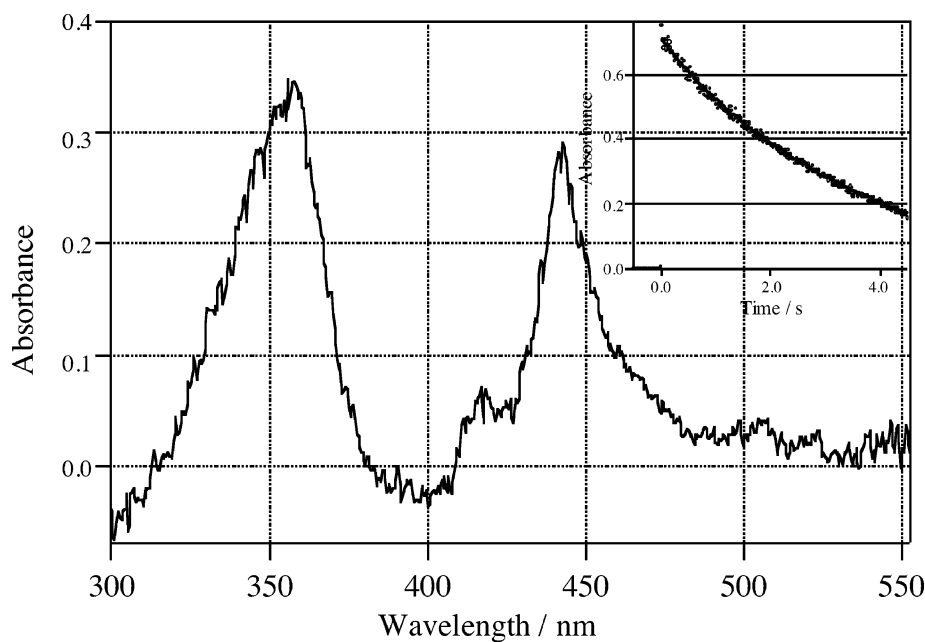


Figure 10. Absorption of transient products formed during irradiation of bis(diazo) compound **2-2N₂** in degassed benzene at room temperature recorded 10 μ s after excitation. The inset shows the time course of the absorption at 450 nm (oscilloscope trace).

Most importantly, polycarbenes consisting of a persistent triplet carbene are also very persistent, surviving up to 160 K and a few seconds in solution at room temperature.²³ Moreover, undesirable bimolecular side reactions, which generate chemical defects among the topologically controlled high-spin ($S = 1$) centers for extended spin alignment, are rigorously avoided.

Although high-spin organic materials with a lifetime of the second order are still ephemeral for practical use, in the light

of the fact that a more persistent triplet carbene surviving days under ambient conditions is close to being realized, it will not be long before a stable high-spin polycarbene is available.²⁴

Experimental Section

General Methods. ¹H and ¹³C NMR spectra were recorded on a JEOL JNM-AL300FT/NMR spectrometer in CDCl₃ with Me₄Si as an internal reference. IR spectra were measured on a JASCO-Herschel FT/IR-410 spectrometer, and UV-vis spectra were recorded on a JASCO CT-560 spectrophotometer. The mass spectra were recorded

(23) All three species shown here decayed by a second-order fashion. In these cases, the lifetime could not be determined and hence half-life, $t_{1/2}$, was used as a rough measure of the stability under these conditions. The half-life is very much dependent upon the conditions, such as the concentration of the species, and cannot be regarded as a definitive value to discuss the stability in a quantitative manner. So the half-life reported here simply indicated that the stability of three species may be roughly equal.

(24) It may be difficult to prepare a high-spin polycarbene consisting of the present carbene unit because it has a fairly small D value mostly because of the anthryl group. However, we have prepared an equally stable diazo compound which not only survives a similar coupling reaction but also can generate a triplet carbene with a larger D value.

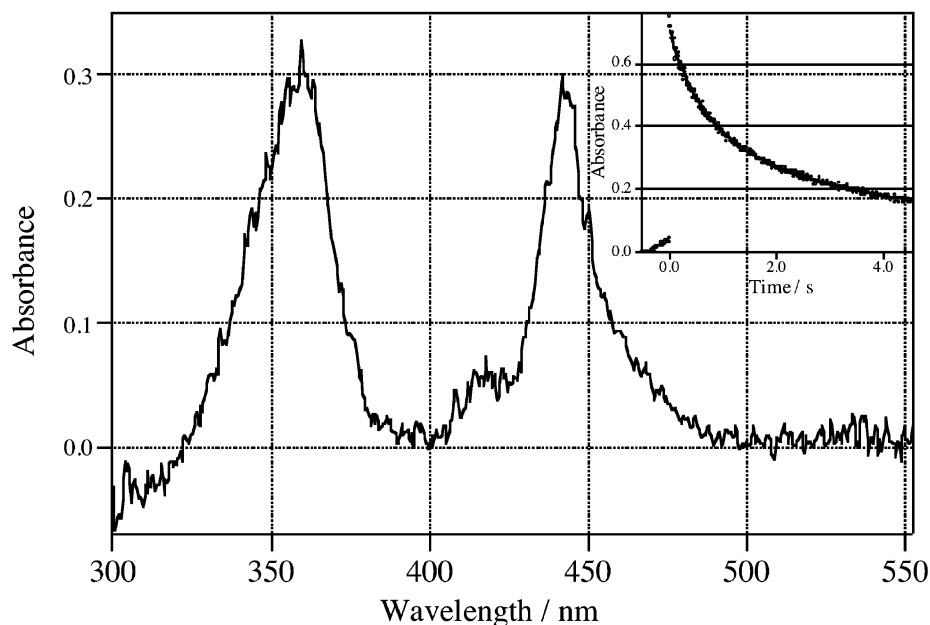


Figure 11. Absorption of transient products formed during irradiation of tris(diazo) compound **3-3N₂** in degassed benzene at room temperature recorded 10 μ s after excitation. The inset shows the time course of the absorption at 450 nm (oscillogram trace).

on a JEOL JMS-600H mass spectrometer. Gel permeation chromatography (GPC) was carried out on a JASCO, model HLC-01 instrument using UV-1570 as a detector. The GPC column was a Shodex H-2001. Thin-layer chromatography was carried out on a Merck Kieselgel 60 PF₂₅₄. Column chromatography was performed on silica gel (Fuji Davidson) for column chromatography or ICN for dry column chromatography.

Unless otherwise noted, all of the reagents employed in this study are commercial products and used after standard purification. Tetrahydrofuran, ethyl ether, toluene, and dioxane were purified by distillation from sodium/benzophenone, and dichloromethane, carbon tetrachloride, and triethylamine were from calcium hydride.

Materials. 9-(4-*tert*-Butyl-2,6-dimethyl)phenylanthracene. To a stirred solution of 4-*tert*-butyl-2,6-dimethylbromobenzene²⁵ (5.0 g, 20.7 mmol) in dry ether (40 mL) was added dropwise a 1.50 M *n*-pentane solution of *tert*-butyllithium (30.4 mL, 45.6 mmol) at -78 °C under argon atmosphere. After being stirred for 1 h, the mixture was allowed to warm to room temperature. A solution of anthrone²⁶ (4.0 g, 20.7 mmol) in dry toluene (80 mL) was added dropwise to the mixture, and the mixture was refluxed overnight. After being cooled to room temperature and addition of saturated aqueous ammonium chloride (40 mL), the mixture was extracted with ether, and the organic layer was washed with water, dried over anhydrous sodium sulfate, and concentrated under reduced pressure to leave a crude product which was purified by column chromatography (silica gel, hexane), followed by a short-path distillation (0.1 mmHg, 68 °C) to give 9-(4'-*tert*-butyl-2',6'-dimethyl)phenylanthracene (3.1 g, 44%) as a pale yellow solid: mp 167 °C; ¹H NMR (300 MHz, CDCl₃, ppm) δ 8.47–7.29 (m, 9H, Anth-H), 7.24 (s, 2H, Ph-H), 1.73 (s, 6H, -Me), 1.44 (s, 9H, -^tBu); ¹³C NMR (75.5 MHz, CDCl₃, ppm) δ 150.3, 137.0, 136.0, 134.4, 131.6, 129.8, 128.6, 126.1, 126.0, 125.5, 125.1, 124.4, 34.5, 31.6, 20.4; EI MS (*m/z*) 338.1 (base, M⁺), 323.2 (41.3, M⁺ - Me). HRMS calcd for C₂₆H₂₆ 338.2035, found *m/z* 338.2034.

9-(4-*tert*-Butyl-2,6-dimethyl)phenyl-10-bromoanthracene. To a stirred solution of the phenylanthracene (3.1 g, 9.0 mmol) in carbon tetrachloride (40 mL) was added bromine (0.5 mL, 9.0 mmol) at 0 °C. The solution was stirred at room temperature overnight. The reaction

mixture was washed with 20% aqueous potassium hydroxide, saturated aqueous sodium thiosulfate, and water, and the organic layer was dried over anhydrous sodium sulfate and concentrated under reduced pressure to leave a residue which was reprecipitated with hexane to give 9-(4'-*tert*-butyl-2',6'-dimethyl)phenyl-10-bromoanthracene (3.3 g, 89%) as a yellow solid: mp 180–181 °C; ¹H NMR (300 MHz, CDCl₃, ppm) δ 8.60–7.35 (m, 8H, Anth-H), 7.24 (s, 2H, Ph-H), 1.72 (s, 6H, -Me), 1.44 (s, 9H, -^tBu); ¹³C NMR (75.5 MHz, CDCl₃, ppm) δ 150.7, 136.8, 134.0, 130.6, 130.5, 128.0, 127.0, 126.5, 125.8, 124.5, 122.1, 124.4, 34.5, 31.5, 20.4; EI MS (*m/z*) 417.6 (base, M + 2), 415.6 (98.0, M⁺), 400.7 (32.3, M⁺ - Me). HRMS calcd for C₂₆H₂₅ 416.1139, found *m/z* 416.1125.

[9-{10-(4-*tert*-Butyl-2,6-dimethyl)phenyl}anthryl](4-bromo-2,6-dimethylphenyl)methanol. To a stirred solution of the bromoanthracene (2.0 g, 4.8 mmol) in dry ether (40 mL) was added dropwise a 2.66 M hexane solution of *n*-butyllithium (2.2 mL, 5.8 mmol) at 0 °C under argon atmosphere. After the mixture was stirred for 3 h, a solution of 4-bromo-2,6-dimethylbenzaldehyde²⁷ (1.0 g, 4.8 mmol) in dry tetrahydrofuran (13 mL) was added dropwise to the mixture, and the mixture was stirred at room temperature overnight. After addition of saturated aqueous ammonium chloride (30 mL), the mixture was extracted with ether, and the organic layer was washed with water, dried over anhydrous sodium sulfate, and concentrated under reduced pressure to leave a crude product which was purified by column chromatography (silica gel, hexane:dichloromethane = 2:1) to give [9-{10-(4'-*tert*-butyl-2',6'-dimethyl)phenyl}anthryl](4-bromo-2,6-dimethylphenyl)methanol (2.0 g, 74%) as a yellow solid: mp 99.5–100.0 °C; ¹H NMR (300 MHz, CDCl₃, ppm) δ 8.49–7.25 (m, 8H, Anth-H), 7.48 (s, 1H, HO-C-H), 7.24 (s, 2H, Anth-Ph-H), 7.18 (s, 2H, Ph-H), 2.41 (d, *J* = 4.04 Hz, 1H, -OH), 2.18 (s, 6H, Ph-Me), 1.72 (s, 6H, Anth-Ph-Me), 1.44 (s, 9H, -^tBu); ¹³C NMR (75.5 MHz, CDCl₃, ppm) δ 150.5, 139.3, 139.1, 138.1, 136.7, 134.7, 132.9, 132.7, 129.81, 129.76, 127.1, 125.9, 125.0, 124.7, 124.5, 120.8, 73.1, 34.5, 31.5, 21.8, 20.2.

[9-{10-(4-*tert*-Butyl-2,6-dimethyl)phenyl}anthryl](4-bromo-2,6-dimethylphenyl)chloromethane. Gaseous hydrochloric acid prepared by adding hydrochloric acid (10 mL) to concentrated sulfuric acid (15 mL) was bubbled into a stirred solution of the methanol (1.5 g, 2.7

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mmol) in dry benzene (20 mL) for 1 h at 5 °C, and the reaction was monitored by ¹H NMR. The reaction mixture was concentrated and dried under reduced pressure to give [9-{10-(4'-*tert*-butyl-2',6'-dimethylphenyl)anthryl}(4-bromo-2,6-dimethylphenyl)chloromethane (1.5 g, 97%) as a yellow solid: ¹H NMR (300 MHz, CDCl₃, ppm) δ 8.49–7.26 (m, 8H, Anth–H), 7.78 (s, 1H, Cl–C–H), 7.24 (s, 2H, Anth–Ph–H), 7.21 (s, 2H, Ph–H), 2.31 (s, 6H, Ph–Me), 1.72 (s, 6H, Anth–Ph–Me), 1.44 (s, 9H, –*t*Bu); ¹³C NMR (75.5 MHz, CDCl₃, ppm) δ 150.6, 139.7, 139.2, 137.1, 136.7, 134.5, 133.0, 129.9, 129.7, 128.3, 127.3, 126.1, 125.0, 124.8, 124.5, 121.6, 59.4, 34.5, 31.5, 22.4, 20.3.

Ethyl *N*-[9-{10-(4-*tert*-butyl-2,6-dimethylphenyl)anthryl}(4-bromo-2,6-dimethylphenyl)carbamate. A mixture of ethyl carbamate (4.6 g, 51.6 mmol) and silver tetrafluoroborate (0.6 g, 2.8 mmol) was heated to 60 °C. A solution of the chloromethane (1.5 g, 2.6 mmol) in dry dioxane (13 mL) was added dropwise to this mixture at the same temperature. After being refluxed overnight, the reaction mixture was filtered and the filtrate was extracted with chloroform, and the organic layer was washed with water, dried over anhydrous sodium sulfate, and concentrated under reduced pressure to leave a crude product which was column chromatographed (silica gel, hexane:dichloromethane = 1:1) to give ethyl *N*-[9-{10-(4'-*tert*-butyl-2',6'-dimethylphenyl)anthryl}(4-bromo-2,6-dimethylphenyl)carbamate (1.2 g, 75%) as a pale brown solid: mp 136.6–137.2 °C; ¹H NMR (300 MHz, CDCl₃, ppm) δ 8.31–7.27 (m, 8H, Anth–H), 7.54 (d, *J* = 9.00 Hz, 1H, N–C–H), 7.24 (s, 2H, Anth–Ph–H), 7.13 (s, 2H, Ph–H), 5.47 (d, *J* = 8.64 Hz, 1H, –NH), 4.22 (q, *J* = 7.17 Hz, 2H, –CH₂–), 2.17 (s, 6H, Ph–Me), 1.70 (s, 6H, Anth–Ph–Me), 1.43 (s, 9H, –*t*Bu), 1.26 (d, *J* = 7.17 Hz, 3H, –CH₂–Me); ¹³C NMR (75.5 MHz, CDCl₃, ppm) δ 155.4, 150.5, 138.7, 138.3, 138.2, 136.7, 134.5, 133.1, 129.8, 129.7, 127.3, 126.4, 125.0, 124.5, 123.7, 120.1, 61.4, 53.8, 34.5, 31.5, 22.5, 20.3, 14.7.

Ethyl *N*-Nitroso-*N*-[9-{10-(4-*tert*-butyl-2,6-dimethylphenyl)anthryl}(4-bromo-2,6-dimethylphenyl)methyl]carbamate. Nitrogen dioxide (5.0 g) was bubbled into dry carbon tetrachloride (20 mL) at –20 °C under stirring. Sodium acetic acid (9.0 g, 109.7 mmol) and a solution of the carbamate (1.2 g, 1.9 mmol) in dry carbon tetrachloride (15 mL) were added to the mixture. The mixture was allowed to warm to room temperature for 2 h and was poured into ice. This mixture was extracted with chloroform, and the organic layer was washed with water, dried over anhydrous sodium sulfate, concentrated, and dried under reduced pressure to give ethyl *N*-nitroso-*N*-[9-{10-(4'-*tert*-butyl-2',6'-dimethylphenyl)anthryl}(4-bromo-2,6-dimethylphenyl)methyl]carbamate (1.4 g, quant.) as a yellow solid: ¹H NMR (300 MHz, CDCl₃, ppm) δ 7.89 (s, 1H, N–C–H), 7.63–7.22 (m, 8H, Anth–H), 7.24 (s, 2H, Anth–Ph–H), 7.16 (s, 2H, Ph–H), 4.11 (q, *J* = 7.17 Hz, 2H, –CH₂–), 1.96 (s, 6H, Ph–Me), 1.70 (s, 6H, Anth–Ph–Me), 1.44 (s, 9H, –*t*Bu), 0.81 (d, *J* = 7.17 Hz, 3H, –CH₂–Me); ¹³C NMR (75.5 MHz, CDCl₃, ppm) δ 153.6, 150.6, 139.1, 138.3, 136.6, 134.9, 134.5, 133.0, 130.7, 129.6, 127.3, 126.55, 126.45, 125.0, 124.5, 123.5, 121.0, 64.3, 56.4, 34.5, 31.5, 20.9, 20.2, 13.4.

[9-{10-(4-*tert*-butyl-2,6-dimethylphenyl)anthryl}(4-bromo-2,6-dimethylphenyl)diazomethane (4). To a stirred solution of the nitroso-carbamate (1.4 g, 2.2 mmol) in dry tetrahydrofuran (15 mL) was added potassium *tert*-butoxide (0.5 mg, 4.7 mmol) at –20 °C under argon atmosphere. After being stirred overnight, the reaction mixture was poured into ice, extracted with ether, and the ethereal layer was washed with water, dried over anhydrous sodium sulfate, concentrated, and dried under reduced pressure to leave a crude product which was purified by column chromatography (alumina, hexane at –20 °C), followed by GPC (chloroform, monitored at 350 nm) to give **4** (0.6 g, 48%) as an orange solid: ¹H NMR (300 MHz, CDCl₃, ppm) δ 8.00–7.25 (m, 8H, Anth–H), 7.28 (s, 2H, Ph–H), 7.25 (s, 2H, Anth–Ph–H), 2.14 (s, 6H, Ph–Me), 1.73 (s, 6H, Anth–Ph–Me), 1.44 (s, 9H, –*t*Bu); ¹³C NMR (75.5 MHz, CDCl₃, ppm) δ 150.6, 138.9, 138.1, 136.8, 134.3, 132.0, 130.2, 130.1, 129.9, 127.2, 126.4, 125.4, 125.1, 124.5, 122.7, 120.8, 57.1, 34.5, 31.5, 21.1, 20.3; IR (KBr, cm^{–1}) ν_{C=N₂} 2041.

[9-{10-(4-*tert*-butyl-2,6-dimethylphenyl)anthryl}(4-phenyl-2,6-dimethylphenyl)diazomethane (1-N₂). A mixture of the diazomethane **4** (50.0 mg, 0.09 mmol), palladium acetate (1.1 mg, 5.0 × 10^{–3} mmol), potassium fluoride (19 mg, 0.33 mmol), 2-(di-*tert*-butylphosphino)biphenyl (4.5 mg, 1.5 × 10^{–2} mmol), benzene boronic acid (18.3 mg, 0.15 mmol), and dry tetrahydrofuran (0.5 mL) was stirred overnight at 40 °C under nitrogen atmosphere. The reaction mixture was passed through a short alumina column, and the filtrate was concentrated and dried under reduced pressure to leave a crude product which was purified by GPC (chloroform, monitored at 350 nm) to afford **1-N₂** (44 mg, 88%) as an orange solid: mp 135.0–140.5 °C (dec); ¹H NMR (300 MHz, CDCl₃, ppm) δ 8.10 (d, *J* = 8.82 Hz, 2H), 7.62 (d, *J* = 7.35 Hz, 2H), 7.54–7.30 (m, 13H), 2.24 (s, 6H, H), 1.75 (s, 6H); ¹³C NMR (75.5 MHz, CDCl₃, ppm) δ 150.5, 140.6, 139.9, 137.9, 137.3, 136.9, 134.4, 130.3, 130.1, 129.8, 128.7, 128.1, 127.2, 127.2, 126.9, 126.3, 125.40, 125.36, 124.5, 123.5, 57.5, 34.5, 31.6, 21.5, 20.3; IR (KBr, cm^{–1}) ν_{C=N₂} 2039.

3,5-Bis{3,5-dimethyl-4-(diazo[9-{10-(4-*tert*-butyl-2,6-dimethylphenyl)anthryl]methyl)phenyl}benzene (2-2N₂). A mixture of the diazomethane **4** (28 mg, 0.05 mmol), palladium acetate (0.6 mg, 3 × 10^{–3} mmol), potassium fluoride (9.5 mg, 0.15 mmol), 2-(di-*tert*-butylphosphino)biphenyl (2.3 mg, 8 × 10^{–3} mmol), 5-trimethylsilylbenzene-1,3-diboronic acid (5.9 mg, 0.025 mmol), and dry tetrahydrofuran (0.3 mL) was stirred overnight at 40 °C under nitrogen atmosphere. The reaction mixture was passed through a short alumina column, and the filtrate was concentrated and dried under reduced pressure to leave a crude product which was purified by GPC (chloroform, monitored at 350 nm) to afford bis(diazo) compound **2-2N₂** (14 mg, 51%) as an orange solid: mp 150–155.0 °C (dec); ¹H NMR (300 MHz, CDCl₃, ppm) δ 8.11 (d, *J* = 8.64 Hz, 4H), 7.80 (s, 1H), 7.71 (s, 2H), 7.60–7.20 (m, 26H), 2.26 (s, 12H), 1.75 (s, 12H), 1.44 (s, 18H), 0.36 (s, 9H); ¹³C NMR (75.5 MHz, CDCl₃, ppm) δ 151.5, 142.6, 141.4, 141.2, 138.9, 138.4, 137.8, 135.4, 131.8, 131.3, 131.1, 130.8, 129.2, 129.1, 128.1, 127.5, 127.2, 126.3, 125.4, 124.4, 58.4, 35.4, 32.5, 22.4, 21.3, 1.0; IR (KBr, cm^{–1}) ν_{C=N₂} 2039.

1,3,5-Tris{3,5-dimethyl-4-(diazo[9-{10-(4-*tert*-butyl-2,6-dimethylphenyl)anthryl]methyl)phenyl}benzene (3-3N₂). A mixture of the diazomethane **4** (56 mg, 0.1 mmol), palladium acetate (0.1 mg, 5 × 10^{–4} mmol), potassium phosphate (42 mg, 0.2 mmol), tetra(*n*-butyl)ammonium bromide (cat.) and benzene triboronic acid²⁸ (6.3 mg, 0.03 mmol), and dry DMF (0.5 mL) was stirred overnight at 40 °C under nitrogen atmosphere. The reaction mixture was passed through a short alumina column, and the filtrate was concentrated and dried under reduced pressure to leave a crude product which was purified by GPC (chloroform, monitored at 350 nm) to afford tris(diazo) compound **3-3N₂** (10.4 mg, 20%) as an orange solid: mp 291–297 °C (dec); ¹H NMR (300 MHz, CDCl₃, ppm) δ 8.11 (d, *J* = 8.82 Hz, 6H), 7.82 (s, 3H), 7.54–7.30 (m, 30H), 2.27 (s, 18H), 1.75 (s, 18H), 1.44 (s, 27H); ¹³C NMR (75.5 MHz, CDCl₃, ppm) δ 150.5, 141.7, 139.8, 137.9, 137.5, 136.8, 134.4, 130.3, 130.14, 130.10, 128.2, 127.2, 126.3, 125.4, 125.3, 124.7, 124.5, 123.5, 57.5, 34.5, 31.6, 21.5, 20.3; IR (KBr, cm^{–1}) ν_{C=N₂} 2039.

5-Trimethylsilylbenzene-1,3-diboronic Acid Dipinacol Ester. A mixture of 5-trimethylsilyl-1,3-dibromobenzene²⁹ (1.0 g, 3.3 mmol), diborane pinacol ester (1.8 g, 7.2 mmol), PdCl₂(dppf) (150 mg, 0.2 mmol), KOAc (220 mg, 19.5 mmol), and DMSO (20 mL) was heated to 80 °C for 4 h. After the mixture was cooled, water (50 mL) was added, and the mixture was extracted with CH₂Cl₂. The organic layer was washed with brine, dried over Na₂SO₄, and the solvent was evaporated. The residue was passed through a short alumina column and then purified by GPC (CHCl₃, monitored at 250 nm) to give 5-trimethylsilylbenzene-1,3-diboronic acid dipinacol ester as a light brown solid (990 mg, 76%): mp 125–128 °C; ¹H NMR (300 MHz,

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CDCl_3 , ppm) δ 8.26 (s, 1H), 8.04 (s, 2H), 1.34 (s, 24H), 0.29 (s, 9H); ^{13}C NMR (75.5 MHz, CDCl_3 , ppm) δ 143.5, 142.9, 141.3, 139.4, 84.6, 26.0, 1.0; EI MS (m/z) 402 (4.4%, M^+), 387 (61%, $\text{M}^+ - \text{Me}$), 84 (100%).

5-Trimethylsilylbenzene-1,3-diboronic Acid. To a solution of the ester (201 mg, 0.5 mmol) in acetone (30 mL) were added NaIO_4 (641 mg, 3.0 mmol), NH_4OAc (231 mg, 3.0 mmol), and water (15 mL), and the mixture was stirred for 48 h. Acetone was evaporated, and the mixture was extracted with ether, the ethereal solution was dried over Na_2SO_4 , and the solvent was evaporated and dried in vacuo to give 5-trimethylsilylbenzene-1,3-diboronic acid as a light brown solid (95 mg, 80%): mp 164–168 °C.

EPR Measurements. The diazo compound was dissolved in 2-methyltetrahydrofuran (10^{-3} M), and the solution was degassed in a quartz cell by three freeze–degas–thaw cycles. The sample was cooled in an optical transmission EPR cavity at 77 K and irradiated with a Wacom 500 W Hg lamp using a cutoff filter ($\lambda > 350$ nm). EPR spectra were measured on a JEOL JES TE 200 spectrometer (X-band microwave unit, 100 kHz field modulation). The signal positions were read by the use of a gaussmeter. The temperature was controlled by a 9650 Microprocessor-based Digital Temperature Indicator/Controller, which provided the measurements with an accuracy within ± 0.1 K and a control ability within ± 0.2 K. Errors in the measurements of component amplitudes did not exceed 5%, and the accuracy of the resonance fields determination was within ± 0.5 mT.

Low-Temperature UV/Vis Spectra. Low-temperature spectra at 77 K were obtained by using an Oxford variable-temperature liquid-nitrogen cryostat (DN 1704) equipped with a quartz outer window and a sapphire inner window. The sample was dissolved in dry 2-MTHF, placed in a long-necked quartz cuvette of 1 mm path length, and degassed thoroughly by repeated freeze–degas–thaw cycles at a pressure near 10^{-5} Torr. The cuvette was flame-sealed, under reduced pressure, placed in the cryostat, and cooled to 77 K. The sample was irradiated for several minutes in the spectrometer with a Halos 300 W high-pressure mercury lamp using a cutoff filter ($\lambda > 350$ nm), and the spectral changes were recorded at the appropriate time intervals. The spectral changes upon thawing were also monitored by carefully controlling the matrix temperature with an Oxford Instrument Intelligent Temperature Controller (ITC 4).

Flash Photolysis. All flash measurements were made on a Unisoku TSP-601 flash spectrometer. Three excitation light sources were used depending on the precursor absorption bands and lifetime of the transient species. They were (i) a cylindrical 150-W Xe flash lamp (100 J/flash with 10 ms pulse duration), (ii) a Quanta-Ray GCR-11 Nd:YAG laser (355 nm pulses of up to 40 mJ/pulse and 5–6 ns duration; 266 nm pulses of up to 30 mJ/pulse and 4–5-ns duration), and (iii) a Lamda Physik LEXTRA XeCl excimer laser (308 nm pulses of up to 200 mJ/pulse and 17 ns duration). The beam shape and size were controlled by a focal length cylindrical lens.

A Hamamatsu 150 W xenon short arc lamp (L 2195) was used as the probe source, and the monitoring beam, guided using an optical

fiber scope, was arranged in an orientation perpendicular to the excitation source. The probe beam was monitored with a Hamamatsu R2949 photomultiplier tube through a Hamamatsu S3701-512Q MOS linear image sensor (512 photodiodes used). Timing of the excitation pulse, the probe beam, and the detection system was achieved through an Iwatsu model DS-8631 digital synchro scope which was interfaced to a NEC 9801 RX2 computer. This allowed for rapid processing and storage of the data and provided printed graphic capabilities. Each trace was also displayed on a NEC CRT N5913U monitor.

A sample was placed in a long-necked Pyrex tube which had a sidearm connected to a quartz fluorescence cuvette and was degassed using a minimum of four freeze–degas–thaw cycles at a pressure near 10^{-5} Torr immediately prior to being flashed. The sample system was flame-sealed under reduced pressure, and the solution was transferred to the quartz cuvette which was placed in the sample chamber of the flash spectrometer. A cell holder block of the sample chamber was equipped with a thermostat and allowed to come to thermal equilibrium. The concentration of the sample was adjusted so that it absorbed a significant portion of the excitation light.

SQUID Measurements. Magnetic susceptibility data were obtained on a Quantum Design MPMS-2A superconducting quantum interference device (SQUID) magnetometer/susceptometer. Irradiation with light from an argon ion laser (488 nm, Omnichrome 543-150BS) through a flexible optical fiber which passes through the inside of the SQUID sample holder was performed inside the sample room of the SQUID apparatus at 5–11 K. One end of the optical fiber was located 40 mm above the sample cell (capsule), and the other was attached to a coupler for the laser. The bottom part of the capsule (6 mm \times 10 mm) without a cap was used as a sample cell. A 80 μL sample of the solution (1.0 mM) in 2-MTHF was placed in the cell, which was held by a straw. The irradiation was carried out until there was no further change of magnetization monitored at 5 K in a constant field of 5 kOe. The magnetization, M_b and M_a , before and after irradiation was measured at 2 and 5 K in a field range 0–50 kOe. The plots of the magnetization [$M = (M_a - M_b)$; F stands for a photolysis factor of diazo compound] versus the magnetic field were analyzed in terms of the Brillouin function.

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Supporting Information Available: MS spectra (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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