

# A Dendrimer Approach to High-Spin Polycarbenes. Conversion of Connectivity from Disjoint to Non-Disjoint by Perturbation of Nonbonding Molecular Orbital Coefficients

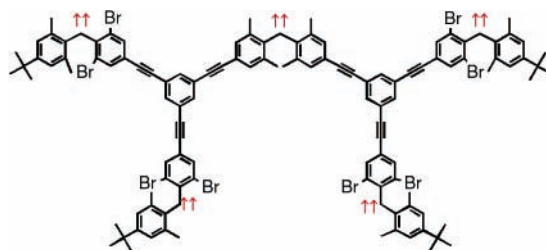
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## ABSTRACT



Pentakis(diazo) compound was prepared by coupling 3,5-bis[4-[diazo(4-*tert*-butyl-2,6-dimethylphenyl)methyl]-3,5-dibromophenylethynyl]-phenylacetylene with bis(4-iodo-2,6-dimethylphenyl)diazomethane under Sonogashira reaction conditions. Pentakis(carbene) generated by irradiation of the pentakis(diazo) compound was shown to have a high-spin state with  $S = 4.4$  at 2.0 K.

Triplet carbenes are regarded as more effective spin sources than radicals since the spin states ( $S = 1$ ) are double that of radicals ( $S = 1/2$ ) and the magnitude of the exchange coupling between the neighboring centers is larger in triplet carbenes than in radicals.<sup>1,2</sup> Moreover, the photolytic production of polycarbenes is possible even in solid solution at cryogenic temperatures if poly(diazo) precursors are avail-

able. Actually, Iwamura and co-workers have prepared a starburst-type nonakis(diazo) compound, which gives a nonakis(carbene) with a nonadecet ground state ( $S = 9$ ) upon irradiation at low temperature.<sup>2</sup>

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 stability for practical application under ambient conditions.

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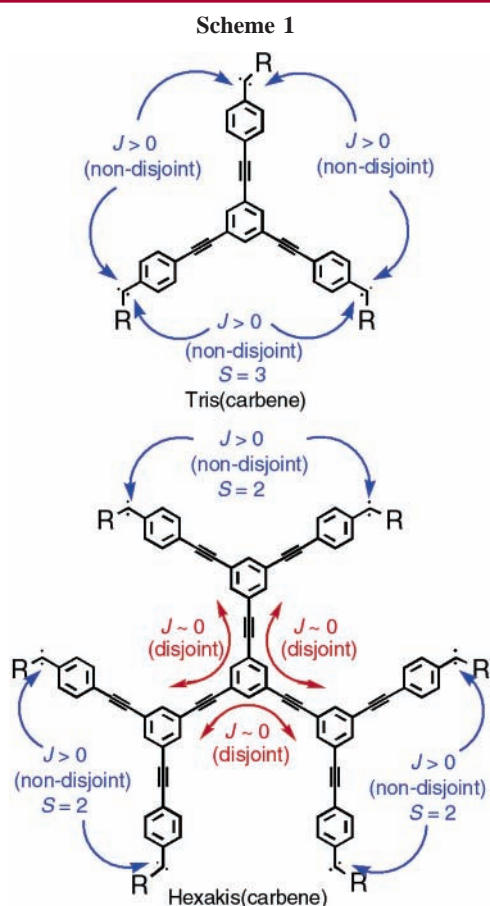
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Second, diazo groups are also generally labile,<sup>3</sup> and, hence, the diazo compound cannot be used as a building block to prepare a more complicated poly(diazo) compound.

We have made great efforts to stabilize a triplet carbene and succeeded in preparing fairly stable ones surviving for days in solution at room temperature.<sup>4,5</sup> We also found that a diphenyldiazomethane prepared to generate a persistent triplet carbene is also persistent for the diphenyldiazo compound and, hence, can be further modified, with the diazo group intact, into a more complicated diazo compound.<sup>6–9</sup>

For instance, (2,4,6-tribromophenyl)(2,6-dibromo-4-*tert*-butylphenyl)diazomethane is stable enough to survive under mild Sonogashira coupling reaction conditions and undergoes a coupling reaction with trimethylsilylacetylene to give (2,6-dibromo-4-trimethylsilylethynylphenyl)(2,6-dibromo-4-*tert*-butylphenyl)diazomethane. Three units of the diazo compound are introduced at the 1-, 3-, and 5-positions of a benzene ring through the ethynyl group by employing a similar coupling reaction to give a tris(diazo) compound, which eventually generates fairly persistent tris(carbene) with a septet ground state upon irradiation (Scheme 1).<sup>6</sup>



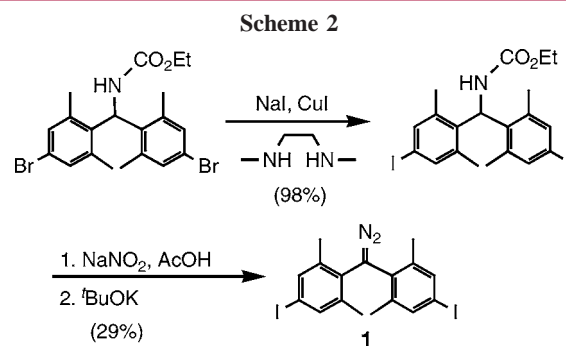
By extending this method, we were able to prepare phenylacetylene dendritic hexakis(diazo) compound having

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peripheral 6 diazo units, which was expected to generate hexakis(carbene) with an  $S = 6$  ground state.<sup>9</sup> However, carbenes generated from the hexakis(diazo) compound were found to have a low spin state of less than 2. The results can be reasonably interpreted in terms of the disjoint–nondisjoint concept based on the MO theory.<sup>10,11</sup> The hexakis(carbene) consists of a dendritic structure, which has three bis(carbene) units on the terminal of each branches. The connectivity of two carbene units within this bis(carbene) unit is nondisjoint, and hence, they interact in a ferromagnetic fashion with the spin quantum number  $S = 2$ . However, the connectivity between three bis(carbene) units through the central benzene ring is disjoint. Thus, there are no magnetic interactions between three bis(carbene) units through the core part in the hexakis(carbene) (Scheme 1).

However, the connectivity can be improved from disjoint to nondisjoint by introducing a new spin system so as to disturb NBMO coefficients in the original spin systems. In the hexakis system, for instance, this will be achieved by incorporating a new carbene unit between the bis(carbene) units and core benzene. To prove this idea, we prepared a model pentakis(diazo) compound where two bis(diazo) units are connected by an interior diazo group so as to make all five carbene units interact ferromagnetically and characterized pentakis(carbene) generated from the pentakis(diazo) compound.

The interior diazo compound used in this study was bis-(4-iodo-2,6-dimethylphenyl)diazomethane (**1**), which was prepared from the corresponding dibromocarbamate<sup>12</sup> according to the procedure outlined in Scheme 2. Coupling of



**1** with 2 equiv of a bis(diazo) compound (**2**),<sup>9</sup> carrying two persistent triplet carbene precursor, resulted in the formation

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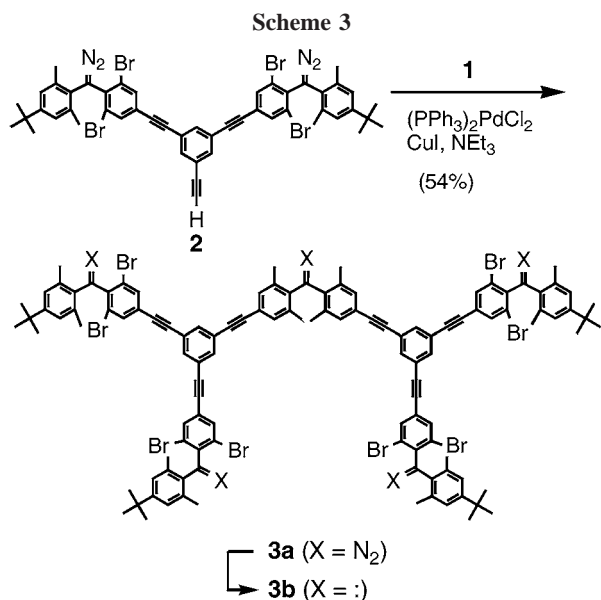
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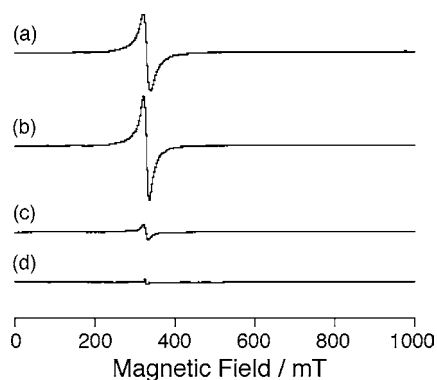
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of a desired pentakis(diazo) compound (**3a**) as red solids in 54% yield under mild Sonogashira coupling reaction conditions (Scheme 3).<sup>13</sup>



Irradiation ( $\lambda > 300$  nm) of **3a** ( $4.0 \times 10^{-3}$  M) in 2-methyltetrahydrofuran (2-MTHF) at 77 K gave ESR spectra that were completely different from those observed for the corresponding triplet diphenylcarbenes.<sup>14–16</sup> The spectra showed rather broad signal centered around ca. 330 mT (Figure 1a). The broad signal is consistent with the



**Figure 1.** (a) ESR spectra obtained by irradiation of pentakis(diazo) compound **3a** in 2-methyltetrahydrofuran at 77 K and (b–d) the same sample observed at 77 K after warming to (b) 90 K, (c) 110 K, and (d) 150 K.

tendency that, as the spin multiplicity became higher, the  $D$  value became smaller.<sup>17</sup>

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Thawing the matrix containing pentakis(carbene) and recoiling again to 77 K to measure the signal could estimate the thermal stability of the pentakis(carbene). This procedure can compensate for the weakening of signals due to Curie's law. When the matrix containing **3b** was warmed gradually in 10 K increments, the signal became sharp around 90 K (Figure 1b). This change was not reversible; when the sample was recooled at 77 K, no change took place, apart from an increase in the signal intensity according to Curie's law. This is interpreted in terms of geometrical change of carbenes often observed for sterically congested carbenes.<sup>14a,15</sup> The signals did not decay appreciably up to 100 K, started to decompose at around 110 K, and disappeared irreversibly above 150 K (Figure 1c,d). The ESR signals of bis(2,6-dimethylphenyl)carbene,<sup>14a</sup> i.e., the interior carbene unit and (2,6-dibromo-4-trimethylsilylethynylphenyl)(4-*tert*-butyl-2,6-dimethylphenyl)carbene,<sup>16</sup> i.e., the exterior carbene unit, were found to disappear in 2-MTHF matrix at 140 and 160 K, respectively. Thus, the thermal stability of pentakis(carbene) (**3b**) is essentially identical with that of these monocarbenes.

When similar irradiation of **3a** ( $7.7 \times 10^{-4}$  M) in a 2-MTHF matrix at 77 K was monitored by UV/vis spectroscopy, a sharp and strong absorption band at 386 nm was observed at the expense of the original absorption due to **3a**. Since ESR signals ascribable to pentakis(carbene) are observed under identical conditions, the absorption spectrum can be assigned to **3b**. Upon thawing the matrix, the band became sharper and shifted to 389 nm at around 110 K and was observable up to 140 K (Figure S2, Supporting Information). This change can be attributed to the geometrical change of the carbenes, as has been revealed in ESR experiments.

To obtain evidence concerning the spin states of the photoproducts from **3a**, the magnetic susceptibility of the photoproducts was measured. A 2-MTHF solution of pentakis(diazo) compound (**3a**, 0.3 mM) 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 at 5 K in a constant field of 5 kOe with the irradiation time for the pentakis(diazo) compound was measured in situ. As the irradiation time was increased, the magnetization values gradually increased and reached a plateau after 20 min. After the magnetization 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,

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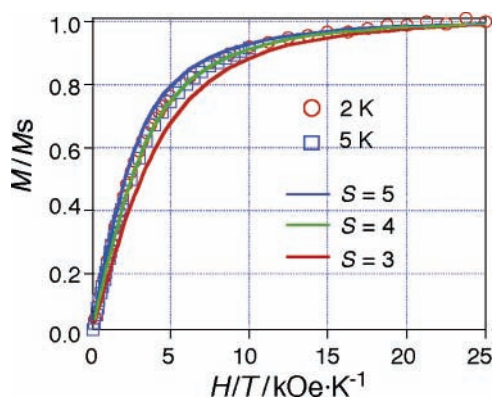
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$M_b$ , were also measured under the same conditions. The magnetization due to the species generated by photolysis was then obtained by subtracting the corresponding values obtained before and after irradiation. Thus, the effect of any paramagnetic impurities could be canceled by this treatment. The plots of the magnetization ( $M$ ) versus the temperature-normalized magnetic field ( $H/T$ ) were analyzed in terms of the Brillouin function as follows<sup>2,18,19</sup>

$$M = M_a - M_b = FNgJ\mu_B B(\chi) \quad (1)$$

where  $F$  is the generation factor for carbene obtained from saturated magnetization ( $M_s$ ),  $N$  is the number of the molecule,  $J$  is the quantum number for the total angular momentum,  $\mu_B$  is Bohr magneton, and  $g$  is the Landé  $g$ -factor. Since the carbenes are composed 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  $H/T$  plot is shown in Figure 2 with theoretical curves with  $S = 3, 4$ , and  $5$ .



**Figure 2.** Plot of  $M/M_s$  vs  $H/T$  of the photoproduct from **3a** measured at 2.0 and 5.0 K. The solid lines represent theoretical curves with  $S = 3, 4$ , and  $5$ .

The observed data were best fitted with eq 1 with  $S = 4.4$  ( $F = 0.91$ ) at 2.0 K and  $S = 4.2$  ( $F = 0.96$ ) at 5.0 K. Although the  $S$  values are somewhat smaller than the theoretical value of 5, the results clearly indicate that the five carbene centers interact ferromagnetically. In other words, the connectivity is switched from disjoint to nondisjoint by the new carbene unit between the bis(carbene) units and core benzene.

Since the magnetization data at two different temperatures were fitted to the same Brillouin function, the sample is considered to be free from ferro- and antiferromagnetic intermolecular interactions. Somewhat smaller values in  $S$  and  $F$  are probably ascribed to a carbene defect due to photodecomposition of carbenes and/or due to purity of precursor **3a**.

The present study clearly demonstrates that the potential problem in the dendrimer approach to generate high-spin polycarbenes is relatively easily solved by changing the “wrong” connectivity through a new carbene center in the appropriate position. The results also indicate that this is realized by the persistent nature of our diazo compounds, which allows us to introduce a diazo unit at a desired position. Thus, a step toward a persistent triplet carbene will eventually lead us to a persistent high-spin polycarbene.

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**Supporting Information Available:** Preparation of **1** and **2a**,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **3a** (Figure S1), UV–vis spectra of **3b** (Figure S2), plot of magnetization vs irradiation time in the photolysis of **3a** (Figure S3), and field dependence of the magnetization of the photoproduct from **3a** (Figure S4). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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