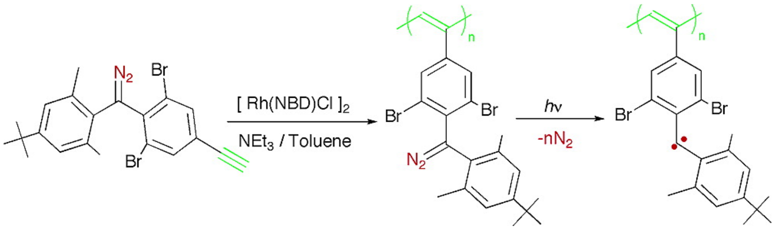
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Communication

Preparation of Poly(phenyl)acetylenes Having Diazo Groups and Magnetic Characterization of Poly(carbene)

Tetsuji Itoh, Yoshinobu Jinbo, Katsuyuki Hirai, and Hideo Tomioka

J. Am. Chem. Soc., **2005**, 127 (6), 1650-1651• DOI: 10.1021/ja0455345 • Publication Date (Web): 19 January 2005



More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 6 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

View the Full Text HTML

Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

J|A|C|S
COMMUNICATIONS

Preparation of Poly(phenyl)acetylenes Having Diazo Groups and Magnetic Characterization of Poly(carbene)

Tetsuji Itoh,† Yoshinobu Jinbo,† Katsuyuki Hirai,‡ and Hideo Tomioka*,†

Chemistry Department for Materials, Faculty of Engineering, and Instrumental Analysis Facilities,
Life Science Research Center, Mie University, Tsu, Mie 514-8507 Japan

Received July 25, 2004; E-mail: tomioka@chem.mie-u.ac.jp

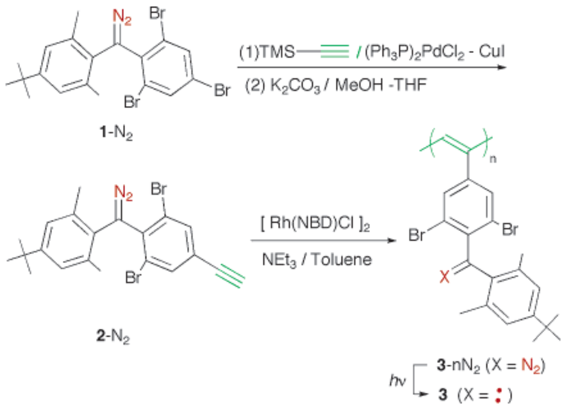
Many attempts have been made in order to realize organic ferromagnetic materials.[1,2] Triplet carbenes are regarded as one of the most effective spin sources since the magnitude of the exchange coupling between the neighboring centers is large.[3] However, these systems have not been employed extensively due to 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 toward stabilization and succeeded in preparing fairly stable ones that survive for days.[4] The second disadvantage that arises is that diazo groups are also generally labile[5] and, hence, are usually introduced at the last step of synthesis.[6]

We found that a diphenyldiazomethane for a persistent triplet carbene is also persistent for the diazo compound[7] and, hence, can be further modified, with the diazo group intact, into a more complicated diazo compound.[8] Thus, the diazo compound can be used as a building block to prepare a polydiazo compound, which can then generate high-spin poly(carbene) with considerable thermal stability. This is a report of the preparation of a poly(phenyl)acetylene bearing diazo unit using Rh-complex-catalyzed polymerization[9,10] and the characterization of poly(carbene) generated from those precursor polydiazo compounds.

(2,6-Dibromo-4-ethynylphenyl)(2,6-dimethyl-4-*tert*-butylphenyl)diazomethane (**2**-N_2)[8c] was selected as a starting diazo precursor for the following reasons. First, it is expected to survive the chemical manipulations required to prepare the corresponding polymer since the diazo carbon is well-shielded by four relatively bulky groups at the ortho positions. Second, it is also expected to generate a fairly persistent triplet carbene unit upon photoexcitation, as it has been shown that **1**-N_2 generates the corresponding triplet carbene (^{3}**1**), which survives for minutes in solution at room temperature.[11] Finally, alkyl groups, i.e., methyl and *tert*-butyl groups, on one side of phenyl ring in **2**-N_2, are expected to both protect the carbenic center and also improve solubility, which will become a serious problem at a higher degree of polymerization.

The starting diazo compound **2**-N_2 was easily prepared from the corresponding brominated diazo compound **1**-N_2 by Sonogashira coupling reaction, followed by deprotection of the TMS group (Scheme 1).[8c] Treatment of **2**-N_2 with [Rh(norbornadiene═NBD)-Cl]$_2$ complex in the presence of triethylamine as a cocatalyst in toluene for 1 day at room temperature followed by quenching by MeOH and filtration gave a red solid. The solid was dissolved in $CHCl_3$ and purified by recycled gel permeation chromatography to obtain a main fraction. The average molecular weight of polymers (**3**-nN_2) was estimated to be approximately 86 000 (190 mer) from GPC calibration using a polystyrene standard. IR spectra of the polymer (**3**-nN_2) showed a strong absorption band at 2100 cm^{-1} due to the C═N═N stretch of the diazo group, whose intensity relative to the other bands was essentially identical with that observed for the starting monomer (**2**-N_2). This clearly indicates that the diazo group is not decayed during the polymerization process.

Scheme 1



A 2-methyltetrahydrofuran solution of **3**-nN_2 was placed inside the sample compartment of a superconducting quantum interference device (SQUID) magnet/susceptometer and 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 over a period of irradiation was measured in situ. As the irradiation time was 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. Thus, the effect of any paramagnetic impurities could be canceled by this treatment. The plots of the magnetization (M/s) versus the temperature-normalized magnetic field (H/T) were analyzed in terms of the Brillouin function as follows:[1c,6,12]

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

where *F* is the photolysis factor of diazo compound, *N* is the number of the molecule, *J* is the quantum number for the total angular momentum, μ_B is the Bohr magneton, and *g* is Landé *g*-factor. Since these 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* versus H/T plots are shown in Figure 1a.

The observed data for the photoproduct from polydiazo compound indicate that the magnetization data at two different

---

† Chemistry Department for Materials.
‡ Instrumental Analysis Facilities.

10.1021/ja0455345 CCC: $30.25

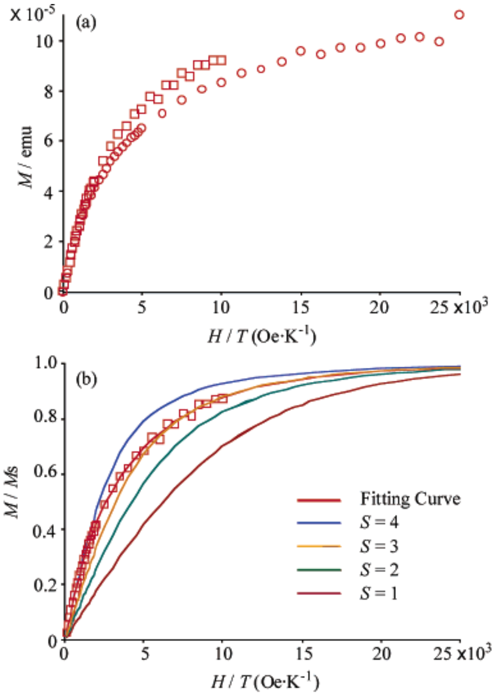


Figure 1. (a) Plot of M vs H/T of the photoproduct from polydiazo compound (**3**-nN$_2$) measured at 2.0 (○) and 5.0 K (□). (b) Plot of M/Ms vs H/T of the photoproduct from polydiazo compound (**3**-nN$_2$) measured at 5.0 K (□). The red lines represent two-component theoretical curves with $S = 9.63$ ($F = 0.15$) and $S = 1.94$ ($F = 0.22$).

temperatures did not fit the same Brillouin function. Since the magnetization is attenuated at lower temperatures (compare M vs H/T plot at 2 and 5 K in Figure 1a), the presence of antiferromagnetic interaction among the unpaired spins is suggested. When a sample concentration as low as 0.5 mM is taken into account, the observed antiferromagnetic interaction can be assigned to an intramolecular interaction rather than an intermolecular one.

Therefore, the data at 5 K where the antiferromagnetic interaction is weaker were analyzed in terms of the Brillouin function (Figure 1b). The data were fitted with eq 1 with $S = 4.90$ ($F = 0.35$). Alternatively, the data were better analyzed by a two-component Brillouin function[13] with $S = 9.63$ ($F = 0.15$) and $S = 1.94$ ($F = 0.22$). Significantly small F values indicate either that the decomposition rate of the precursor diazo functional groups is incomplete or that there are considerable intramolecular antiferromagnetic interactions between the carbene centers. Since the IR analysis of the spent solution showed that most diazo groups disappeared, the latter possibility is more likely.[14]

The observations suggest that a persistent triplet diphenylcarbene unit incorporated into a π-network of the phenylacetylene polymer in a ferromagnetic fashion indeed acts as a spin source to generate a high-spin ground state. However, the estimated spin multiplicities are not as high as that expected from the degree of polymerization. It should be noted that the connectivity of carbene centers on the pendant phenyl group through the polyene backbone is nondisjoint in the Borden/Davidson sense,[15] and hence the spins are expected to interact ferromagnetically. The poly(phenyl)acetylenes bearing stable radical groups have been shown to have a spin multiplicity of 1/2, indicating that through-bond interaction was essentially not observed.[16] This is interpreted as indicating that the polyene structures do not have a planar polyene backbone and also that the dihedral angle between the backbone and the attached phenyl ring is significantly twisted. A defect in the backbone structure due the nature of phenylacetylene polymerization is also suggested.[16c] A similar explanation can be applied for the unexpectedly low spin multiplicities observed for polycarbene **3**. It is interesting to note here that the spin multiplicity of **3** is significantly higher than that of a component spin unit, i.e., triplet carbene ($S = 1$), rather than an almost complete lack of magnetic interaction, as observed for the poly(phenyl)acetylene bearing stable radical units. This is partly ascribable to the higher spin density of the present system composed of triplet carbene units than that composed of doublet radical units and demonstrates the usefulness of triplet carbene as the spin source for constructing high-spin organic molecules.

Acknowledgment. The authors are grateful to the Ministry of Education, Culture, Sports, Science and Technology of Japan for support of this work through a Grant-in-Aid for Scientific Research for Specially Promoted Research (No. 12002007).

Supporting Information Available: Preparation, GPC, IR, NMR, and UV/vis charts of **3**-nN$_2$, plot of magnetization vs irradiation time in the photolysis of **3**-nN$_2$, and field dependence of the magnetization of the photoproduct from **3**-nN$_2$ (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Iwamura, H. *Adv. Phys. Org. Chem*. **1990**, *26*, 179. (b) Dougherty, D. A. *Acc. Chem. Res*. **1991**, *24*, 88. (c) Rajca, A. *Chem. Rev*. **1994**, *94*, 871.
(2) (a) Miller, J. S., Epstein, A. J., Eds. *MRS Bulletin* **2000**, *25*, 21. (b) Miller, J. S., Drillon, M., Eds. *Magnetism: Molecules to Materials II*; Wiley-VCH: Weinheim, Germany, 2001. (c) *Molecular Magnetism*; Itoh, K., Kinoshita, M., Eds.; Kodansha-Gordon and Breach: Tokyo, 2000.
(3) (a) Koga, N.; Iwamura, H. In *Carbene Chemistry*; Bertrand, G., Ed.; Fontis Media: Lausanne, 2002; pp 271−296. (b) Matsuda, K.; Nakamura, N.; Takahashi, K.; Inoue, K.; Koga, N.; Iwamura, H. *Molecule-Based Magnetic Materials*; ACS Symposium Series 644; American Chemical Society: Washington, DC, 1996; p 142.
(4) (a) Tomioka, H. *Acc. Chem. Res*. **1997**, *30*, 315. (b) Tomioka, H. In *Advances in Carbene Chemistry*; Brinker, U., Ed.; JAI Press: Greenwich, CT, 1998; Vol. 2, pp 175−214. (c) Tomioka, H. In *Carbene Chemistry*; Bertrand G., Ed.; Fontis Media S. A.; Lausanne, 2002; pp 103−152.
(5) Regitz, M.; Maas, G. *Diazo Compounds−Properties and Synthesis*; Academic Press: Orlando, 1986.
(6) Matsuda, K.; Nakamura, N.; Inoue, K.; Koga, N.; Iwamura, H. *Bull. Chem. Soc. Jpn*. **1996**, *69*, 1483 and references therein.
(7) Tomioka, H.; Hattori, M.; Hirai, K.; Sato, K.; Shiomi, D.; Takui, T.; Itoh, K. *J. Am. Chem. Soc*. **1998**, *120*, 1106.
(8) (a) Itoh, T.; Hirai, K.; Tomioka, H. *J. Am. Chem. Soc*. **2004**, *126*, 1130. (b) Ohtsuka, Y.; Itoh, T.; Hirai, K,; Tomioka, H.; Takui, T. *Org. Lett*. **2004**, *6*, 847. (c) Maemura, T.; Ohtsuka, Y.; Wildt, H.; Hirai, K.; Tomioka, H. *Eur. J. Org. Chem*. **2004**, 2991. (d) Itoh, T.; Jinbo, Y.; Hirai, K.; Tomioka, H. *J. Org. Chem*. **2004**, *69*, 4238. (e) Itoh, T.; Morisaki, F.; Kurono, M.; Hirai. K.; Tomioka, H. *J. Org. Chem*. **2004**, *69*, 5870.
(9) Masuda, T.; Yoshimura, T.; Fujimori, J.; Higashimura, T. *J. Chem. Soc., Chem. Commun*. **1987**, 1805.
(10) Kishimoto, Y.; Eckerle, P.; Miyatake, T.; Kainosho, M.; Ono, A.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc*. **1999**, *121*, 12035 and references therein.
(11) Tomioka, H.; Watanabe, T.; Hattori, M.; Nomura, N.; Hirai, K. *J. Am. Chem. Soc*. **2002**, *124*, 474.
(12) R. L. *Magnetochemistry*; Springer-Verlag: Berlin, 1986.
(13) See for instance: Rajca, A.; Wongsriratanakul, J.; Rajca, S.; Cerny, L. *Chem. Eur. J*. **2004**, *10*, 3144.
(14) However, rather significant experimental errors in analyzing a small quantity (0.05 mL) of a very dilute (0.5 mM) sample should also be taken into account.
(15) Borden, W. T.; Davidson, E. R. *J. Am. Chem. Soc*. **1977**, *99*, 4587.
(16) (a) Miura, Y.; Matsumoto, M.; Ushitani, Y.; Taki, Y.; Takui, T.; Itoh, K. *Macromol*. **1993**, *26*, 6673. (b) Nishide, H.; Kaneko, T.; Igarashi, M.; Tsuchida, E. Yoshioka, N.; Lahti, P. *Macromolecules* **1994**, *27*, 3082. (c) Lahti, P. M.; Inceli, A. L.; Rossitto, F. C. *J. Polym. Sci., Part A: Polym. Chem*. **1997**, *35*, 2167.

JA0455345