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Preparation of Sterically Congested Di(4-pyridyl)diazomethanes and Characterization of Triplet Carbenes from Them

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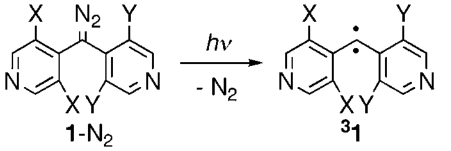
ABSTRACT



$\mathbf{1}$-N_2 $\quad$ $^3\mathbf{1}$

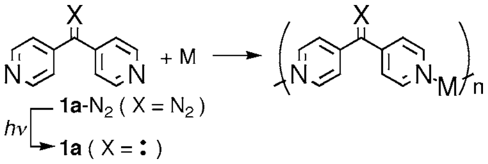
a: X = Y = H; **b**: X = Cl, Y = H; **c**: X = Y = Cl

Di(4-pyridyl)diazomethanes having two and four ortho chlorine groups were prepared, and the triplet carbenes generated from them were characterized by ESR and UV/vis at low temperature and time-resolved UV/vis at room temperature. An appreciable increase in the stability of triplet carbenes is achieved by introducing ortho chlorine groups.

Many attempts have been made to prepare purely organic spin systems.[1] Such approaches have several problems, which prevent the formation of usable systems. For instance, a "bottom-up" synthetic approach to obtaining molecular magnets is faced with synthetic limitations, especially when the orders of the alignment of spins become higher. On the other hand, efforts to increase the number of aligned spins are hampered by the development of antiferromagnetic intra and/or interchain interactions between the radical centers.

To overcome these problems, heterospin systems comprising of 2p spins of organic radicals and 3d spins of magnetic metal ions have been proposed.[2,3] The strategy is based on the supramolecular chemistry exhibited by pyridine− and polypyridine−metal ions.[4] For instance, magnetic interaction between radical centers and metal ions can be realized through a pyridyl ligand to generate a high spin unit (Scheme 1). This system allows us to extend the dimension of the spin network from one (1D) to two (2D) and three (3D) by simple self-assembly between pyridyl groups and metal ions.[5]

Scheme 1



Pyridines having a triplet carbene unit have been successfully employed to generate high heterospin polycarbenes with

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(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. (d) *Magnetic Properties of Organic Materials*; Lahti, P. M., Ed.; Marcel Dekker: New York, 1999.

(2) Koga, N.; Iwamura, H. In *Carbene Chemistry*; Bertrand, G., Ed.; Fontis Media: Lausanne, 2002; pp 271−296.

(3) (a) Koga, N.; Iwamura, H. In ref 1c, pp 629−659. (b) Koga, N.; Iwamura, H. *Mol. Cryst. Liq. Cryst.* **1997**, *305*, 415. (c) Iwamura, H.; Koga, N. *Mol. Cryst. Liq. Cryst.* **1999**, *334*, 437. (d) Iwamura, H.; Koga, N. *Pure Appl. Chem.* **1999**, *71*, 231.

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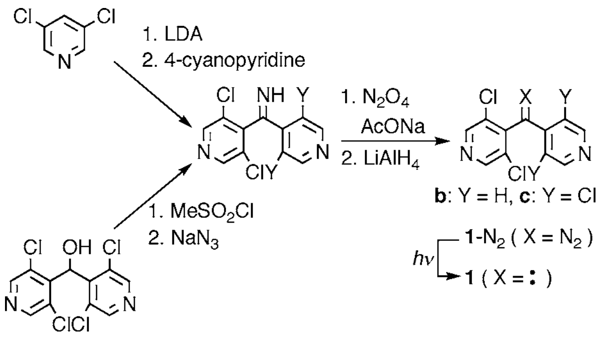
2D- and/or 3D-spin networks.[2,6] However, the chemical stability of the triplet carbene in these systems is ignored. In this respect, it is desirable to design and prepare a persistent triplet pyridylcarbene. We report here our attempts to generate and characterize triplet di(4-pyridyl)carbenes (DPyCs, ^{3}**1b** and **c**) having two and four chlorine groups at the ortho positions as a kinetic protector.[7]

Most sterically congested diaryldiazomethanes have been successfully prepared by base treatment of the corresponding *N*-(nitroso)methylcarbamates.[8] However, all attempts to prepare the desired precursor diazomethanes, [4-(3,5-dichloro)-pyridyl](4-pyridyl)diazomethane (**1b**-N_2) and bis[4-(3,5-dichloro)pyridyl]diazomethane (**1c**-N_2), were unsuccessful by this procedure. We thus chose the second route, which is the nitrosation followed by the reduction of the corresponding ketimines by lithium aluminum hydride (LAH).[8] The desired [4-(3,5-dichloro)pyridyl](4-pyridyl)ketimine was prepared by the conventional method. Thus, treatment of 3,5-dichloropyridine with lithium diisopropylamine (LDA) followed by addition of 4-cyanopyridine gave the ketimine in good yield. Nitrosation of the ketimine followed by reduction with LAH gave the corresponding diazo compound (**1b**-N_2) as a yellow solid (Scheme 2). Tetrachlorinated ketimine could not be prepared similarly but was obtained by treatment of the corresponding methanesulfonate with sodium azide. Nitrosation of the ketimine followed by reduction gave **1c**-N_2 as a yellow solid (Scheme 2). All diazomethanes were purified by repeated cycles of gel permeation chromatography followed by preparative TLC.

Scheme 2



Irradiation (λ > 300 nm) of **1c**-N_2 (2.0×10^{-2} M) in propanetriol triacetate (PT)[9] glass at 77 K gave ESR signals with typical fine structure patterns for unoriented triplet species,[10,11] i.e., ^{3}**1c**. Signals at 109.0, 476.9, and 531.8 mT are assigned to a low-field *z* and a set of high-field *x* and *y* transitions, respectively, from which the zero-field splitting (ZFS) parameters were obtained as $D = 0.409$ cm^{-1} and $E = 0.013$ cm^{-1} ($E/D = 0.032$).

The thermal stability of the triplet carbenes could be estimated by thawing the matrix containing triplet carbenes gradually and recooling again to 77 K to measure the signal. This procedure can compensate for the weakening of signals due to Curie's Law. When the matrix containing ^{3}**1c** was warmed gradually in 10 K increments, the ESR signals of ^{3}**1c** disappeared at around 200 K.

Similar measurements were carried out with **1b**-N_2 and the data are summarized in Table 1. Data for the "parent" triplet di(4-pyridyl)carbene (^{3}**1a**) are included for the sake of comparison.

Table 1. Spectroscopic Data for Di(4-pyridyl)carbenes[a]

carbenes	$\|D\|$ (cm^{-1})	$\|E\|$ (cm^{-1})	E/D	λ_{max} (nm)	T_d[b] (K)
1a	0.437	0.020	0.046	300, 500	160
1b	0.421	0.019	0.043	512, 467	180
1c	0.409	0.013	0.032	360, 500	200

[a] Measured in PT at 77 K. [b] Temperature at which the ESR spectra of triplet di(4-pyridyl)carbenes disappeared.

The zero-field splitting (ZFS) parameters *D* and *E* give information on the molecular and electronic structures of triplet carbenes.[10,11] The *D* value is related to the separation between the unpaired electrons. The *E* value, when weighted by *D*, (i.e., *E*/*D*), is a measure of the deviation from axial symmetry. For diarylcarbenes, this value thus depends on the magnitude of the central C−C−C angle. Put more simply, the more the two electrons are delocalized in carbenes with a conjugated carbene π-system, the smaller the value of the repulsive interaction *D* will be. On the other hand, increasing the bond angle at the carbene center leads to a higher *p*-orbital contribution and a smaller value for *E*. Although the values *D* and *E* depend on the electronic distribution, it has been shown that there is a good correlation between the *E*/*D* ratio and the bond angle at the divalent carbon atom.

Inspection of the data in Table 1 reveals the effect of ortho chlorine groups on the structures and stabilities of triplet DPyC. Both *D* and *E*/*D* values decrease from ^{3}**1a** to ^{3}**1b** to ^{3}**1c**. The observed decrease in the *D* and *E*/*D* values is then explained as indicating that the carbene bond angle expands as more chlorine groups are introduced at the ortho positions,

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(4) (a) Lehn, J.-M. *Supramolecular Chemistry*; VCH Publisher: New York, 1995. (b) Nierengarten, J.-F.; Dietrich-Buchecker, C. O.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1994**, *116*, 375. (c) Leininger, J.-F.; Olenyuk, B.; Stang, P. J. *Chem. Rev.* **2000**, *100*, 853.

(5) Iwamura, H.; Inoue, K.; Koga, N. *New J. Chem.* **1998**, 201.

(6) (a) Karasawa, S.; Kumada, H.; Iwamura, H.; Koga, N. *J. Am. Chem. Soc.* **2001**, *123*, 9685. (b) Karasawa, S.; Koga, N. *Polyhedron* **2001**, *20*, 1387.

(7) For reviews of persistent triplet carbenes, see: (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 *Advances in Strained and Interesting Organic Molecules*; Halton, B., Ed.; JAI Press: Greenwich, CT, 2000; Vol. 8, pp 83−112. (d) Tomioka, H. In *Carbene Chemistry*; Bertrand, G., Ed.; Fontis Media, S. A.: Lausanne, 2002; pp 103−152.

(8) (a)Zimmerman, H. E.; Paskovich, D. H. *J. Am. Chem. Soc.* **1964,** *86*, 2149. (b) Regitz, M.; Maas, G. *Diazo Compounds-Properties and Synthesis*; Academic Press: Orlando, 1986.

(9) Because of inherent instable nature of triplet di(4-pyridyl)carbenes, a viscous matrix such as propanetriol triacetate was required to obtain ESR signal at 77 K.

(10) For reviews of the EPR and UV/vis spectra of triplet carbenes, see: (a) Sander, W.; Bucher, G.; Wierlacher, S. *Chem. Rev.* **1993**, *93*, 1583. (b) Trozzolo, A. M.; Wasserman, E. In *Carbenes*; Jones, M., Jr., Moss, R. A., Eds.; Wiley: New York, 1975; Vol. 2. pp 185−206.

(11) Wasserman, E.; Hutton, R. S. *Acc. Chem. Res.* **1977**, *10*, 27.

most probably as a result of steric repulsion between the ortho substituents and increased delocalization of the electrons. In other words, as more chlorine groups are introduced at ortho positions, triplet DPyCs are more thermodynamically stabilized. The ortho chlorine groups are also expected to stabilize triplet DPyCs kinetically, by protecting the carbenic center from external reagents.[12] In accord with this interpretation, the thermal stability of triplet DpyCs increased significantly in this order, as judged from the temperature at which ESR signals and UV/Vis absorption bands (vide infra) disappear (*T*d).

To determine the effects of *o*-chlorine groups on the kinetics of triplet DPyCs in solution at room temperature, time-resolved UV/Vis spectroscopic measurements of **1**-N_2 were carried out. Irradiation of **1** in PT matrix at 77 K was first monitored by UV/Vis spectroscopy, to determine the spectroscopic features of triplet DPyCs. Irradiation ($\lambda > 300$ nm) of **1c**-N_2 (2.0×10^{-2} M) in PT at 77 K resulted in the appearance of new absorption bands centered at 500 and 560 nm at the expense of the original absorption due to **1c**-N_2 (Figure 1). The new bands are very weak and could not be detected when the initial concentration of diazo compound was adjusted for usual UV/vis measurements, i.e., in the order of 10^{-4} M. Generally, UV/vis spectra of triplet diphenylcarbenes consist of two identifiable features, an intense UV band with a maximum at around 290−320 nm and weak structured bands at around 400−500 nm.[10] The observed absorption bands are appreciably different from those observed for typical triplet diphenylcarbenes. However, since strong ESR signals ascribable to a triplet carbene are observed under identical conditions, the absorption spectrum can be assigned to triplet carbene ^{3}**1c**. When the PT matrix containing ^{3}**1c** was gradually warmed, the absorption bands due to ^{3}**1c** started to decompose at around 210 K and disappeared completely at 230 K. Similar measurements were carried out with **1a**-N_2 and **1b**-N_2 and the absorption maxima are summarized in Table 1.

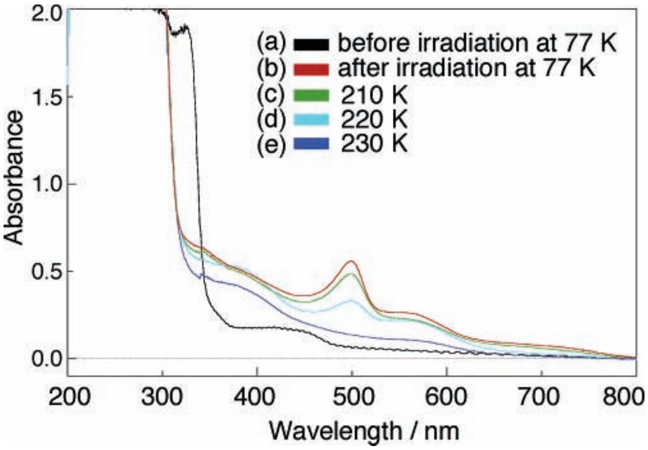

Figure 1. UV−vis spectral changes observed in the photolysis of diazo compound **1c**-N_2. (a) UV−vis spectrum of **1c**-N_2 in PT at 77 K. (b) Same sample after irradiation ($\lambda > 300$ nm). (c−e) Same sample after warming the matrix to (c) 210, (d) 220, and (e) 230 K.

Laser flash photolysis(LFP) of **1**-N_2 was then carried out.[13] LFP of **1c**-N_2 in a degassed benzene solution at room temperature with a 10 ns, 70−90 mJ, 308 nm pulse from a XeCl laser produced no apparent new transient absorption band. This is obviously because of the inherent weak nature of the absorption band due to ^{3}**1c** (vide supra). However, when LFP was carried out on a nondegassed benzene solution containing **1c**-N_2, a new broad absorption band at 370 nm appeared (Figure 2). The spent solution was found to contain bis[4-(3,5-dichloro)pyridyl]ketone (**1c**-O) as the main product. It is well documented that diarylcarbenes with triplet ground states are readily trapped by oxygen to generate the corresponding diaryl ketone oxides, which are readily observed directly either by matrix isolation spectroscopy or by flash photolysis techniques, and show a broad absorption band centered at 390−450 nm.[14,15]

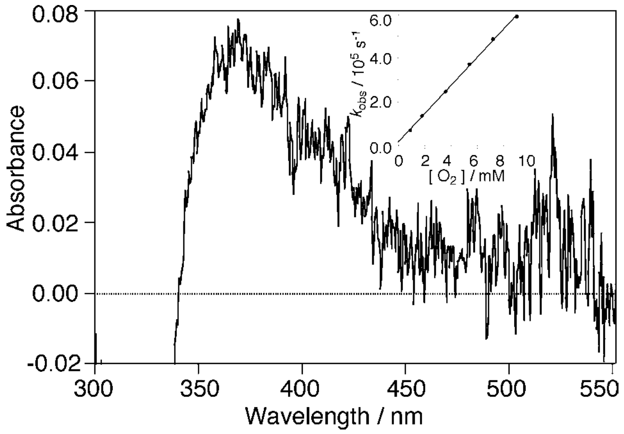

Figure 2. Transient absorption spectrum obtained in LFP of diazo compound **1c**-N_2 in nondegassed benzene with 308-nm excimer laser recorded 1 μs after the pulse. The inset shows a plot of the growth rate of the oxide (**1c**-O_2) monitored at 370 nm as a function of the concentration of oxygen.

Thus, the observations can be interpreted to indicate that the triplet carbene ^{3}**1c** is trapped by oxygen to form the carbonyl oxide (**1c**-O_2). The apparent build-up rate constant, k_{obs}, of the carbonyl oxide increases as the concentration of oxygen increases. The rate constant k_{obs} is expressed as given in eq 1

$$k_{obs} = k_0 + k_{O_2}[O_2] \tag{1}$$

where k_0 represents the rate of decay of ^{3}**1c** in the absence of oxygen and k_{O_2} is the quenching rate constant of ^{3}**1c** with

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[12] Tomioka, H.; Hirai, K.; Fujii, C. *Acta Chim. Scand*. **1993**, *46*, 680. (b) Tomioka, H.; Hirai, K.: Nakayama, T. *J. Am. Chem. Soc*. **1993**, *115*, 1285. (c)Kawano, M.; Hirai, K.; Tomioka, H.; Ohashi, Y. *J. Am. Chem. Soc*. **2001**, *123*, 6904.

oxygen. As shown in the inset of Figure 2, the plot of the observed pseudo-first-order rate constant for the formation of **1c**-O_2 against [O_2] is linear. From the slope of this plot, the rate constant for the quenching of ^{3}**1c** by oxygen was determined to be 6.5×10^7 M^{-1} s^{-1}. The intercept of the slope (k_0) was determined to be 1.7×10^4 s^{-1}. The lifetime of ^{3}**1c** was thus estimated to be 60.0 μs.[16]

Similar measurement was carried out with other di(4-pyridyl)diazomethanes (**1a**-N_2 and **1b**-N_2) and kinetic data are summarized in Table 2.

Table 2. Kinetic Data for Reaction of Triplet Di(4-pyridyl)carbenes with Oxygen[a]

carbenes	λ_{max}[b] (nm)	k_o (s^{-1})	$\tau_{carbene}$[c] (μs)	k_{O_2} (M^{-1} s^{-1})
1a	425	1.9×10^6	0.53	1.9×10^9
1b	410	7.9×10^5	1.3	6.6×10^8
1c	370	1.7×10^4	60	6.5×10^7

[a] Measured in benzene at 20 °C. [b] Absorption maxima of the corresponding carbonyl oxide (**1**-O_2). [c] $\tau_{carbene} = 1/k_o$.

Inspection of the data in Table 2 indicates that chlorine groups at the ortho positions effectively stabilize DPyCs only when they are introduced at all the ortho positions. The half-life is increased only slightly when two chlorine groups are introduced, but it is increased by 2 orders of magnitude when all the ortho hydrogens are replaced with chlorine groups. The reaction with the most efficient quencher of triplet carbene, i.e., oxygen,[14,15] is also significantly retarded when four ortho chlorine groups are introduced.

It is interesting to compare the effect of chlorine groups on triplet DPyCs with that on triplet diphenylcarbenes (DPCs).[12] It has been shown that the lifetime of triplet bis(2,4,6-trichlorophenyl)carbene is 18 ms,[12b] which is some 4 orders of magnitude greater than that of the "parent" triplet diphenylcarbene ($\tau = 1$ μs). Thus, the effect of *o*-Cl on ^{3}DPyCs is notably smaller than that on ^{3}DPCs.

It is interesting to note here that the ZFS parameter of parent ^{3}DPC ($D = 0.4055$ cm^{-1}) is smaller than that of parent ^{3}DPyC, ^{3}**1a** ($D = 0.437$ cm^{-1}). In addition, the rate of the decrease in D values on introduction of four *o*-Cl groups in ^{3}DPyC, i.e., on going from ^{3}**1a** ($D = 0.437$ cm^{-1}) to ^{3}**1c** ($D = 0.409$ cm^{-1}), is ca. 6%, which is apparently smaller than the corresponding decrease in DPC, i.e., on going from ^{3}DPC ($D = 0.4055$ cm^{-1}) to chlorinated ^{3}DPC ($D = 0.364$ cm^{-1})[12] (ca 10%). These results suggest that in ^{3}DPyCs, unpaired electrons are more localized on the carbene center than in ^{3}DPCs, and are not effectively delocalized to the aromatic ring, even on introduction of *o*-Cl groups.

We have shown that the triplet DpyC, a unit for high heterospin polycarbenes, can be stabilized by steric protection to some extent, but that this carbene is more difficult to stabilize than triplet DPCs.

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Supporting Information Available: EPR spectra of **1a**, **1b**, and **1c** (Figures S1, S2, and S3), UV/vis spectra of **1a** and **1b** (Figures S4 and S5), time-resolved UV−vis spectra of **1a**-O_2 and **1b**-O_2 (Figures S6 and S7). Preparation of **1b**-N_2 and **1c**-N_2. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) For details of our LFP equipments, see; Tomioka, H.; Okada, H.; Watanabe, T.; Banno, K.; Komatsu, K.; Hirai, K. *J. Am. Chem. Soc*. **1997**, *119*, 1582.

(14) For review, see: (a) Sander, W. *Angew. Chem., Int. Ed. Engl*. **1990**, *29*, 344. (b) Bunnelle, W. *Chem. Rev*. **1991**, *91*, 336.

(15) Scaiano, J. C.; McGimpsey, W. G.; Casal, H. L. *J. Org. Chem*. **1989**, *54*, 1612.

(16) Carbonyl oxide formation has been used to monitored carbenes that are transparent in the useful UV region. See, for instance; Morgan, S.; Platz, M. S.; Jones, M., Jr.; Myers, D. R. *J. Org. Chem*. **1991**, *56*, 1351.