

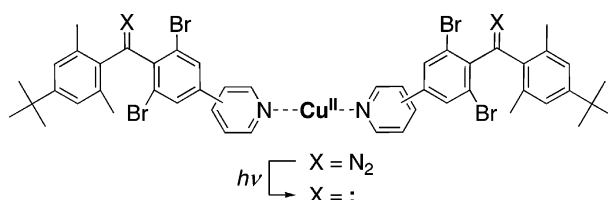
Preparation of Sterically Congested Diphenyldiazomethanes Having a Pyridine Ligand and Magnetic Characterization of Photoproducts of Their 2:1 Copper Complexes

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To confirm whether high-spin species can be generated as a result of ferromagnetic interaction between the 3d spin of metal ions and the 2p spins of triplet carbene through the pyridyl group located remote from the carbene center, [2,6-dibromo-4-(3- and 4-pyridyl)phenyl](4-*tert*-butyl-2,6-dimethylphenyl)diazomethanes were prepared and the corresponding carbenes were generated either in the absence or presence of $\text{Cu}(\text{hfac})_2$. These were characterized by ESR and UV/vis in a matrix at low temperature, and by laser flash photolysis in solution at room temperature. These studies indicated that although both carbenes generated a fairly stable complex with copper ions, the 4-pyridyl isomer formed a high-spin species as a result of ferromagnetic interaction between the 3d spin of metal ions and the 2p spins of triplet carbene. Such an interaction in the corresponding 3-isomer is likely to be antiferromagnetic. This is further confirmed by magnetic measurements using a Superconducting Quantum Interference Device (SQUID). The results demonstrate that extension of this method will enable stable high-spin polycarbenes to be obtained.

Introduction

Molecular magnetism, in which the spins of unpaired electrons in π -orbitals of light atoms such as carbon, nitrogen, and oxygen are mainly responsible for the magnetic properties, is attracting an ever-increasing

amount of interest. Many attempts to prepare organic ferromagnetic materials have been made.^{1,2} The spin sources used for such studies are mostly thermodynamically stable radicals such as phenoxy,³ triphenylmethyls,⁴ and nitroxides,⁵ mainly due to their ease of preparation and use. These radicals have some potential problems. For instance, exchange coupling between neighboring nitroxides is weak. 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.^{6,7} Iwamura and co-workers have prepared a "starburst"-type nona(diazo) compound, a

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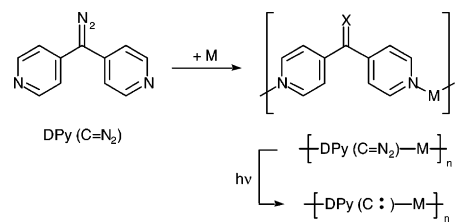
precursor of nonacarbene, and have demonstrated that the nine diazo groups are photolyzed at low temperature to give a nonadecet ground state ($S = 9$).⁷

However, these systems have two disadvantages that hinder their extension to usable magnetic materials. First, a triplet carbene unit is highly unstable and lacks stability for practical applications under ambient conditions.⁸ To overcome this difficulty, we attempted to stabilize triplet carbenes, and succeeded in preparing fairly stable ones that survive for several days in solution at room temperature.^{9,10} The next step is to explore a way of connecting them, while retaining a robust π -spin polarization.

The second disadvantage is that diazo groups, generally employed as precursors for carbenes, are also, in general, labile,¹¹ and hence cannot be used as building blocks for the preparation of more complicated poly(diazo) compounds. We found 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-trimethylsilylethynylphenyl)diazomethane. Three units of the diazo compound are then 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.¹² Thus it is potentially possible to prepare a poly(diazo) compound by extending this method.¹³

Another method for preparing poly(diazo) compounds is to use heterospin systems comprised of 2p spins of organic radicals and 3d spins of magnetic metal ions.^{14,15}

SCHEME 1



The strategy is based on the supramolecular chemistry exhibited by pyridine- and polypyridine-metal ions.¹⁶ For instance, bis(4-pyridyl)diazomethane, DPy(C=N₂), formed a polymeric chain structure [DPy(C=N₂)-M-] by ligation with coordinatively unsaturated metal ions (M). The 3d spins on metal ions in the chain do not interact with each other, but once triplet bis(4-pyridyl)carbene, DPy(C:), is generated upon irradiation, they start to interact with each other through the 2p spins on the carbene center, thereby generating a high-spin system comprised of 2p and 3d spins (Scheme 1).¹⁴

This suggests that if a pyridyl group is introduced on a phenyl ring of a sterically congested diphenyldiazomethane, a precursor for a persistent triplet carbene, a polymeric diazo compound chain should be attainable after coordination with metal ions. However, it needs to be confirmed whether the 2p spins of triplet carbene, generated upon photolysis of the chain, can indeed interact magnetically with the 3d spin of metal ions through the pyridyl group located remote from the carbene center. If so, the overall magnetic properties will also be affected by the position of the coordinating nitrogen in the pyridine ring. Iwamura and co-worker have investigated the exchange coupling of the spins of copper(II) ion coordinated with the ring nitrogen atoms and *N-tert*-butylaminoxyl radical attached as a substituent on the pyridine and *N*-phenylimidazole rings and shown the 2p spins of *N-tert*-butylaminoxyl radicals indeed interact magnetically with the 3d spin of metal ions but the magnitude of interaction in the complex using *N*-phenylimidazole rings is much smaller than that observed for the complex using pyridine ring. This indicates that the interaction through a remote π -system is possible but is considerably weakened due to the presence of many intervening π -bonds.¹⁷ However, the mode and magnitude of similar interactions of the 2p spins of triplet carbene through a distant ligating site is not known.

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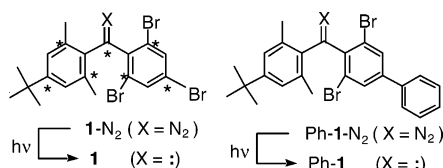
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SCHEME 2



To examine these issues, we have prepared diphenyldiazomethanes having pyridyl groups and have characterized the magnetic properties of the photoproducts formed from these diazo compounds.

Results and Discussion

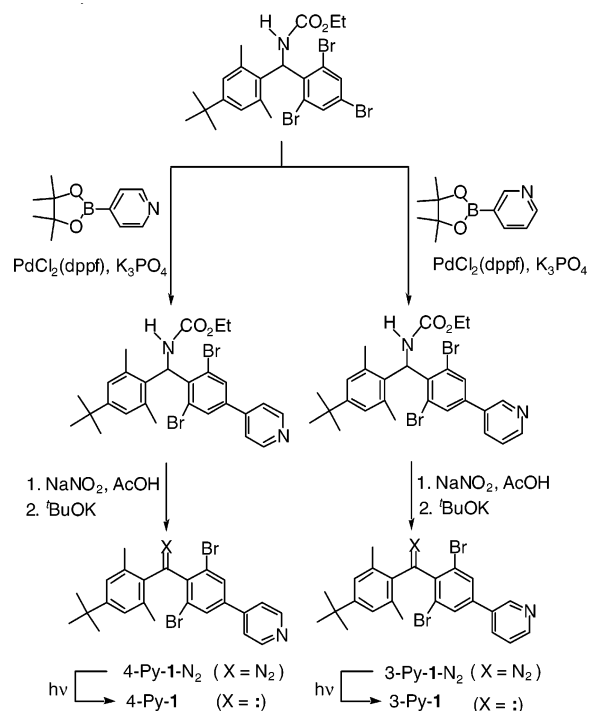
(A) Design and Preparation of Precursor Diazomethane. A diphenyldiazomethane unit used in this study was (2,4,6-tribromophenyl)(4-*tert*-butyl-2,6-dimethylphenyl)diazomethane, **1-N₂**, which can generate a fairly persistent triplet diphenylcarbene (**31**).¹⁸ Before preparing a desired precursor, the spin densities of organic spin sources need to be considered. The nonbonding molecular orbitals (NBMOs) of **31** were studied using the simple Hückel molecular orbital method, in which the atoms having nonzero NBMO coefficients have been stated. To a first approximation, the spin densities are assumed to be generated on the atoms with such nonzero coefficients. Thus, ligand pyridyl groups need to be introduced at the ortho and/or para positions, which have NBMO spin densities such that the interactions of the spins are transmitted effectively to a ligand.^{19,20} We therefore decided to introduce pyridyl groups at the para position of **1-N₂**, for synthetic reasons (Scheme 2).

The spin densities at the bridging groups are also important factors to take into account. The nonbonding molecular orbitals (NBMOs) of the isomeric carbenes 3- and 4-pyridylcarbene suggest that, while in the para isomer 4-pyridylcarbene, nonzero NBMO coefficients are expected to be on the pyridyl nitrogen, zero NBMO coefficients are expected on the pyridyl nitrogen atom in the meta isomer 3-pyridylcarbene, and hence the magnitude of the spin interactions is expected to be small. The sign of the spin polarization of the π -electrons on the nitrogen atom is also different between the two isomers.

These factors will affect the overall spin states if the 2p and 3d spins interact magnetically. To test this idea, we prepared sterically congested diaryldiazomethanes having a 3- and 4-pyridyl group (3- and 4-Py-**1-N₂**, respectively) as a ring substituent, and characterized the magnetic properties of the complex formed as a result of coordination with Cu(II) ions followed by irradiation.

All attempts to prepare a desired diazo compound by reacting pyridylboronic acid with the diazomethane

SCHEME 3



under Suzuki coupling conditions²¹ were unsuccessful. However, the coupling reaction of the precursory carbamate took place smoothly to give [2,6-dibromo-4-(3- and 4-pyridyl)phenyl](4-*tert*-butyl-2,6-dimethylphenyl)methylcarbamate, which was converted to the corresponding diazo compounds (3- and 4-Py-**1-N₂**) by a routine method (Scheme 3).

(B) Spectroscopic Studies of Metal-Free Diazomethanes (3- and 4-Py-1-N₂**).** Before examining the magnetic properties of the species generated by photolysis of a complex between the desired diazo compounds Py-**1-N₂** and metal ions, we characterized free carbenes from 3- and 4-Py-**1-N₂**.

Electron Spin Resonance (ESR). Irradiation ($\lambda > 350$ nm) of 4-Py-**1-N₂** (2.7×10^{-2} M) in 2-methyltetrahydrofuran (2-MTHF) at 77 K gave ESR signals of randomly oriented triplet molecules (Figure 1a). The signals were analyzed in terms of the zero-field splitting (ZFS) parameters with $D = 0.420$ cm⁻¹ and $E = 0.0290$ cm⁻¹ ($E/D = 0.069$).²² The values showed unequivocally that the triplet signals are due to triplet [2,6-dibromo-4-(4-pyridyl)phenyl](4-*tert*-butyl-2,6-dimethylphenyl)carbene (4-Py-**31**) generated by photodissociation of 4-Py-**1-N₂**. Similar irradiation of 3-Py-**1-N₂** (3.9×10^{-2} M) in 2-MTHF gave triplet signals ascribable to triplet [2,6-dibromo-4-(3-pyridyl)phenyl](4-*tert*-butyl-2,6-dimethylphenyl)carbene (3-Py-**31**) with ZFS parameters of $D = 0.410$ cm⁻¹ and $E = 0.0270$ cm⁻¹ ($E/D = 0.066$) (Figure 1b).

These values can be compared with those reported for the triplet carbene before pyridination, (4-*tert*-butyl-2,6-

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(22) ESR signals of brominated diarylcarbenes are generally very broad¹⁸ and hence not all transitions are clearly observed. To determine ZFS parameters, we employed computer simulation.

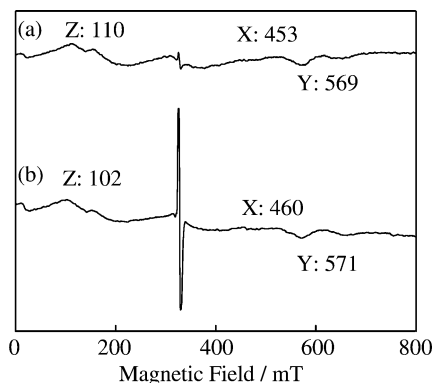


FIGURE 1. ESR spectra obtained by irradiation of compound 4-Py-1-N₂ (a) and 3-Py-1-N₂ (b) in 2-methyltetrahydrofuran at 77 K. The signal at 334 mT is ascribable to a doublet species fortuitously produced during the photolysis of diazo compound.

dimethylphenyl)(2,4,6-tribromophenyl)carbene (³1) ($D = 0.423 \text{ cm}^{-1}$ and $E = 0.0326 \text{ cm}^{-1}$, $E/D = 0.0771$)¹⁷ and a phenylated analogue, (2,6-dibromo-4-phenylphenyl)(4-*tert*-butyl-2,6-dimethylphenyl)carbene (Ph-³1) ($D = 0.348 \text{ cm}^{-1}$ and $E = 0.0326 \text{ cm}^{-1}$, $E/D = 0.0937$).²³

The structure of triplet carbenes is characterized by ESR ZFS parameters D and E .²⁴ The D value is related to the separation between the unpaired electrons. The E value, when weighted by D , is a measure of the deviation from axial symmetry. For diarylcarbenes, this value will thus depend on the magnitude of the central C–C–C angle. Since the E value depends on the magnitude of the central angle, the reduction in E indicates that the carbene adopts a structure with an expanded C–C–C angle upon annealing. This interpretation is supported by the observation that a substantial reduction in E is usually accompanied by a significant reduction in D , indicating that the electrons are becoming more delocalized.

The ZFS parameters of Py-³1, especially the D values, are closer to those reported for the triplet carbene before pyridination (³1) and apparently larger than those for the phenylated analogue Ph-³1. This suggests that the extent of delocalization of unpaired electrons into pyridyl groups at para positions is not significant compared to that of the phenyl ring.

The ESR signals not only were stable at this temperature but disappeared irreversibly when the matrix was thawed to room temperature. The thermal stability of the triplet carbenes could be estimated by thawing the matrix containing triplet carbenes gradually and then recooling it to 77 K, to measure the signal. This procedure can compensate for weakening of signals due to Curie's law.²³ The characteristic bands due to Py-³1 started to decay slowly at 100 K and decayed rather sharply at 120 K. The triplet signals of brominated DPCs are generally weak and broad. The signals of Py-³1 were not strong

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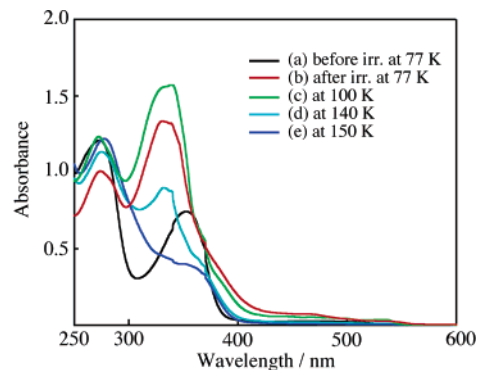


FIGURE 2. UV/vis spectra obtained by irradiation of diazo compound 4-Py-1-N₂: (a) spectra of 4-Py-1-N₂ in 2-methyltetrahydrofuran at 77 K; (b) the same sample after irradiation ($\lambda > 350 \text{ nm}$); (c–e) the same sample after thawing to 100 (c), 140 (d), and 150 K (e).

enough to allow thermal stability. Instead, the thermal stability of Py-³1 was estimated more accurately by monitoring the UV/vis spectra of ³1 as a function of temperature (vide infra).

UV/Visible Spectroscopy (UV/Vis). Optical spectroscopic monitoring in the frozen medium gave analogous results. Irradiation ($\lambda > 350 \text{ nm}$) of 4-Py-1-N₂ ($5.4 \times 10^{-4} \text{ M}$) in 2-MTHF at 77 K resulted in the appearance of new absorption bands at the expense of the original absorption due to 4-Py-1-N₂. The new spectrum consists of two identifiable features: an intense UV band with a maximum at 333 nm and weak, broad bands extending from 410 to 550 nm (Figure 2). These features are usually present in the spectrum of triplet diarylcarbenes.²⁵ Since ESR signals due to triplet carbene were observed under identical conditions, we can safely assign the absorption spectrum to the triplet carbene 4-Py-³1. The bands can be compared with those observed for carbene before pyridination, ³1, which exhibited rather weak bands at 337 and 349 nm. The rather strong bands in the longer wavelength region exhibited by Py-³1 are similar to those observed for the phenylated analogue, Ph-³1, and show the role of the pyridyl groups at the para position.

The glassy solution did not exhibit any changes until the matrix temperature was raised to 100 K, but the bands started to disappear rather sharply at around 140 K, and disappeared irreversibly when the temperature was raised to 150 K. The thermal stability is thus essentially similar to that observed for ³1 and Ph-³1. Similar results were obtained in the photolysis of the meta isomer, 3-Py-1-N₂ (Figure 3). The absorption spectrum and thermal stability of 3-Py-³1 are essentially identical with those observed for the corresponding 4-isomer.

Laser Flash Photolysis (LFP). Laser flash photolysis (LFP) of 4-Py-1-N₂ ($1.5 \times 10^{-4} \text{ M}$) in degassed benzene at room temperature produced a transient species showing a strong absorption band at 380 nm (Figure 4). Due to overlap of the absorption maxima of the diazo precursor 4-Py-1-N₂, the sample was not sufficiently transparent for adequate monitoring in the 300–370 nm region.

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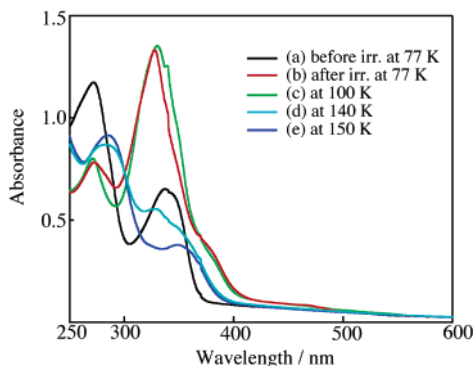


FIGURE 3. UV/vis spectra obtained by irradiation of diazo compound 3-Py-1-N₂: (a) spectra of 3-Py-1-N₂ in 2-methyltetrahydrofuran at 77 K; (b) the same sample after irradiation ($\lambda > 350$ nm); (c–e) the same sample after thawing to 100 (c), 140 (d), and 150 K (e).

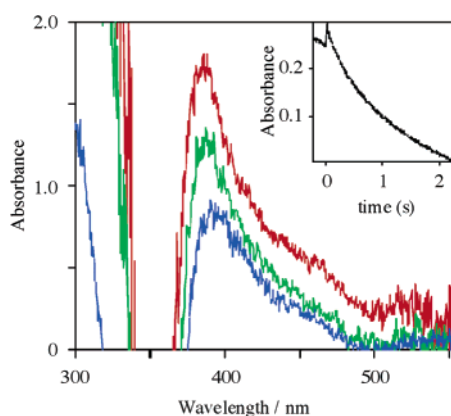


FIGURE 4. Absorption of transient products obtained upon 308-nm excitation of diazo compound 4-Py-1-N₂ in degassed benzene at room temperature recorded 10 μ s (red), 100 ms (green), and 1 s (blue) after excitation. The inset shows the time course of the absorption at 350 nm (oscillogram trace).

Therefore, direct comparison of the transient bands with those observed in the matrix at low temperature was not possible. It is likely that we are observing the tailing part of the absorption band due to 4-Py-³1. This assignment was supported by trapping experiments (vide infra). All absorption bands decayed in a similar manner. The inset in Figure 4 shows the decay of 4-Py-³1 in the absence of trapping reagents, which is found to be second order ($2k/\epsilon l = 1.6 \text{ s}^{-1}$). The rough lifetime of 4-Py-³1 was estimated in the form of the half-life, $t_{1/2}$, to be 0.8 s.

When LFP was carried out on a nondegassed benzene solution of 4-Py-1-N₂ (1.5×10^{-4} M), the half-life of 4-Py-³1 decreased dramatically, and a broad absorption band with a maximum at 420 nm appeared at the expense of the absorption due to 4-Py-³1 (Figure S1, Supporting Information). The spent solution was found to contain the corresponding ketone 4-Py-1-O. It is well documented^{26,27} that diarylcarbenes with triplet ground states are readily trapped by oxygen to generate the corresponding diaryl ketone oxides, which are easily observed directly, either by matrix isolation or by flash photolysis,

(26) See for review: Sander, W. *Angew. Chem., Int. Ed. Engl.* **1990**, 29, 344. (b) Bunnelle, W. *Chem. Rev.* **1991**, 91, 336.

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

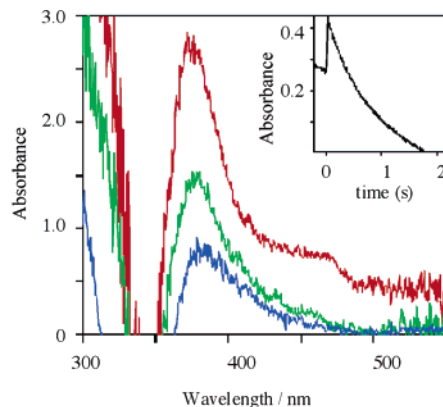
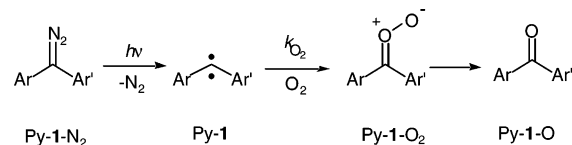


FIGURE 5. Absorption of transient products obtained upon 308-nm excitation of diazo compound 3-Py-1-N₂ in degassed benzene at room temperature recorded 10 μ s (red), 100 ms (green), and 1 s (blue) after excitation. The inset shows the time course of the absorption at 340 nm (oscillogram trace).

SCHEME 4



and show a broad absorption band centered at 390–450 nm. Thus, the observations can be interpreted as indicating that 4-Py-³1 is trapped by oxygen to form the carbonyl oxide (4-Py-1-O₂), which confirms that the transient absorption quenched by oxygen is due to 4-Py-³1 (Scheme 4).

The apparent build-up rate constant, k_{obs} , of the carbonyl oxide (4-Py-1-O₂) is essentially identical with that of the decay of 4-Py-³1, and k_{obs} is expressed as given in eq 1

$$k_{\text{obs}} = k_0 + k_{\text{O}_2}[\text{O}_2] \quad (1)$$

where k_0 represents the rate of decay of 4-Py-³1 in the absence of oxygen and k_{O_2} is the rate constant for the quenching of 4-Py-³1 by oxygen. A plot of the observed pseudo-first-order rate constant of the formation of the oxide against [O₂] is linear (Figure S1, Supporting Information). From the slope of this plot, k_{O_2} was determined to be $2.2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$.

Similar LFP of the meta isomer 3-Py-1-N₂ (1.5×10^{-4} M) gave a transient absorption band with a maximum at 380 nm, which decayed in a second-order manner ($2k/\epsilon l = 1.3 \text{ s}^{-1}$) with a half-life of 0.8 s (Figure 5). The rate constant for the quenching by oxygen, k_{O_2} , was determined to be $2.6 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ (Figure S2, Supporting Information).

Once again, these values are comparable to that observed for the triplet carbene before pyridination, ³1 ($t_{1/2} = 0.55 \text{ s}$),¹⁸ and that for the phenylated analogue Ph-³1 ($t_{1/2} = 0.5 \text{ s}$),²³ suggesting that the introduction of the pyridyl group does not decrease the stability of the triplet state.

(C) Spectroscopic Studies of Photoproducts of Complex between Py-1-N₂ and Cu(hfac)₂. All of the above observations suggest that we now have a fairly

persistent triplet carbene unit that has a pyridine ligand bridgeable with metal ions. The next step is to characterize the magnetic properties of the photoproducts of the complex between Py-1-N₂ and a metal ion.

It has been demonstrated that the sign and magnitude of the exchange coupling between metal ions and an organic radical depend not only on the periodicity of the ligand π -orbitals, but also on the orbitals occupied by the unpaired d electrons of the metal ions.^{14a} For instance, ferromagnetic interaction is observed between the carbenes and the copper ions in the [Cu(hfac)₂{4-DPy(C:)}] (hfac = hexafluoroacetylacetonate) system, while anti-ferromagnetic interaction is observed between the carbenes and the manganese ions in the [Mn(hfac)₂{4-DPy(C:)}] system. This is explained in terms of the difference in the overlapping mode of the magnetic orbitals in the metal ions and the nitrogen atom on the pyridine ligands. In the Cu(II) complexes, the magnetic orbital is $d_{x^2-y^2}$ and orthogonal to the $p\pi$ -orbital at the pyridyl nitrogen, in which the spin is polarized due to the presence of the triplet carbene. Hund's rule would predict the coupling to be ferromagnetic. On the other hand, in the Mn(II) complexes, the magnetic orbital that interacts with carbene is d_{xz} and hence the interaction with the $2p\pi$ -orbital at the pyridine nitrogen is a π -type magnetic one. In this case, the unpaired electrons are expected to couple antiferromagnetically.

Thus, if Cu(II) is used as a metal ion, a ferromagnetic interaction would be expected in the complex with 4-Py-³1. Since the sign of the spin polarization of the π -electrons on the nitrogen atom in 3-Py-³1 may be opposite to that of 4-Py-³1, an antiferromagnetic interaction will be induced between the carbene center and the copper ion. We thus chose Cu(hfac)₂ as a metal ion for this work.

ESR. Solutions of 4-Py-1-N₂ (13.6×10^{-3} M) in 2-MTHF and Cu(hfac)₂ (6.8×10^{-3} M) in 2-MTHF were mixed at a 2:1 molar ratio at room temperature, and the mixture was allowed to stand overnight.

The solution was placed in the cryostat of the low-temperature ESR cavity. ESR signals at 260, 275, 291, 312, and 321 mT, which are characteristic of the magnetic orbital $d_{x^2-y^2}$ in the Cu(II) ion of Cu(hfac)₂,²⁸ were seen before irradiation. When the solution was irradiated ($\lambda > 350$ nm) at 77 K, rather broad signals gradually appeared at around 331 mT, at the expense of the signals due to the isolated Cu(II) ion in Cu(hfac)₂ (Figure 6). The original signals due to Cu(II) were recovered when the sample was warmed to room temperature and recooled. Similar ESR spectral changes have been observed for the 2:1 complex of (phenyl)(4-pyridyl)carbene with the Cu(II) ion, which has been shown to have a ferromagnetic interaction between the carbene and the copper ion. The observation that no significant signals due to isolated triplet carbene 4-Py-³1 were observed suggests that the pyridine moiety binds with Cu(hfac)₂ essentially in a nearly quantitative manner under these cryogenic conditions.

To estimate the thermal stability of the signals, the sample was warmed to a desired temperature, allowed to stand at this temperature for 5 min, and recooled to 77 K to measure the ESR signals. The new signals started to disappear at 120 K but were observable up to

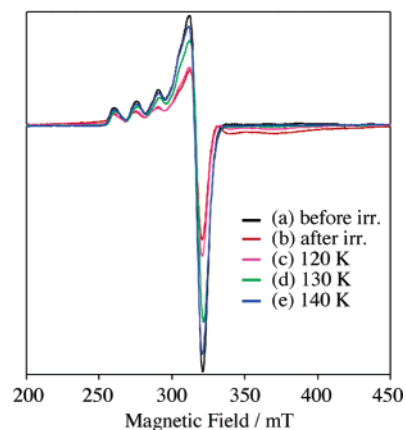


FIGURE 6. ESR spectra obtained by irradiation of 4-Py-1-N₂ and Cu(hfac)₂ in 2-MTHF mixed in a 2:1 molar ratio: (a, b) ESR spectrum before (a) and after (b) irradiation ($\lambda > 350$ nm) at 77 K; (c–e) ESR spectra observed at 77 K in 2-methyltetrahydrofuran after warming the matrix to 120 (c), 130 (d), and 140 K (e).

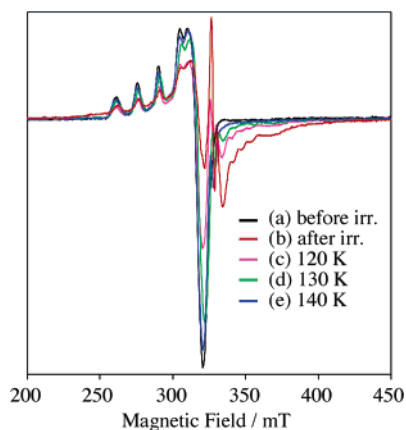


FIGURE 7. ESR spectra obtained by irradiation of 3-Py-1-N₂ and Cu(hfac)₂ in 2-MTHF mixed in a 2:1 molar ratio: (a, b) ESR spectrum before (a) and after (b) irradiation ($\lambda > 350$ nm) at 77 K; (c–e) ESR spectra observed at 77 K in 2-methyltetrahydrofuran after warming the matrix to 120 (c), 130 (d), and 140 K (e).

130 K. The signals were replaced by those due to the Cu(II) ion at around 140 K.

It should be noted that the signals of di(4-pyridyl)carbene–Cu(hfac)₂ disappeared irreversibly at temperatures higher than 60 K. Thus, the remarkable thermal stability of the 4-Py-1–Cu complex is seen.

Similar irradiation of a Cu(II) complex of the meta isomer 3-Py-1-N₂ (2.6×10^{-3} M) gave a different spectrum. Upon irradiation at 77 K, rather sharp signals at 325–354 mT were observed, at the expense of the signals due to the isolated Cu(II) ion. Once again, the original signals due to Cu(II) were recovered when the sample was warmed to room temperature and recooled (Figure 7), and no significant signals due to isolated triplet carbene ³1 were observed. The shape of the signals is completely different from that observed for the 4-Py-³1–Cu(II) complex. Upon warming the matrix, the sharp signals started to decrease at around 120 K and were replaced by those due to the Cu(II) ion at around 140 K.

Although the spectral changes upon irradiation of the

(28) Sugiura, Y. *Inorg. Chem.* **1978**, *17*, 2178.

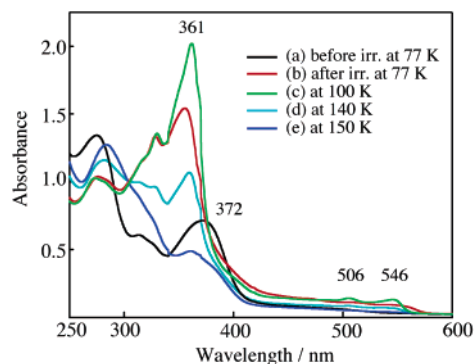


FIGURE 8. UV/vis spectra obtained by irradiation of 4-Py-1-N₂ and Cu(hfac)₂ in 2-MTHF mixed in a 2:1 molar ratio: (a, b) UV/vis spectra before (a) and after (b) irradiation at 77 K; (c–e) the same sample after thawing to 100 (c), 140 (d), and 150 K (e).

Py-1-N₂Cu complexes differed between the two isomers, they were not clear enough to judge the difference in the mode of magnetic interaction.

UV/Vis. Irradiation of a 2:1 mixture of 4-Py-1-N₂ and Cu(hfac)₂ in 2-MTHF (2.7×10^{-4} M) at 77 K gave rise to new absorption bands at the expense of the original absorption due to the complex. The new spectrum again consists of two identifiable features, an intense UV band with an apparent maximum at 361 nm and weak, broad bands with apparent maxima around 506 and 546 nm (Figure 8). Since the ESR signals most likely ascribable to the carbene–Cu complex are observed under identical conditions, we can assign the absorption spectrum to the complex. These bands can be compared with those of the metal-free triplet carbene 4-Py-³1 (337 nm and broad bands at 400–550 nm). A similar slight red shift of the characteristic absorption due to carbene after complexation with Cu(hfac)₂ has also been noted in di(4-pyridyl)-carbene–Cu(hfac)₂ systems. The glassy solution did not exhibit any changes for hours at this temperature, but all the bands disappeared irreversibly when the temperature was raised to 150 K. Thus, remarkable thermal stability of the 4-Py-1–Cu complex is once again noted.

Similar irradiation of a 2:1 mixture of 3-Py-1-N₂ and Cu(hfac)₂ in 2-MTHF (1.3×10^{-4} M) at 77 K gave rise to new absorption bands at the expense of the original absorption due to the complex (Figure 9). In this case, the new spectrum is very similar to that of the metal-free triplet carbene 3-Py-³1, with little shift. This may be interpreted in terms of weak interaction between the carbene center and the copper ion and/or a difference in the mode of magnetic interaction. The absorption bands disappeared irreversibly at a temperature around 150 K.

Superconducting Quantum Interference Device (SQUID) Measurements. To obtain the spin quantum numbers of the Py-1-Cu complex more definitively, the magnetic properties before and after photolysis of the Py-1-N₂–copper complex in 2-MTHF solutions were studied using a SQUID magneto/susceptometer.

The 2-MTHF solution of the 2:1 4-Py-1-N₂–copper complex (3.0×10^{-4} M) was placed inside the sample compartment of a SQUID magneto/susceptometer and was irradiated at 5–10 K by light ($\lambda = 488$ nm) from an Ar ion laser through an optical fiber. The development of magnetization (M /emu) at 5 K in a constant field of 5

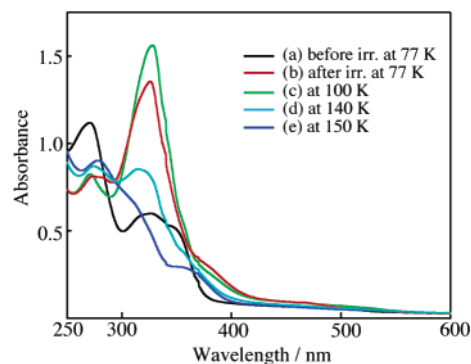


FIGURE 9. UV/vis spectra obtained by irradiation of 3-Py-1-N₂ and Cu(hfac)₂ in 2-MTHF mixed in a 2:1 molar ratio: (a, b) UV/vis spectra before (a) and after (b) irradiation at 77 K; (c–e) the same sample after thawing to 100 (c), 140 (d), and 150 K (e).

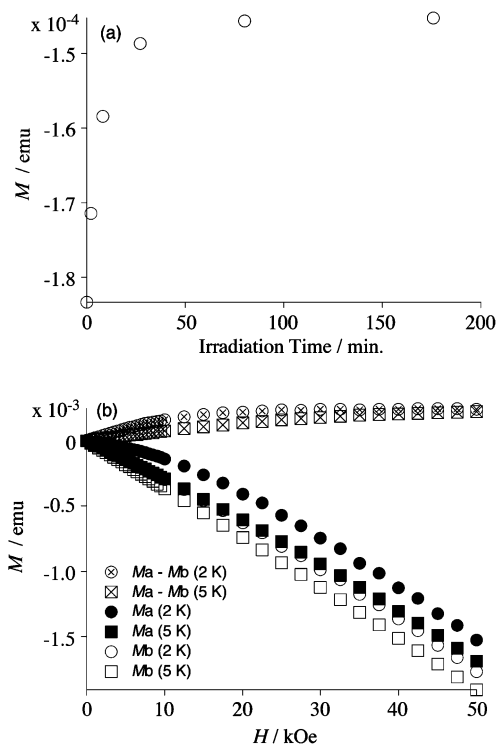


FIGURE 10. (a) Plot of magnetization (M in emu) as a function of irradiation time observed in the photolysis of 4-Py-1-N₂ and Cu(hfac)₂ in 2-MTHF mixed in a 2:1 molar ratio measured at 5.0 K and 5 kOe. (b) Field dependence of the magnetization of the photoproduct from a 2:1 complex of 4-Py-1-N₂ with Cu(hfac)₂ in 0.3 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 $M = M_a - M_b$.

kOe with irradiation time was measured in situ for the sample and is shown in Figure 10a. 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 (Figure 10b).

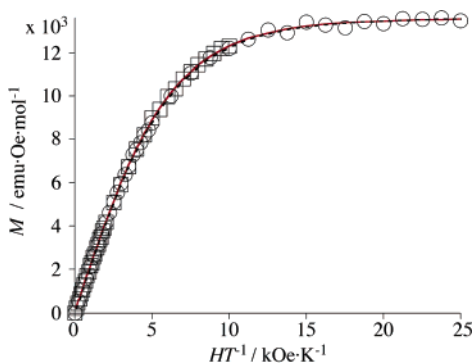


FIGURE 11. Plot of M vs H/T of the photoproduct from a 2:1 complex of 4-Py-1-N₂ with Cu(hfac)₂ measured at 2.0 (○) and 5.0 (□) K. The red and broken lines show fitting curves by eqs 4 and 5, respectively.

Magnetization of the copper complex before and after irradiation is expressed as follows:

$$M_b = M_{\text{Cu}} + M_{\text{dia}} \quad (2)$$

$$M_a = FM_{\text{comp}} + (1 - F)M_{\text{Cu}} + M_{\text{dia}} \quad (3)$$

where M_{comp} and M_{Cu} are the magnetization due to the carbene–Cu complexes and the diazo–copper complexes, respectively, and F is a photolysis factor. The magnetization (M) due to the species generated by photolysis was obtained as the difference between M_a and M_b : $M = M_a - M_b = F(M_{\text{comp}} - M_{\text{Cu}})$. Thus, the effect of diamagnetic and any paramagnetic impurities could be canceled out by this treatment.

The experimental data were analyzed by best-fitting the Brillouin function $B(\chi)$ as given by eq 4:²⁹

$$M = M_a - M_b = F(M_{\text{comp}} - M_{\text{Cu}}) = F\{Ng\mu_B SB(\chi) - Ng'\mu_B B(\chi')/2\} \quad (4)$$

where $\chi = gS\mu_B H/(k_B T)$, $\chi' = g'\mu_B H/(2k_B T)$, and the other symbols have their usual meaning. The g' value for the complexes of Cu(hfac)₂ with 4-Py-1-N₂ was 2.14, which was obtained from the ESR spectrum before irradiation, under similar conditions. The experimental data (M vs H/T) for the 4-Py-1-N₂–copper complex after irradiation were fitted with eq 4 with $S = 2.01 \pm 0.01$ and $F = 0.82 \pm 0.01$. The fitting curve is shown in Figure 11 as a red line.³⁰

The estimated S value was thus slightly lower than the theoretical one for when two carbene centers ($S = 2$) interact with a copper(II) ion ($S = 1/2$) ferromagnetically ($S = 2.5$). The lower S value may be due to a diminished spin density at the pyridyl nitrogen located remote from the carbene center. However, the magnetization data at two different temperatures were fitted to the same Brillouin function (Figure 11), and hence the sample generated by irradiation of the 4-Py-1-N₂–copper complex is considered to be a ground state, at least at 5 K.

Then the lower S value is probably ascribed to a carbene defect due to incomplete photolysis of the diazo compounds or decomposition of carbenes. If one assumes

that three kinds of magnetic species, the biscarbene complex ($S = 5/2$), a one-carbene defected monocarbene complex ($S = 3/2$), and a two-carbene defected noncarbene complex ($S = 1/2$) exist in the matrix after irradiation, the magnetization expression is written as:

$$M_b = M_{\text{Cu}} + M_{\text{dia}}$$

$$M_a = F_{\text{bis}}M_{\text{bis}} + F_{\text{mono}}M_{\text{mono}} + (1 - F_{\text{bis}} - F_{\text{mono}})M_{\text{Cu}} + M_{\text{dia}}$$

$$M = M_a - M_b = F_{\text{bis}}M_{\text{bis}} + F_{\text{mono}}M_{\text{mono}} - (F_{\text{bis}} + F_{\text{mono}})M_{\text{Cu}} = F_{\text{bis}}\{(5/2)Ng\mu_B B(\chi_{\text{bis}})\} + F_{\text{mono}}\{(3/2)Ng\mu_B B(\chi_{\text{mono}})\} - (F_{\text{bis}} + F_{\text{mono}})\{Ng'\mu_B B(\chi')/2\} \quad (5)$$

where $\chi_{\text{bis}} = (5/2)g\mu_B H/(k_B T)$, $\chi_{\text{mono}} = (3/2)g\mu_B H/(k_B T)$, and F_{bis} and F_{mono} are the molar fractions of biscarbene and monocarbene complexes, respectively. When the experimental data (M vs H/T) were analyzed in terms of eq 5, the fitted curve (broken line) with $F_{\text{bis}} = 0.33 \pm 0.01$ and $F_{\text{mono}} = 0.59 \pm 0.02$ exactly traced the experimental data (solid line in Figure 11).³⁰ In other words, the resulting 4-Py-³1–copper complex is comprised of a 33:59:8 mixture of copper ion complexed with biscarbene, monobarbene, and noncarbene.³¹

The overall results for the field dependence of M for the complex of Cu(hfac)₂ with 4-Py-³1 suggest that the generated carbene centers interact ferromagnetically with copper(II) ions, as was expected.

The data obtained for the photoproducts from similar irradiation of the 2-MTHF solution of the 2:1 3-Py-1-N₂–copper complex (1.0 mM) were also analyzed using the Brillouin function (Figures 12 and 13). The experimental data (M vs H/T) for the 3-Py-1-N₂–copper complex after irradiation were analyzed in terms of eq 4 with a fitting curve with $S = 1.00 \pm 0.03$ and $F = 0.60 \pm 0.03$ (Figure 13).³⁰ The S value of the 3-Py-³1–copper complex is distinctly lower than that of the 4-Py-³1–copper complex. Although this value corresponds to the theoretical one for magnetically isolated carbene 3-Py-³1, it is notable that the saturation magnetization (M_s) at 2.5×10^4 Oe/K is 3.26×10^3 emu·Oe/mol. This value corresponds to only 29% of that expected for magnetically isolated carbene. This may be due to incomplete photodecomposition of 3-Py-1-N₂. However, the degree of photolysis was estimated to be >95% by comparing the $n-\pi^*$ absorption of the diazo moiety in the UV/vis spectra before and after the SQUID measurement. In addition, ESR results for the 3-Py-³1–copper complex indicated that the carbene centers interacted magnetically with the copper ion.

Thus, the low S and M_s values can be explained in terms of the antiferromagnetic interaction between the carbene centers and the copper ion in the complex. Coordination of a Cu(II) ion to the pyridyl ligand of 4-Py-

(31) This does not mean that the sample with the same composition is formed in ESR and UV/vis measurements since the conditions under which the complex is generated are intrinsically very different among the three methods, SQUID, ESR and UV/vis, in terms of the sample concentration, generation temperatures, light source, sample conditions, and so on. So we think that it is unlikely that the sample with the same compositions under these circumstances should be formed under three different spectroscopic measurements.

(29) Carlin, R. L. *Magnetochemistry*; Springer-Verlag: Berlin, Germany, 1986.

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

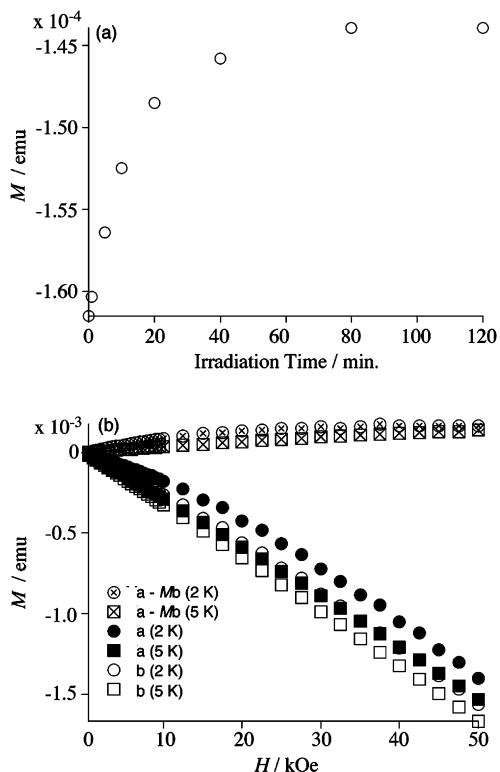


FIGURE 12. (a) Plot of magnetization (M in emu) as a function of irradiation time observed in the photolysis of 3-Py-1-N₂ and Cu(hfac)₂ in 2-MTHF mixed in a 2:1 molar ratio measured at 5.0 K and 5 kOe. (b) Field dependence of the magnetization of the photoproduct from a 2:1 complex of 3-Py-1-N₂ with Cu(hfac)₂ in 0.3 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 $M = M_a - M_b$.

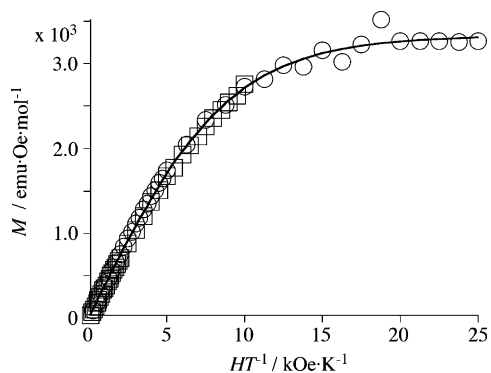


FIGURE 13. Plot of M vs HT^{-1} of the photoproduct from a 2:1 complex of 3-Py-1-N₂ with Cu(hfac)₂ measured at 2.0 (○) and 5.0 (□) K. The solid line shows the fitting curve by eq 4.

³¹ induces a ferromagnetic exchange interaction, due to a spin polarization mechanism and the interaction arising from the orthogonal relationship of singly occupied $d_{x^2-y^2}$ orbitals on the Cu(II) ion with the π -orbitals on the nitrogen atom of the pyridine. On the other hand, the sign of the polarization of the π -electrons on the nitrogen atom for 3-Py-³¹ may be opposite to that of 4-Py-³¹. Therefore, an antiferromagnetic interaction should be induced between the carbene center and the copper ion to give low S and M_S values.

Conclusions

The present results demonstrate that the 2p spins of triplet carbene can interact magnetically with the 3d spin of metal ions, through the pyridyl group located remote from the carbene center. Interestingly, the regiospecificity in the exchange coupling of magnetic metal ions observed for bis(pyridyl)carbene systems where the spins are “directly” transmitted to the ligand nitrogen atom is retained in the present system. Thus a ferromagnetic interaction is observed for the copper ion complex with the 4-pyridyl isomer, while an antiferromagnetic interaction is observed in the corresponding 3-isomer.

It is interesting to compare the present results with that observed for the complex of Cu(hfac)₂ and *N*-{4-(*N*-oxyl-*tert*-butylamino)phenyl}imidazole (4-NOIm).¹⁷ Since the magnitude of the exchange coupling between a triplet carbene and a neighboring radical center is expected to be larger than that between radicals, one may expect the magnitude of the interaction in the present complex is larger than that observed for the complex using *N*-{4-(*N*-oxyl-*tert*-butylamino)phenyl}imidazole. Unfortunately we were not able to estimate the value at present. However, it should be noted here that the magnetic measurements for the complex of Cu(hfac)₂ and 4-NOIm were made in the crystalline state in which the chain of the complex is expected to be held tightly, while the present measurements were made in a frozen solution where the chain may be more flexible. It has been shown that the apparent spin quantum number of the ferromagnetic chains consisting of a 1:1 complex between bis-(4-pyridylcarbene)(DPy) and copper ions amounts to $S = 33.6$, but this value drops down to 6.4 when it is measured in a frozen solution of 2-MTHF. Thus we need to do magnetic measurements on a crystalline sample of Py-1-N₂-copper complex before we draw meaningful conclusions concerning this issue.

The carbene-copper complex showed remarkable stability, surviving temperatures up to 140 K in the 2-MTHF matrix, while the analogous copper ion complex with an unprotected pyridylcarbene decays at temperatures higher than 60 K. The results suggest that it should be possible to prepare a persistent high-spin polycarbene by extending this method. Since we have a fairly stable triplet carbene that can survive for a week in solution at room temperature, it should not be long before we can achieve a fairly stable high-spin polycarbene.

Experimental Section

Preparation of [2,6-Dibromo-4-(4-pyridyl)phenyl](4-*tert*-butyl-2,6-dimethylphenyl)diazomethane (4-Py-1-N₂). To a mixture of ethyl *N*-[2,4,6-tribromophenyl(4-*tert*-butyl-2,6-dimethylphenyl)methyl]carbamate^{13f} (100 mg, 0.18 mmol), 2-(4-pyridyl)-4,4,5,5-tetramethyl-1,3-dioxaborolane³² (108 mg, 0.53 mmol), [1,1'-bis(diphenylphosphino)ferrocene]palladium dichloride dichloromethane complex (PdCl₂(dppf)·CH₂Cl₂) (14 mg, 0.018 mol) and potassium phosphate (63 mg, 0.30 mmol) were added anhydrous 1,4-dioxane (2.5 mL) under Ar atmosphere and the mixture was stirred at 100 °C for 2 days. The mixture was then filtered and the filtrate was extracted with diethyl ether. The organic layer was washed with water, dried over anhydrous sodium sulfate, and concentrated under reduced pressure to leave a crude product that was column

(32) Coudret, C. *Synth. Commun.* **1996**, *26*, 3543.

chromatographed (silica gel, hexane:diethyl ether = 1:1) to give ethyl *N*-[[2,6-dibromophenyl-4-(4-pyridyl)phenyl](4-*tert*-butyl-2,6-dimethylphenyl)methyl]carbamate (32 mg, 32%) as a yellow semisolid; ^1H NMR (300 MHz, CDCl_3 , ppm) δ 8.68 (br s, 2H), 7.81 (s, 2H), 7.44 (d, $J = 4.41$ Hz, 2H), 6.99 (s, 2H), 6.49 (d, $J = 8.82$ Hz, 1H), 5.38 (d, $J = 8.64$ Hz), 4.26–4.13 (m, 2H), 2.23 (s, 6H), 1.29 (s, 9H), 1.27 (t, $J = 4.41$ Hz, 3H); ^{13}C NMR (75.5 MHz, CDCl_3 , ppm) δ 155.0, 150.6, 150.5, 144.7, 139.0, 138.9, 136.9, 132.5, 132.4, 127.0, 126.9, 125.3, 61.2, 58.1, 34.1, 31.2, 21.3, 14.8; EI-MS m/z (rel intensity) 576 ($M + 4$, 1.3), 574 ($M + 2$, 2.0) 572 (M^+ , 1.5), 495 (97.6), 493 (96.6), 57 (100); HRMS calcd for $\text{C}_{27}\text{H}_{30}\text{Br}_2\text{N}_2\text{O}_2$ 572.0673, found m/z 572.0647.

To a stirred and cooled solution of the carbamate (94 mg, 0.16 mmol) in acetic anhydride (6 mL) and acetic acid (4.5 mL) was added sodium nitrite (226 mg, 3.28 mmol) in portions at 0 °C over a period of 2.5 h and the mixture was stirred for 1 day at room temperature after addition was complete. The mixture was poured into ice and was extracted with diethyl ether. The ethereal layer was washed with aqueous sodium carbonate water, dried over anhydrous sodium sulfate, and concentrated under reduced pressure to give ethyl *N*-nitroso-*N*-[[2,6-dibromophenyl-4-(4-pyridyl)phenyl](4-*tert*-butyl-2,6-dimethylphenyl)methyl]carbamate (85 mg, 86%) as a brown semisolid; ^1H NMR (300 MHz, CDCl_3 , ppm) δ 8.69 (br s, 2H), δ 7.84 (s, 2H), 7.46 (d, $J = 4.41$ Hz, 2H), 6.99 (s, 2H), 6.93 (s, 1H), 4.38–4.36 (m, 2H), 2.23 (s, 6H), 1.28 (s, 9H), 1.25 (t, $J = 3.31$ Hz, 3H).

To a stirred solution of the nitrosocarbamate (85 mg, 0.14 mmol) in dry tetrahydrofuran (5 mL) was added potassium *tert*-butoxide (32 mg, 0.28 mmol) at –20 °C under argon atmosphere. After being stirred overnight, the reaction mixture was poured into ice and extracted with ether, and the ethereal layer was washed with water, dried over anhydrous sodium sulfate, and concentrated under reduced pressure to leave a crude product that was purified by column chromatography (alumina, hexane at –20 °C), followed by GPC (chloroform, monitored at 320 nm) to give [2,6-dibromo-4-(4-pyridyl)phenyl](4-*tert*-butyl-2,6-dimethylphenyl)diazomethane (4-Py-1-N₂) (15 mg, 21%) as an orange semisolid; ^1H NMR (300 MHz, CDCl_3 , ppm) δ 8.71 (br s, 2H), 7.86 (s, 2H), 7.47 (br s, 2H), 7.10 (s, 2H), 2.20 (s, 6H), 1.31 (s, 9H); ^{13}C NMR (75.5 MHz, CDCl_3 , ppm) δ 151.0, 150.63, 150.58, 144.7, 139.1, 137.5, 133.0, 131.6, 126.0, 125.8, 124.7, 63.5, 34.3, 31.3, 21.2; IR (NaCl, cm^{-1}) $\nu_{\text{C}=\text{N}_2}$ 2053.

Preparation of [2,6-Dibromo-4-(3-pyridyl)phenyl](4-*tert*-butyl-2,6-dimethylphenyl)diazomethane (3-Py-1-N₂). To a mixture of ethyl *N*-[[2,4,6-tribromophenyl(4-*tert*-butyl-2,6-dimethylphenyl)methyl]carbamate³³ (100 mg, 0.18 mmol), 2-(3-pyridyl)-4,4,5,5-tetramethyl-1,3-dioxaborolane³³ (108 mg, 0.53 mmol), [1,1'-bis(diphenylphosphino)ferrocene]palladium dichloride dichloromethane complex ($\text{PdCl}_2(\text{dppf})\cdot\text{CH}_2\text{Cl}_2$) (14 mg, 0.018 mol) and potassium phosphate (63 mg, 0.30 mmol) was added anhydrous 1,4-dioxane (2.5 mL) under Ar atmosphere and the mixture was stirred at 100 °C for 2 days. The mixture was then filtered and the filtrate was extracted with diethyl ether. The organic layer was washed with water, dried over anhydrous sodium sulfate, and concentrated under reduced pressure to leave a crude product that was column chromatographed (silica gel, hexane:diethyl ether = 1:1) to give ethyl *N*-[[2,6-dibromophenyl-4-(3-pyridyl)phenyl](4-*tert*-butyl-2,6-dimethylphenyl)methyl]carbamate (36 mg, 36%) as a yellow semisolid; ^1H NMR (300 MHz, CDCl_3 , ppm) δ 8.79 (br s, 1H), 8.62 (br d, $J = 4.23$ Hz, 1H), 7.81 (dt, $J = 8.08$, 1.84 Hz, 1H), 7.77 (s, 2H), 7.39–7.35 (m, 2H), 6.99 (s, 2H), 6.50 (d, $J = 8.64$ Hz, 1H), 5.39 (d, $J = 8.64$ Hz, 1H), 4.26–4.11 (m, 2H), 2.24 (s, 6H), 1.29 (s, 9H), 1.27 (t, $J = 6.98$ Hz, 3H); ^{13}C NMR (75.5 MHz, CDCl_3 , ppm) δ 155.0, 150.6, 149.5, 148.0, 138.7, 138.0, 137.0, 134.2, 132.6, 132.5, 127.0, 126.9, 126.6, 125.2, 61.2, 58.0, 34.1, 31.2, 21.9, 14.8; EI-MS m/z (rel intensity) 576

($M + 4$, 1.3), 574 ($M + 2$, 2.0) 572 (M^+ , 1.5), 495 (97.6), 493 (96.6), 57 (100); HRMS calcd for $\text{C}_{27}\text{H}_{30}\text{Br}_2\text{N}_2\text{O}_2$ 572.0673, found m/z 572.0649.

To a stirred and cooled solution of the carbamate (17 mg, 0.030 mmol) in acetic anhydride (1.2 mL) and acetic acid (0.9 mL) was added sodium nitrite (50 mg, 0.72 mmol) in portions at 0 °C over a period of 2.5 h and the mixture was stirred for 1 day at room temperature after addition was complete. The mixture was poured into ice and extracted with diethyl ether. The ethereal layer was washed with aqueous sodium carbonate water, dried over anhydrous sodium sulfate, and concentrated under reduced pressure to give ethyl *N*-nitroso-*N*-[[2,6-dibromophenyl-4-(3-pyridyl)phenyl](4-*tert*-butyl-2,6-dimethylphenyl)methyl]carbamate (19 mg, quant.) as a brown semisolid; ^1H NMR (300 MHz, CDCl_3 , ppm) δ 8.80 (br s, 1H), 8.64 (br d, $J = 4.23$ Hz, 1H), 7.86 (dt, $J = 8.08$, 1.84 Hz, 1H), 7.77 (s, 2H), 7.45–7.38 (m, 2H), 6.99 (s, 2H), 6.93 (d, $J = 8.64$ Hz, 1H), 4.38–4.36 (m, 2H), 2.23 (s, 6H), 1.28 (s, 9H), 1.25 (t, $J = 6.98$ Hz, 3H).

To a stirred solution of the nitrosocarbamate (19 mg, 0.030 mmol) in dry tetrahydrofuran (5 mL) was added potassium *tert*-butoxide (8 mg, 0.07 mmol) at –20 °C under argon atmosphere. After being stirred overnight, the reaction mixture was poured into ice and extracted with ether, and the ethereal layer was washed with water, dried over anhydrous sodium sulfate, and concentrated under reduced pressure to leave a crude product that was purified by column chromatography (alumina, hexane at –20 °C), followed by GPC (chloroform, monitored at 320 nm) to give [2,6-dibromo-4-(3-pyridyl)phenyl](4-*tert*-butyl-2,6-dimethylphenyl)diazomethane (3-Py-1-N₂) (2 mg, 28%) as an orange semisolid; ^1H NMR (300 MHz, CDCl_3 , ppm) δ 8.82 (br s, 1H), 8.64 (br d, $J = 4.23$ Hz, 1H), 7.84 (dt, $J = 8.08$, 1.84 Hz, 1H), 7.81 (s, 2H), 7.41–7.36 (m, 2H), 7.10 (s, 2H), 2.20 (s, 6H), 1.31 (s, 9H); ^{13}C NMR (75.5 MHz, CDCl_3 , ppm) δ 150.9, 149.5, 147.9, 140.0, 137.4, 134.2, 134.1, 131.9, 131.6, 126.9, 126.0, 125.9, 124.8, 63.4, 34.3, 31.3, 21.2; IR (NaCl, cm^{-1}) $\nu_{\text{C}=\text{N}_2}$ 2054.

Irradiation for Product Analysis. In a typical run, a solution of the diazo compound (ca. 10 mg) in solvent was placed in a Pyrex tube and irradiated with a high-pressure, 300-W mercury lamp until all the diazo compound was destroyed. The irradiation mixture was concentrated on a rotary evaporator below 20 °C. Individual components were isolated by preparative TLC and identified by NMR and MS (see the Supporting Information).

EPR Measurements. The diazo compound was dissolved in 2-methyltetrahydrofuran 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 500 W Xe lamp using a Pyrex filter. EPR spectra were measured on a 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 Digital Temperature Indicator/Controller, providing the measurements accuracy within ± 0.1 K and the control ability within ± 0.2 K. Errors in the measurements of component amplitudes did not exceed 5%, 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 a variable-temperature liquid-nitrogen cryostat 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 300-W high-pressure mercury lamp using a Pyrex filter, and the spectral changes were recorded at appropriate time intervals. The

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spectral changes upon thawing were also monitored by carefully controlling the matrix temperature with a Temperature Controller.

Flash Photolysis. All flash measurements were made on a 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- μ s pulse duration), (ii) a 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) an 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 150 W xenon short arc lamp 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 photomultiplier tube through a linear image sensor (512 photodiodes used). Timing of the excitation pulse, the probe beam, and the detection system was achieved through a digital synchro scope that was interfaced to a computer. This allowed for rapid processing and storage of the data and provided printed graphic capabilities. Each trace was also displayed on a monitor.

A sample was placed in a long-necked Pyrex tube that had a sidearm connected to a quartz fluorescence cuvette and 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 Superconducting Quantum Interference Device (SQUID) magnetometer/susceptometer. Irradiation with light from an argon ion laser (488 nm) through a flexible optical fiber that 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 50–60 μ L sample solution (0.3–1.0 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 5 K in a field range of 0–50 kOe. The plots of the magnetization [$M = (M_a - M_b)$] versus the magnetic field were analyzed in terms of the Brillouin function.

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Supporting Information Available: General methods, analytical and spectroscopic data for photoproducts of diazo compounds, transient absorption spectra obtained in LFP of 4- and 3-Py-1-N₂ in nondegassed benzene, and UV–vis spectra measure before and after SQUID measurements. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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