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Triplet Diphenylcarbenes Protected by Trifluoromethyl and Bromine Groups. A Triplet Carbene Surviving a Day in Solution at Room Temperature

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Abstract: Two types of diphenyldiazomethanes having two trifluoromethyl and two bromine groups at the ortho positions, either in unsymmetrical or in symmetrical fashion, that is, (2,6-dibromo-4-phenylphenyl)-[4-phenyl-2,6-bis(trifluoromethyl)phenyl]diazomethane (*U*-**1**$-N_2$) and bis(2-bromo-4-phenyl-6-trifluoromethylphenyl)diazomethane (*S*-**1**$-N_2$), are prepared. Triplet diphenylcarbenes (*U*-^{3}**1** or *S*-^{3}**1**) are generated from those precursors and are characterized by ESR, UV/vis spectroscopy at low temperature, as well as time-resolved UV/vis spectroscopy at room temperature. Those carbenes are shown to be at least 2 orders of magnitude less reactive than the most stable triplet diphenylcarbene thus far known, that is, bis(2,6-dibromo-4-phenylphenyl)carbene. It has been also shown that *S*-^{3}**1** is significantly more stable than *U*-^{3}**1** even though both have the same two kinds of substituents. It is suspected that the perpendicular alignment of the two most bulky groups is a more effective way to shield the carbenic center than the planar one. By this way, triplet substituted diphenylcarbene surviving nearly a day in solution at room temperature is realized for the first time.

Triplet carbenes are highly reactive organic radicals that are also notoriously difficult to stabilize.[1] To isolate the triplet carbene with its electronic integrity (one centered diradical) intact, steric protection is the ideal method. Attempts to stabilize triplet diphenylcarbenes by introducing various substituents at the ortho positions have been made.[2] This strategy, however, encounters a limitation when alkyl groups are employed as protecting groups. Triplet carbenes abstract hydrogen even from very poor sources of electrons such as CH bonds. Thus, *tert*-butyl groups, which have been successfully used to protect many reactive centers, are almost useless to stabilize triplet carbene center.[3] The bromine group was found to be a very effective protector.[4] Triplet bis(2,6-dibromo-4-*tert*-butylphenyl)carbene was shown to have a half-life of 16 s in solution at room temperature,[4c] ca. 8 orders of magnitude greater than "parent" diphenylcarbene (DPC). This is partly because the van der Waals radius of bromine groups is similar to that of methyl while the C−Br bond length is longer than C−C(Me). More importantly, halides are usually reactive toward singlet carbene, but they are not reactive with the triplet state.[5] Product analysis studies indicate that the main decay pathway is dimerization at the carbenic center.[4] This indicates that the carbene center is not completely shielded and hence carbene still has a space in which to undergo coupling with each other. To realize stable triplet carbene, we need to explore kinetic protectors that are bulky yet unreactive toward triplet carbenes.

The trifluoromethyl (CF_3) group has been regarded as an ideal kinetic protector of carbene because it is much bigger than methyl and bromine groups and C−F bonds are known to be almost the only type of bond unreactive toward carbenic center.[6] Ideally stable triplet DPC may be realized if one can generate DPC having four CF_3 groups at all of the ortho positions. However, it is synthetically almost impossible to prepare the precursor diphenyldiazomethane (DDM). Sterically congested DDMs are usually prepared from the corresponding diphenylmethyl halides by way of the methylcarbamates. The four ortho CF_3 groups introduced on the diphenylmethyl halides are

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(1) (a) Regitz, M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 674. (b) Dagani, R. *Chem. Eng. News* **1991**, *Jan. 28*, 19; **1994**, *May 2*, 20. (c) Heinemann, C.; Müller, T.; Apeloig, Y.; Schwartz, H. *J. Am. Chem. Soc.* **1996**, *118*, 2023. (d) Beohme, C.; Frenking, G. *J. Am. Chem. Soc.* **1996**, *118*, 2039. (e) Wentrup, C. *Science* **2001**, *292*, 1846. (f) Roth, H. D. *Nature* **2001**, *412*, 598. (g) Kirmse, W. *Angew. Chem., Int. Ed.* **2003**, *42*, 2117.

(2) See for reviews: (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.

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(4) (a) Tomioka, H.; Watanabe, T.; Hirai, K.; Furukawa, K.; Takui, T.; Itoh, K. *J. Am. Chem. Soc.* **1995**, *117*, 6376. (b) Tomioka, H.; Hattori, M.; Hirai, K. *J. Am. Chem. Soc.* **1996**, *118*, 8723. (c) Tomioka, H.; Watanabe, T.; Hattori, M.; Nomura, N.; Hirai, K. *J. Am. Chem. Soc.* **2002**, *124*, 474. (d) Hirai, K.; Iikubo, T.; Tomioka, H. *Chem. Lett.* **2002**, 1226.

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(6) Tomioka, H.; Taketsuji, H. *J. Chem. Soc., Chem. Commun.* **1997**, 1745.

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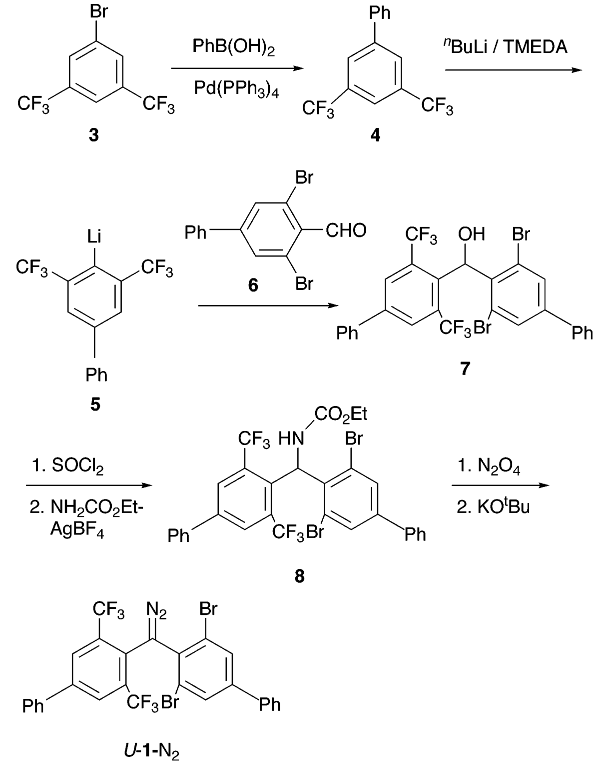
Scheme 1

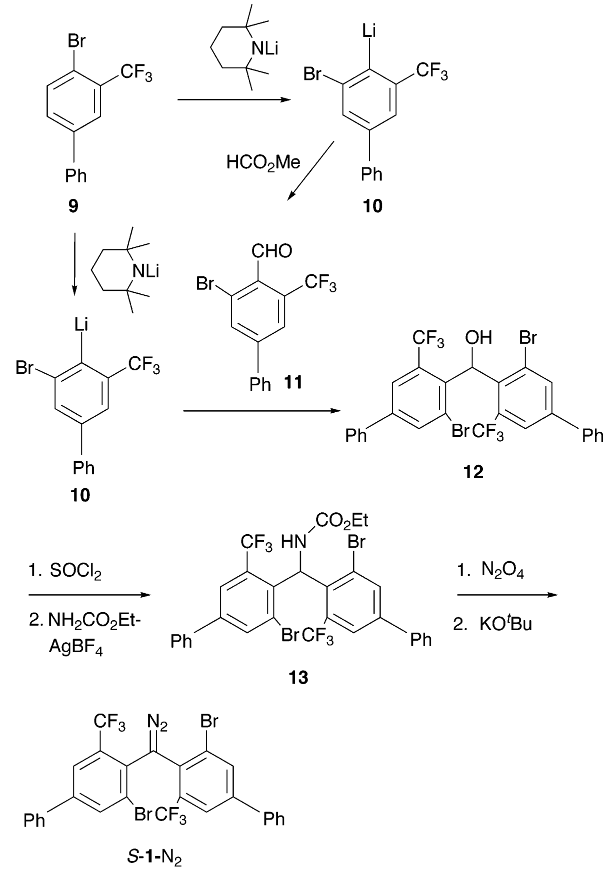


expected to shield the methyl carbon so tightly that the carbon has little space to accept a reagent for further modification. Bis[2,6-bis(trifluoromethyl)phenyl]methanol, a precursor for the desired diazomethane, was found to be completely inert to a further treatment. Thus, we decided to use bromine group as an auxiliary group and to attempt to prepare a precursor DDM having as many CF_3 groups as possible. We were able to prepare two kinds of DDMs having two CF_3 groups in addition to two bromine groups at all of the ortho positions. They are unsymmetrically substituted, having each of those two protectors in each of the phenyl rings, that is, (2,6-dibromo-4-phenylphenyl)-[4-phenyl-2,6-bis(trifluoromethyl)phenyl]diazomethane (*U*-**1**$-N_2$), and symmetrically substituted, having both groups in each one of the phenyl rings, that is, bis(2-bromo-4-phenyl-6-trifluoromethylphenyl)diazomethane (*S*-**1**$-N_2$). We wish to report here that DPCs generated from those precursor DDMs were very persistent, surviving a day in solution at room temperature.[7]

Results

Preparation of Precursor Diazomethanes. The diazomethanes that we used in this study are prepared according to the reaction procedure outlined in Schemes 1 and 2. The preparation of the unsymmetrical one was rather straightforward. Thus, 1,3-bis(trifluoromethyl)benzene having a phenyl group at position 5, prepared from the corresponding bromide (**3**) by the Suzuki coupling reaction, was converted to the 2-lithio derivative by simply treating with butyllithium/*N*,*N*,*N*′,*N*′-tetramethylethylenediamine (BuLi/TMEDA), which was then reacted with 2,6-dibromo-4-phenylbenzaldehyde to give the diarylmethyl alcohol (**7**). The alcohol was then converted to the corresponding DDM (*U*-**1**$-N_2$) by way of a carbamate[8] (Scheme 1).

Scheme 2



To prepare the symmetrical one, that is, *S*-**1**$-N_2$, 2-bromo-6-trifluoromethylphenyllithium was desired. The isomerization of 2-bromo-5-phenyl-3-trifluoromethylphenyllithium to 2-bromo-4-phenyl-6-trifluoromethylphenyllithium (**10**) at low temperature, a reaction originally reported by Schlosser,[9] worked quite well. Thus, treatment of 4-bromo-3-trifluoromethylbiphenyl (**9**) with lithium tetramethylpiperidine (LTMP), followed by the addition of methyl formate, gave 2-bromo-4-phenyl-6-trifluoromethylbenzaldehyde (**11**). The reaction of aldehyde **11** with a mixture of biphenyl **9** with LTMP gave the desired diarylmethyl alcohol (**12**). The alcohol was converted to *S*-**1**$-N_2$ by way of chloride and carbamate (**13**) as summarized in Scheme 2.

All of the diazomethanes were purified by silica gel chromatography at −10 °C followed by repeated chromatography on a gel permeation column. They were rather stable for diazomethane and could be stored in a refrigerator for several months without any appreciable decomposition.

We thus generated triplet carbenes (*U*-^{3}**1** or *S*-^{3}**1**) by irradiation of the precursor diazo compound (**1**$-N_2$) and characterized them by ESR, UV/vis spectroscopy at low temperature, as well as time-resolved UV/vis spectroscopy at room temperature. The structures and reactivities of **1** will be compared to the most stable triplet diphenylcarbene thus far known, that is, bis(2,6-dibromo-4-phenylphenyl)carbene **2**^{4d} (Scheme 3).

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[7] (a) Preliminary reports on the present study were published; Hirai, K.; Tomioka, H. *J. Am. Chem. Soc.* **1999**, *121*, 10213. (b) Here, we used a phenyl group instead of a *tert*-butyl group at the para-positions. The effect of the phenyl group on the stability of persistent triplet diphenylcarbenes has been investigated. See ref 4d.

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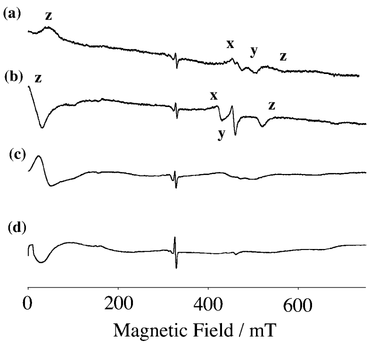
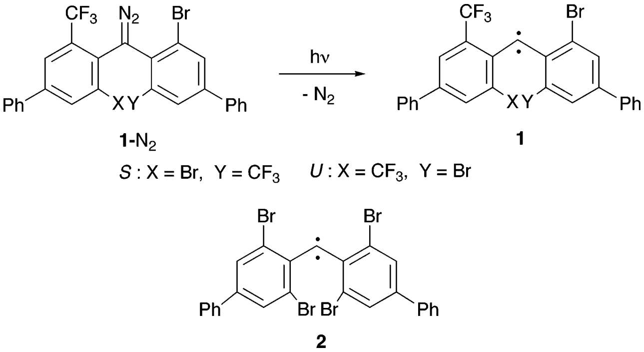


Figure 1. (a) ESR spectrum obtained by irradiation of diazo compound *U*-**1**$-N_2$ in 2-methyltetrahydrofuran at 77 K. (b) The same sample measured at 77 K after thawing to 110 K. (c) ESR spectrum obtained by irradiation of diazo compound *S*-**1**$-N_2$ in 2-methyltetrahydrofuran at 77 K. (d) The same sample measured at 77 K after thawing to 110 K.

Scheme 3



Spectroscopic Studies. (a) ESR Studies in Rigid Matrixes at Low Temperature. Irradiation ($\lambda > 300$ nm) of (2,6-dibromo-4-phenylphenyl)[4-phenyl-2,6-bis(trifluoromethyl)phenyl]diazomethane (*U*-**1**$-N_2$) in 2-methyltetrahydrofuran (2-MTHF) at 70 K gave rise to ESR signals with a typical fine structure pattern for unoriented triplet species[10] (Figure 1a). The signals are analyzed in terms of the zero-field splitting (zfs) parameters to be $D = 0.358$ cm^{-1} and $E = 0.0281$ cm^{-1} ($E/D = 0.079$), showing unequivocally that triplet signals are due to triplet (2,6-dibromo-4-phenylphenyl)[4-phenyl-2,6-bis(trifluoromethyl)phenyl]carbene (*U*-^{3}**1**).

The EPR signals not only were stable at this temperature but also survived even at 110 K. However, as the samples were warmed, a new set of triplet peaks appear at the expense of the original peaks (Figure 1b) with the zfs parameters of $D = 0.327$ cm^{-1} and $E = 0.0266$ cm^{-1} ($E/D = 0.081$). Cooling the sample to 77 K did not reverse this change. This is usually interpreted in terms of geometrical changes (vide infra).[11,12]

Similar irradiation of other precursor diazomethanes, bis(2-bromo-4-phenyl-6-trifluoromethylphenyl)diazomethane (*S*-**1**$-$N$_2$), in 2-MTHF glass at 20 K also gave rise to ESR spectra (Figure 1c) characteristic of randomly oriented triplet molecules.[10] The signal at 23.0 mT is assigned to a low-field *Z* transition, but those ascribable to high-field *X*, *Y*, and *Z* transitions are extremely weak.

Table 1. ESR[a] and UV/Vis[b] Spectral Data

triplet carbenes	*D* (cm^{-1})	*E* (cm^{-1})	*E*/*D*	λ_{max} (nm)	T_d[c] (K)
U-^{3}**1**	0.358	0.0281	0.079	357, 506	240
	(0.327	0.0266	0.081)		
S-^{3}**1**			*d*	358, 494	260
^{3}**2**	0.359	0.0301	0.0838	352, 497	170
	(0.402	0.0044	0.0109)		

[a] Measured in 2-MTHF at 77 K. Values in the parentheses are those measured after thawing to 100 K. [b] Measured in 2-MTHF. [c] Temperature at which absorption bands due to triplet carbenes disappeared in 2-MTHF. [d] ZFS parameters could not be determined (see text).

ESR signals sometimes become sharper when the measurements are made after the sample is warmed and recooled. This is partly because as the temperature is raised, the matrix softens and allows the carbene to assume a single preferred orientation rather than several slightly distorted orientations dictated by the trapping of the precursor in the frozen matrix.[11,12] Also, in the case of sterically congested triplet diarylcarbenes, a new set of triplet signals often appears at the expense of the original peaks, as in the case of *U*-^{3}**1**. However, the measurements after warming the sample to 110 K did not result in an increase in signal intensity to allow us to confidently determine the zfs parameters. Nevertheless, the signal due to the low-field *Z* transition suggests that triplet signals are due to triplet bis(2-bromo-4-phenyl-6-trifluoromethylphenyl)carbene (*S*-^{3}**1**) generated by photodissociation of *S*-**1**$-N_2$.

The *D* and *E* values are reported in Table 1, which includes *D* and *E* values observed for bis(4-phenyl-2,6-dibromophenyl)carbene ^{3}**2**[4d] for the sake of comparison.

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 weakening of signals due to the Currie law.[13] However, the triplet signals of brominated DPCs are generally weak and broad. The signals of ^{3}**1** were thus not strong enough to allow such estimation. Instead, thermal stability of ^{3}**1** was estimated in more accurately by monitoring the UV/vis spectra of ^{3}**1** as a function of temperature (vide infra).

(b) UV/Vis Studies in Rigid Matrixes at Low Temperature. Photolysis ($\lambda > 300$ nm) of *U*-**1**-N$_2$ in 2-MTHF glass at 77 K resulted in the appearance of new bands at the expense of the original absorption due to the starting diazo compound (Figure 2Ab). The new bands consist of two identifiable features, a strong and sharp maximum at 357 nm and a broad and weak band with apparent maximum at around 506 nm. These features, rather strong absorption bands in the UV region and a weak and broad band in the visible region, are usually present in the spectrum of triplet DPCs.[10] The glassy solution did not exhibit any changes for hours when kept at 77 K, but disappeared irreversibly when it was allowed to warm to room temperature and cooled to 77 K. On the basis of these observations coupled with ESR data, the absorption spectrum can be attributed to triplet carbene (*U*-^{3}**1**).

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(10) See for reviews of the EPR and UV/vis spectra of triplet carbenes: (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.

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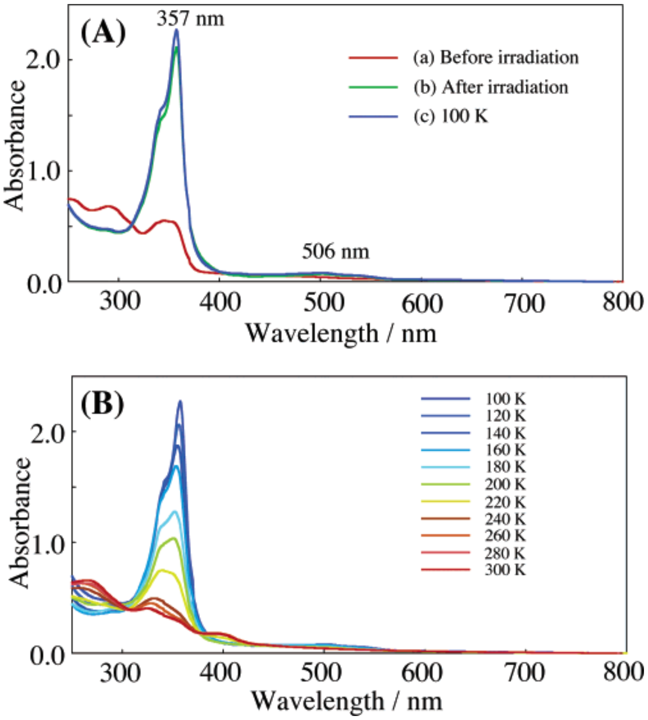

Figure 2. UV/vis spectra obtained by irradiation of diazo compound *U*-**1**−N_2. (A) (a) Spectrum of *U*-**1**−N_2 in 2-methyltetrahydrofuran at 77 K. (b) The same sample after irradiation (λ > 350 nm). (c) The same sample after thawing to 100 K. (B) UV/vis spectral change measured at 10 K increments upon thawing the same sample from 100 to 300 K. For the sake of simplicity, the spectral changes are shown in 20 K increments.

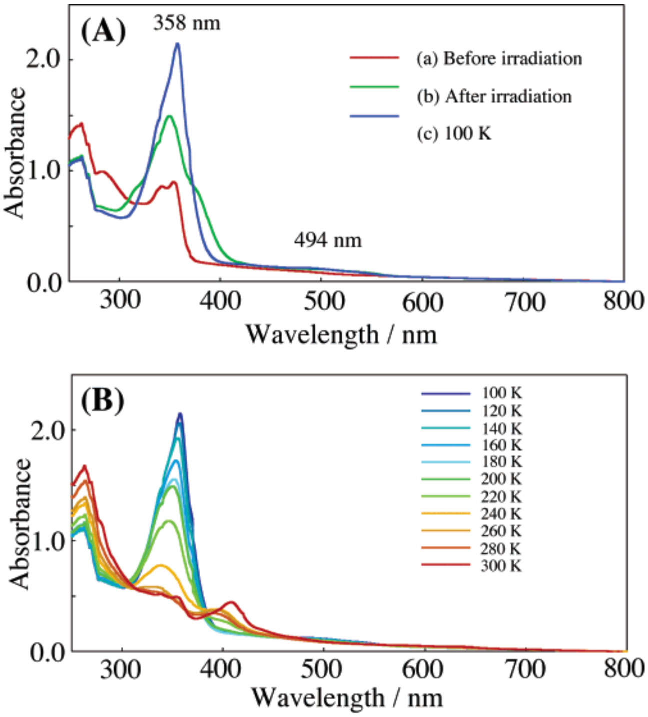

Figure 3. UV/vis spectra obtained by irradiation of diazo compound *S*-**1**−N_2. (A) (a) Spectrum of *S*-**1**−N_2 in 2-methyltetrahydrofuran at 77 K. (b) The same sample after irradiation (λ > 300 nm). (c) The same sample after thawing to 100 K. (B) UV/vis spectral change measured at 10 K increments upon warming the same sample from 100 to 300 K. For the sake of simplicity, the spectral changes are shown in 20 K increments.

The thermal stability is then estimated by raising the sample temperature in 10 K increments to the desired temperature, allowing it to stand for 5 min, and measuring the absorption bands. The characteristic bands due to *U*-^{3}**1** became sharp at 100 K. Similar changes in the UV/vis spectra upon thawing the matrix were also observed for other sterically congested diarylcarbenes and are generally interpreted in terms of geometrical changes of the carbenes (vide infra).[10−12] The bands started to decay slowly at 120 K, decayed rather sharply at around 200 K, and were observable up to 240 K.

Similar absorption but increased stabilities was noted for *S*-^{3}**1**. Photolysis (λ > 300 nm) of *S*-**1**−N_2 in 2-MTHF glass at 77 K resulted in the appearance of new bands showing a strong and sharp maximum at 358 nm and a broad and weak band with apparent maximum at around 494 nm, ascribable to *S*-^{3}**1** (Figure 3Ab). The characteristic bands due to *S*-^{3}**1** became sharp with a slight shift of the maximum from 358 to 368 nm at 100 K. The bands started to decay slowly at around 140 K, decayed rather sharply at 220 K, but were observable up to 260 K (Figure 3B).

It should be noted here that absorption bands of most triplet DPCs in 2-MTHF disappear in the temperature range 100−105 K[10] where the viscosity of the matrix changes dramatically from 10^7 to 10^3 P.[14] Even the absorption bands of relatively stable triplet diphenylcarbene ^{3}**2** disappear only up to 130 K in 2-MTHF.[4d]

This observation clearly demonstrates anomalous stability of ^{3}**1** for a triplet diphenylcarbene, where *S*-^{3}**1** is slightly more stable than *U*-^{3}**1**.

(c) Laser Flash Photolysis Studies in Solution at Room Temperature. To know the stability of the present carbenes more accurately, the lifetime is estimated in a degassed benzene at room temperature, in which we have measured the lifetime of a series of sterically congested diarylcarbenes.[2] The lifetime of the present carbenes **1** was too long to monitor by the laser flash photolysis (LFP) technique, which has been routinely used for such a study. Thus, a conventional UV/vis spectroscopic method was more conveniently employed in this case.

Brief irradiation of *U*-**1**−N_2 in degassed benzene at 20 °C with a 70−90 mJ, 308 nm pulse from XeCl excimer laser produced transient absorption bands, showing a strong maximum at 340 nm (Figure 4). The maximum of the band was shifted to a shorter wavelength than that observed in the photolysis of *U*-**1**−N_2 in 2-MTHF at 77 K. However, the transient bands were markedly quenched by oxygen to give the corresponding ketone oxide (vide infra), and hence we assigned the bands to *U*-^{3}**1**. The absorption bands decay very slowly, and the transient bands did not disappear completely even after 2 h under these conditions. The decay was found to be second order ($2k/\epsilon l$ = 3.26×10^{-3} s^{-1}). The approximate half-life ($t_{1/2}$) of *U*-^{3}**1** is estimated to be 11 min.

Similar irradiation of *S*-**1**−N_2 also produced transient bands at 344 nm (Figure 5). Although the maximum was again shifted to a shorter wavelength than that observed in photolysis of *S*-**1**−N_2 in 2-MTHF at 77 K, the bands were markedly quenched by oxygen to give the corresponding ketone oxide (vide infra) and hence were assigned to *U*-^{3}**1**. The spectrum attributable to *S*-^{3}**1** decayed much slower than that of the unsymmetrical one, *U*-^{3}**1**, and did not disappear completely even after standing a day.

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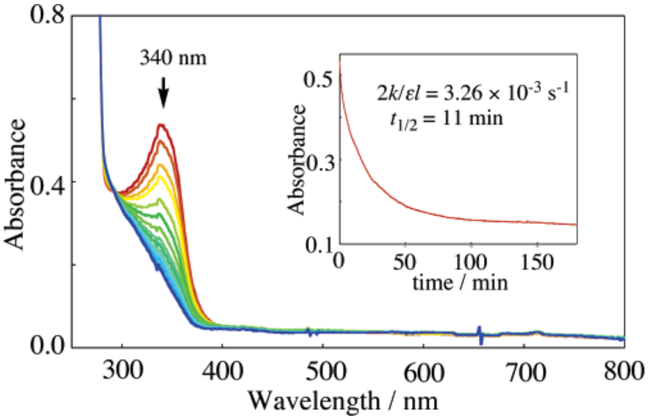


Figure 4. Absorption of transient products formed during irradiation of diazo compound *U*-**1**−N_2 in degassed benzene at room temperature recorded from immediately after irradiation to 300 min after excitation. The inset shows the time course of the absorption at 340 nm.

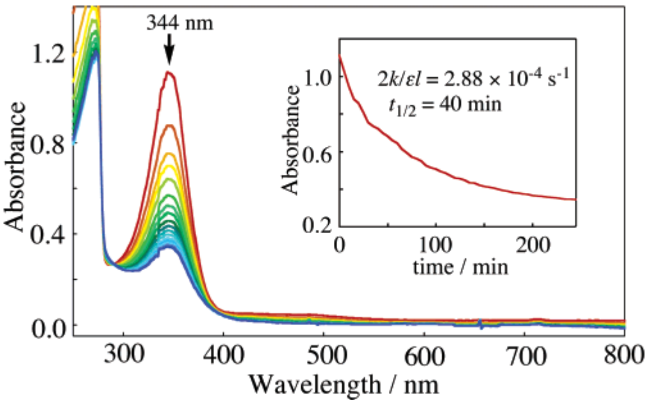


Figure 5. Absorption of transient products formed during irradiation of diazo compound *S*-**1**−N_2 in degassed benzene at room temperature recorded from immediately after irradiation to 300 min after excitation. The inset shows the time course of the absorption at 344 nm.

Triplet substituted diphenylcarbene surviving a day is realized for the first time. The decay was also found to be second order ($2k/\epsilon l = 2.88 \times 10^{-4}$ s^{-1}). The approximate half-life ($t_{1/2}$) of *S*-^{3}**1** is estimated to be 40 min.

The half-life ($t_{1/2}$) is just a measure of lifetime and cannot be regarded as a quantitative scale for reactivity. In this respect, the rate constant of the triplet carbene with a typical triplet quencher can be employed as a more quantitative scale of the reactivity. It is well-documented that carbenes with triplet ground states are readily trapped with oxygen or a good hydrogen donor such as 1,4-cyclohexadiene (CHD).[15] Therefore, the rate constants of the trapping reactions by O_2 and CHD, that is, k_{O2} or k_{CHD}, respectively, are used as a more quantitative scale to estimate the reactivities of the triplet carbenes.

LFP of *U*-**1**−N_2 in a nondegassed benzene solution resulted in a dramatic decrease in the lifetime of *U*-^{3}**1** and a concurrent appearance of a new absorption band at 420 nm (Figure 6). The spent solution was found to contain the corresponding benzophenone. It is well-documented[16,17] that diarylcarbenes with triplet ground states are readily trapped by oxygen to generate the corresponding diaryl ketone oxides, which show a broad absorption band centered at 390−450 nm (Scheme 4). Thus, our observations can be interpreted as indicating that the transient absorption quenched by oxygen is due to *U*-^{3}**1**. The rate of increase in the band at 420 nm is practically the same as the rate of decrease of the peak due to *U*-^{3}**1**, showing that *U*-^{3}**1** is quenched with oxygen to form carbonyl oxide (*U*-**1**−O_2). The rate constant (k_{O_2}) for the quenching of *U*-^{3}**1** by O_2 is determined to be 4.6×10^5 M^{-1} s^{-1} from a plot of the observed pseudo-first-order growth rate of *U*-**1**−O_2 as a function of [O_2] (Figure 7a). This is some 4 orders of magnitude smaller than that observed with the “parent” ^{3}DPC ($k_{O_2} = 5.0 \times 10^9$ M^{-1} s^{-1})[17f] and 1 order of magnitude smaller than that observed with the most stable triplet diphenylcarbene thus far known, that is, bis(4-phenyl-2,6-dibromophenyl)carbene **2**.[4d]

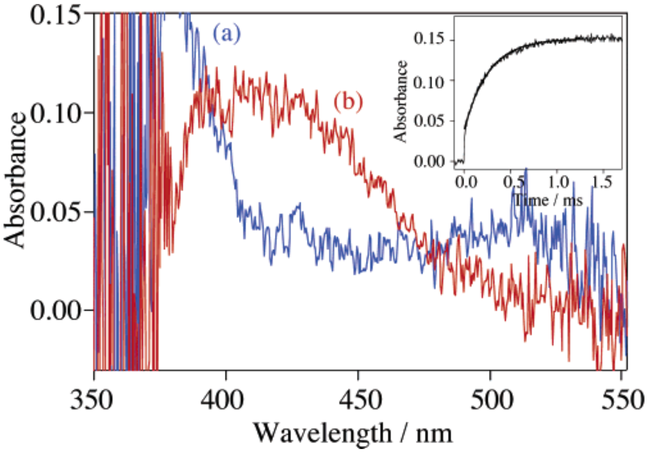
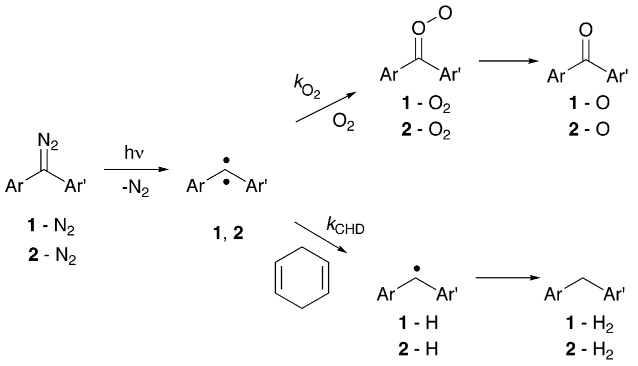


Figure 6. Transient absorption spectra obtained in LFP of *U*-**1**−N_2 (a) in degassed benzene and (b) in nondegassed benzene with a 308-nm excimer laser recorded 500 μs after the pulse. The inset shows oscillogram traces monitored at 420 nm.

Scheme 4



When a degassed benzene solution of *U*-**1**−N_2 containing 1,4-cyclohexadiene (CHD) was excited, a new species was formed, showing an absorption with $\lambda_{max} = 400$ nm, formed as the 344 nm signal of *U*-^{3}**1** decayed (Figure 8). The decay of *U*-^{3}**1** was again found to be kinetically correlated with the growth of the new species. Thus, this new signal was attributable to the corresponding diarylmethyl radical (*U*-**1**−H) formed as

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(15) See for reviews of the general reaction of triplet carbenes: Tomioka, H. In *Reactive Intermediate Chemistry*; Moss, A. M., Platz, M. S., Jones, M., Jr., Eds.; Wiley: New York, 2004; pp 375−461.

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

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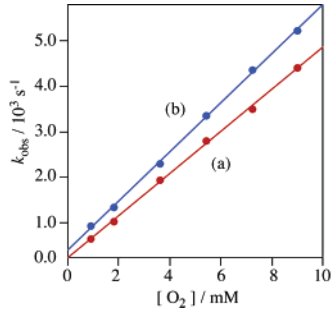

Figure 7. Plot of the growth of the diaryl ketone oxides (a: red) *U*-**1**$-O_2$ and (b: blue) *S*-**1**$-O_2$ monitored at 420 nm as a function of the concentration of oxygen.

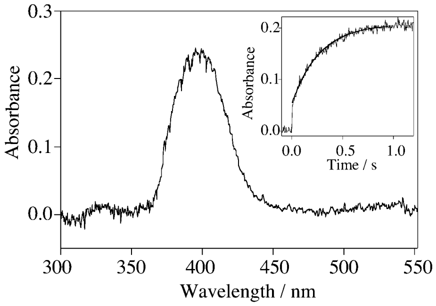

Figure 8. Transient absorption spectra obtained in LFP of *U*-**1**$-N_2$ in degassed benzene in the presence of 1,4-cyclohexadiene with a 308-nm excimer laser recorded 500 ms after the pulse. The inset shows oscillogram traces monitored at 410 nm.

a result of H abstraction of *U*-^{3}**1** from the diene, because it is now well-documented[15,18,19] that triplet arylcarbenes, generated in good hydrogen donor solvents, undergo H abstraction leading to the corresponding radicals (Scheme 4), which show transient absorptions at longer wavelengths than those of the precursor carbenes. The excellent hydrogen donor properties of CHD have been well recognized.[20] The spent solution was found to contain the diarylmethane as the main product. A plot of the observed pseudo-first-order rate constant of the formation of the radical against [CHD] is linear (Figure 9a), and the slope of this plot yields the absolute rate constant for the reaction of *U*-^{3}**1** with the diene, $k_{CHD} = 6.7$ M^{-1} s^{-1}, which is approximately 6 orders of magnitude smaller than that observed with the “parent” ^{3}DPC ($k_{CHD} = 1.0 \times 10^7$ M^{-1} s^{-1}).[19f]

Again, similar measurements were done for the other carbenes (*S*-^{3}**1**) (Figures S1 and S2), and the results are summarized in Table 2. It is interesting to note here that carbenes (*S*-^{3}**1**) showed essentially identical reactivities toward those typical triplet quenchers, that is, oxygen and CHD even though the stability of *S*-^{3}**1** estimated in degassed benzene and in 2-MTHF is significantly larger than its positional isomer *U*-^{3}**1**.

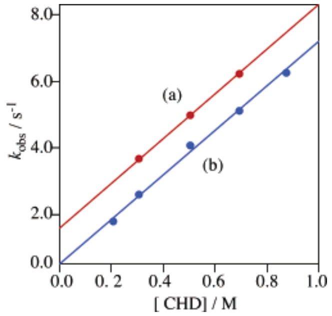

Figure 9. Plot of the growth of the diarylmethyl radicals (a: red) *U*-**1**$-$H and (b: blue) *S*-**1**$-$H monitored at 410 nm as a function of the concentration of 1,4-cyclohexadiene.

Table 2. Kinetic Data[a]

triplet carbenes	$2k/\epsilon l$ (s^{-1})	$t_{1/2}$ (min)	k_{O_2} (M^{-1} s^{-1})	k_{CHD} (M^{-1} s^{-1})
U-^{3}**1**	3.26×10^{-3}	11	4.6×10^5	6.7
S-^{3}**1**	2.88×10^{-4}	40	5.4×10^5	6.7
^{3}**2**	3.5×10^{-1}	0.2	7.5×10^6	2.8×10^2

[a] Measured in degassed benzene at room temperature.

Product Analysis Studies. Most of the sterically congested triplet DPCs decay mainly by undergoing dimerization at the carbenic center to give tetra(aryl)ethenes as the main product, when generated in degassed benzene at room temperature in the absence of appropriate triplet carbene quenchers such as oxygen and hydrogen donors, for instance, bis(2,4,6-trichlorophenyl)carbene produced tetrakis(2,4,6-trichlorophenyl)ethylene in ~80% yield when generated in benzene. In other words, unless this simple coupling process is not prevented, it is not possible to realize really stable triplet carbene. Triplet carbene ^{3}**2** also decayed by dimerization to give tetrakis(2,6-dibromo-4-phenylphenyl)ethylene, which underwent cyclization to give phenanthrene derivatives.

Photolysis of **1**$-N_2$ in degassed benzene gave a complex mixture. ^{1}H NMR spectra of the irradiation mixtures were too complicated to further characterize the structure. However, some of the fractions obtained by GPC of the photomixture showed a mass peak corresponding to the dimer of carbene **1** (Figures S3 and S4). ^{1}H NMR spectra of the fraction (Figures S5 and S6) were also extremely complicated, but are not likely to be assignable to those expected to be formed as a result of dimerization at the carbene center (or phenanthrene derivative to be derived from the dimer).

The complexity of the spectra can be explained in terms of possible isomerism in the carbene dimer even if the simple carbene dimer, that is, tetra(aryl)ethene, is formed. For instance, two isomers, syn and anti, can be expected for the carbene dimer produced in the photolysis of *U*-**1**$-N_2$. Close inspection of ^{1}H NMR spectra of the dimer suggested that the spectra could be best explained in terms of a 6:4 mixture of two isomers. On the other hand, such geometrical isomerism is not expected for the carbene dimer from photolysis of *S*-**1**$-N_2$. The inspection of the molecular models however indicated that rotational isomerism (atropisomerism) is plausible due to the steric repulsion between two bulky ortho-substituents, that is, bromine and trifluoromethyl groups in this case. Unfortunately, aromatic proton signals in this case are too complex to allow us to estimate the ratio of possible isomers.

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(18) For reviews, see: (a) Platz, M. S., Ed. *Kinetics and Spectroscopy of Carbenes and Biradicals*; Plenum: New York, 1990. (b) Jackson, J. E.; Platz, M. S. In *Advances in Carbene Chemistry*; Brinker, U., Ed.; JAI Press: Greenwich, CT, 1994; Vol. 1, pp 87−160.

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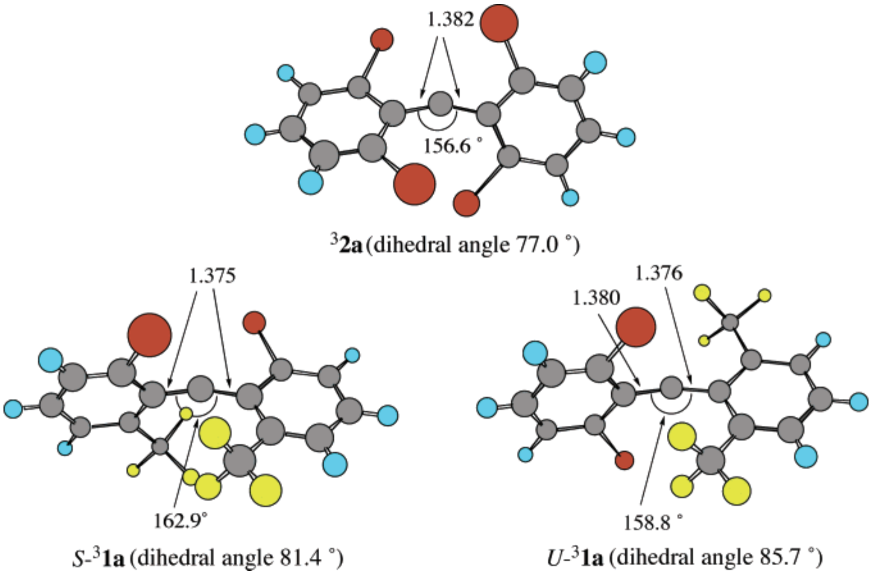

Figure 10. Selected geometrical parameters (distance in Å and angle in deg) for triplet bis(2,6-dibromophenyl)carbene (^{3}**2a**), [2,6-bis(trifluoromethyl)-phenyl](2,6-dibromophenyl)carbene (*U*-^{3}**1a**), and bis(2-bromo-6-trifluoromethylphenyl)carbene (*S*-^{3}**1a**) at B3LYP/6-31G* level of theory.

It has been also shown that triplet arylcarbenes start to decay by undergoing coupling at aromatic rings where considerable spin density must build up, as the carbenic center is sterically more tightly shielded. This usually resulted in a complex mixture.

Discussion

Comparison between ^{3}1 and ^{3}2. Effect of Trifluoromethyl Group As Opposed to Bromine Group as a Kinetic Protector. The kinetic and ESR data for ^{3}**1** are to be compared to those observed for the longest-lived triplet carbene thus far known, that is, bis(2,6-dibromo-4-phenylphenyl)carbene (^{3}**2**) [4d] (Tables 1 and 2).

It is clear that reactivities toward typical triplet quenchers, that is, oxygen and CHD, decrease by approximately 1 and 2 orders of magnitude, respectively, as two *o*-bromine groups in ^{3}**2** are replaced with two CF_3 groups. Similarly, the lifetimes in degassed benzene also increase by approximately 2 orders of magnitude. CF_3 is thus shown to be an excellent kinetic protector of triplet carbene.

We have shown that the inspection of X-ray crystal structures of precursory diphenyldiazomethanes (DDMs) shows how steric shielding of the ortho substituents affects the structures and stabilities of triplet DPCs.[21] It is noted that, as ortho substituents are introduced on DDMs, the dihedral angle (ω) between two phenyl rings increases, while the diazo carbon angle (θ) changes very little. For instance, θ/ω values of bis(4-bromophenyl)-diazomethane and bis(2,4,6-tribromophenyl)diazomethane are 126.9°/45.6° and 127.0°/70°, respectively.[21] In this way, the procarbenic carbon is shielded more effectively from external reagents by the protector substituents. Unfortunately, we were not able to determine the crystal structure of either *S*- or *U*-**1**−N_2 due to disorder issues. However, the crystal structure of (2,6-dibromo-4-*tert*-butylphenyl)[2,6-bis(trifluoromethyl)-4-*tert*-butylphenyl]diazomethane, a *p*-*tert*-butyl analogue of *U*-**1**−N_2, gave some insights on how the structure is affected when two bromine groups are replaced with trifluoromethyl groups. Thus, in this case, ω is increased to 80.8° while θ is still 127.8°. This indicates that the CF_3 group shields the carbon more effectively.[21]

Even though the distance between C(aromatic) and C(trifluoromethyl) is significantly shorter (1.6 Å) than that of C−Br (1.9 Å),[22] three fluorine atoms make the van der Waals radius of the trifluoromethyl group much larger than those of the methyl and bromine groups. Therefore, the phenyl rings are forced to rotate around the $C(=N_2)-C(Ar)$ bond to relieve the compression, which results in a larger dihedral angle. This motion will result in the more effective shielding of procarbenic carbon.

To obtain more direct insights into the difference between the structures of three triplet carbenes, triplet bis(2,6-dibromophenyl)carbene (^{3}**2a**), (2,6-dibromophenyl)[2,6-bis(trifluoromethyl)phenyl]carbene (*U*-^{3}**1a**), and bis(2-bromo-6-trifluoromethylphenyl)carbene (*S*-^{3}**1a**) (as models for ^{3}**2**, *U*-^{3}**1**, and *S*-^{3}**1**, respectively) are optimized by DFT calculations.[23,24] The optimized geometries at UB3LYP/6-31G* level of theory indicate that the carbene angle (θ)/the dihedral angle (ω) between two phenyl rings of tetrabrominated DPC ^{3}**2a** is 156.6°/77.0° but those for both *U*-^{3}**1a** and *S*-^{3}**1a** are 158.8°/85.7° and 162.9°/81.4°, respectively (Figure 10).[25]

These predictions indicate that both *U*-^{3}**1a** and *S*-^{3}**1a** have bent structures with a slightly wider angle of the carbene carbon and dihedral angles than those of ^{3}**2**. The inspection of the optimized geometries also indicates that, while both *U*- and *S*-^{3}**1a** have nearly perpendicular structures, that of ^{3}**2** is twisted from the perpendicular to a staggered one. Thus, the carbene center is better shielded in ^{3}**1a** than in ^{3}**2**.

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(25) Schaefer and co-workers optimized the structure of triplet (2,6-dibromo-4-*tert*-butylphenyl)[4-iso-propyl-2,6-bis(trifluoromethyl)phenyl]carbene, a 4-alkylated analogue of *U*-^{3}**1**, and also showed that this carbene has a bent structure with the central bond angle of 167° at the B3LYP/6-311G(d,p) level. Woodcock, H. L.; Moran, D.; Schleyer, P. von R.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **2001**, *123*, 4331.

The ESR data are not in complete agreement with the theoretical prediction. The ESR spectra of carbenes are characterized by two parameters *D* and *E*.[10,26] The *D* value is related to the separation between the unpaired electrons. The value of *E*, when weighted by *D*, is a measure of the deviation of the carbene from axial symmetry, or, more plainly, it describes the extent to which the molecule is bent. The calculations predict that opening of the carbene−carbon bond angle strongly destabilizes the singlet but requires very little additional energy for the triplet, thus making the singlet−triplet splitting larger.[27,28] The *E*/*D* value for *U*-^{3}**1** in 2-MTHF at 77 K is slightly smaller than that for ^{3}**2** under identical conditions (Table 1).

However, it has been well-documented that sterically congested diarylcarbenes generated in rigid matrix often have the bent geometry and the conformation dictated by those of the precursor and that even if the thermodynamically most stable geometry and/or conformation of the carbene is different from those at the birth, the rigidity of the matrix prevents it from assuming its minimum energy structure. When the matrix is softened upon annealing, the carbene can relax to a more stable geometry depending on the softness of the media.[11,12,29] Therefore one needs to compare the ZFS parameters of triplet DPC in its relaxed state. When the matrix containing ^{3}**2** was warmed, *X* and *Y* lines of the spectrum moved closer together, resulting in a smaller *E* value.[4d] The substantial reduction in the *E* value upon annealing the matrix indicates that the carbene relaxes to a structure with a wider C−C−C angle presumably to gain relief from steric compression.

On the other hand, changes in ESR signals for ^{3}**1** upon warming the matrix are small (Figure 1). Only a slight shift of *X* and *Y* lines in the ESR signals upon annealing the matrix to 110 K is observed for *U*-^{3}**1**. These observations are not expected from the assumption that steric compression in ^{3}**1** is expected to be much severer than that in ^{3}**2** in the light of the bulkiness of trifluoromethyl group as opposed to bromine. Part of the reason for this is the fact that the ESR spectra of brominated carbenes are notoriously broad and weak, and hence ZFS parameters may not be precise enough to allow one to examine the structural feature in details.

Comparison between *U*-^{3}1 and *S*-^{3}1. Positional Effect of Trifluoromethyl Group as a Kinetic Protector. It is interesting to note here that *S*-^{3}**1** with bromine and trifluoromethyl groups at the ortho positions of each of two phenyl rings showed significantly greater stability than *U*-^{3}**1** having two bromine groups at the ortho positions of one phenyl ring and two trifluoromethyl groups at the ortho positions of the other phenyl ring in degassed benzene solution. This indicates that, even if the same two kinds of *o*-substituents are introduced, the effect on the stability of triplet DPCs depends on how those groups are introduced.

What is the origin for this difference? The structure of triplet diarylcarbene is usually characterized by the ZFS parameters (vide supra). However, it is not possible to compare the value between the two, as the values for *S*-^{3}**1** were not determined.

It would be very informative to inspect the X-ray crystal structure of precursor diazomethanes. Unfortunately, X-ray crystal structural analysis of both *U*-**1**−N_2 and *S*-**1**−N_2 showed a slightly disordered structure about the ortho substituents. The structural parameters ω/θ for *U*-**1**−N_2 and *S*-**1**−N_2 obtained from the partially disordered crystal structure are 83.9°/128.3° and 78.7°/128.7°, respectively (Figure S7). DFT calculations of *S*-**1a**−N_2 and *U*-**1a**−N_2 (Figure S8) show, however, that the two DDMs have a similar bond angle ($\theta = 127.5°$) and dihedral angle ($\omega = \sim 70°$). Although the disordered structure indicates that ω is slightly larger in *U*-**1**−N_2 than in *S*-**1**−N_2, it is likely that those two groups are too large to further affect the structure of DDMs.

Inspection of the optimized geometries of *U*-^{3}**1a** and *S*-^{3}**1a** (Figure 10) also indicates that there is only a slight difference between the two carbenes. The carbene bond angle is slightly larger for *S*-^{3}**1a** (162.9°) than for *U*-^{3}**1a** (158.8°), while the dihedral angle is larger for *U*-^{3}**1a** ($\omega = 85.7°$) than for *S*-^{3}**1a** ($\omega = 81.4°$). The C−C distances between the aromatic and carbene carbon (d1 and d2) are slightly shorter for *U*-^{3}**1a** (1.376 and 1.380 Å) than for *S*-^{3}**1a** (1.375 and 1.375 Å). Spin densities on the carbene carbon are slightly smaller for *S*-^{3}**1a** (1.377) than for *U*-^{3}**1a** (1.397).

This is in accord with the observation that both carbenes showed essentially identical reactivities toward oxygen and CHD. A significant difference in the stability observed in benzene is ascribable to the difference in the decay pathway under these conditions. In the absence of proper trapping reagents, triplet carbenes decay mainly by dimerization. So, the difference in the stability is due to that in the rate of dimerization. If one assumes ^{3}**1** has nearly perpendicular geometry, in *U*-^{3}**1**, the two carbon atoms of the most effective kinetic protector, CF_3 groups, are fixed in the same plane, while in *S*-^{3}**2** they are located in a perpendicular manner. Presumably, the perpendicular alignment of the two most bulky groups is a more effective way to shield the carbenic center than the planar one from the dimerization. This change in the alignment may not be important for the attack of a smaller and reactive reagent such as oxygen and 1,4-cyclohexadiene.

Conclusion

The present study revealed that CF_3 groups are an effective kinetic protector for triplet diphenylcarbenes. From a synthetic viewpoint, it is probably impossible to prepare precursor diphenyldiazomethane with four CF_3 groups at all of the ortho positions. Auxiliary protector is shown to be successfully employed to solve this problem. In this case, a manner to introduce the two kinds of protector is found to be crucial to further stabilize triplet carbene toward self-dimerization. In this way, triplet substituted diphenylcarbene surviving nearly a day in solution at room temperature is realized for the first time. This is the most persistent triplet diphenylcarbene thus far reported.

Experimental Section

General Information. IR spectra were measured on a JASCO FT/IR-410 spectrometer, and UV/vis spectra were recorded on a JASCO V-560 spectrometer. The mass spectra were recorded on a JEOL JMS-600H mass spectrometer. ^{1}H and ^{13}C NMR spectra were determined

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[26] A large number of triplet carbenes have been characterized by ESR spectroscopy since the pioneering work of Wasserman et al.: (a) Wasserman, E.; Hutton, R. S. *Acc. Chem. Res.* **1977**, *10*, 27. (b) Wasserman, E.; Snyder, L. C.; Yager, W. A. *J. Chem. Phys.* **1964**, *41*, 1763.

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with a JEOL JNM-AL300 FT/NMR spectrometer in $CDCl_3$ or C_6D_6 with Me_4Si as an internal reference. Thin-layer chromatography was done on a Merck Kieselgel 60 PF_{254}. Column chromatography was carried out on a silica gel (Merck for dry column chromatography) or on an aluminum oxide (ICN, neutral activity grade I, inactivated with 5% H_2O). GPC was undertaken with a JASCO PU-986 chromatograph with a UV-970 UV/vis detector using a Shodex GPC H-2001 (20 mm × 50 cm).

Materials. Preparation of [3,5-Bis(trifluoromethyl)-1,1′-biphenyl-4-yl](3,5-dibromo-1,1′-biphenyl-4-yl)diazomethane (*U*-1-N_2). To a mixture of 4-amino-3,5-dibromo-1,1′-biphenyl (3.27 g, 10 mmol)[31] in water (4 mL) and acetic acid (6.5 mL) was added concentrated sulfuric acid (2.8 g, 28 mmol) under stirring. The mixture was heated to complete dissolution and then cooled to 10 °C. The aniline sulfate was diazotized at 10 °C with an aqueous solution of sodium nitrite (0.77 g, 11 mmol). To a mixture of copper(II) sulfate (1.92 g, 12 mmol) in water (7.5 mL) and ice (5.0 g) was added KCN (3.25 g, 50 mmol) in water (7.5 mL), while the temperature was kept below 20 °C by adding more ice. The voluminous precipitate that initially formed dissolved. Finally, $NaHCO_3$ (6.7 g, 80 mmol) and benzene (10 mL) were added. To this mixture was added dropwise the above solution of the diazonium compound with vigorous stirring at 50−55 °C over 20 min. After an additional 30 min of stirring, the mixture was extracted with benzene, and washed with 2 N NaOH solution and brine. The organic phase was concentrated, and the crude product was chromatographed on silica gel using *n*-hexane−CH_2Cl_2 (2:1) as an eluent to give 3,5-dibromo-4-cyanobiphenyl (**14**) as a brown solid (1.75 g, 52%): mp 131−133 °C; ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 7.84 (s, 2H), 7.57−7.48 (m, 5H); ^{13}C NMR (75.5 MHz, $CDCl_3$, ppm) δ 147.7, 136.7, 130.3, 129.7, 129.4, 127.2, 126.9, 116.9, 116.1; EI MS (*m*/*z*) 339 (M + 2, 49.6%), 337 (M^+, base), 335 (40.7%), 117 (43.9%), 88 (12.5%), HRMS calcd for $C_{13}H_7NBr_2$ 334.8944, found *m*/*z* 334.8947; IR (KBr, cm^{-1}) 2229 (ν_{CN}).

A solution of DIBAL−H in hexane (0.93 M, 5.4 mL, 5.0 mmol) was added dropwise to a solution of 1.41 g (4.19 mmol) of **14** in 12 mL of CH_2Cl_2. The solution was stirred under Ar at ambient temperature for 30 min and was then diluted with 10 mL of Et_2O and cooled in ice. Ten milliliters of 3 N HCl was carefully added, and the mixture was vigorously stirred at 40 °C for 1 h. The organic fraction was washed with brine, dried over Na_2SO_4, and evaporated. The crude product was chromatographed on silica gel using *n*-hexane−CH_2Cl_2 (1:1) as an eluent to give 3,5-dibromobiphenyl-4-carboaldehyde (**6**) as a light brown solid (1.25 g, 88%): mp 93.5−95.0 °C; ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 10.42 (s, 1H), 8.07 (s, 1H), 8.06 (s, 1H), 7.62 (d, *J* = 7.72 Hz, 2H), 7.54−7. 26 (m, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$, ppm) 190.8, 147.1, 136.8, 132.1, 130.5, 129.4, 129.2, 127.2, 125.5; EI-MS (*m*/*z*) 342 (M + 4, 51.9%), 340 (M + 2, base), 338 (M^+, 50.1%), 232 (17.0%), 230 (17.0%), 151 (33.2%); HRMS calcd for $C_{13}H_8OBr_2$ 337.8941, found *m*/*z* 337.8949.

To a solution of 0.77 g (2.66 mmol) of 3,5-bis(trifluoromethyl)-biphenyl (**4**)[32] and 0.80 mL (5.32 mmol) of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine in dry Et_2O (2.5 mL) was added dropwise ^{n}BuLi (2.66 M in hexane, 2.00 mL, 5.32 mmol) at −20 °C. The solution was stirred overnight at room temperature and refluxed for 2 h, and then a solution of **6** (0.90 g, 2.66 mmol) in dry THF (3 mL) was added dropwise at 0 °C. The mixture was refluxed for 4 h and was quenched by addition of saturated aqueous ammonium chloride. The mixture was extracted with ether, washed with water, dried over Na_2SO_4, and the solvent was removed under reduced pressure. The residue was chromatographed on silica gel using *n*-hexane−CH_2Cl_2 (2:1) as an eluent to give (3,5-dibromobiphenyl-4-yl)[3,5-bis(trifluoromethyl)biphenyl-4-yl]methanol (**7**) as a white solid (1.04 g, 46%): mp 81.0−84.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 8.16 (s, 2H), 7.80 (s, 2H), 7.70−7.41 (m, 10H), 6.86 (d, *J* = 6.61 Hz, 1H), 3.49 (d, *J* = 6.61 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$, ppm) δ 143.1, 141.6, 138.1, 137.9, 137.3, 136.9, 132.7, 132.2 (q, *J* = 30.5 Hz), 129.2, 129.1, 129.0, 128.9, 128.6, 127.1, 127.0, 124.5, 124.1 (q, *J* = 274.7 Hz), 72.5; EI-MS (*m*/*z*) 632 (M + 4, 5.1%), 630 (M + 2, 9.7%), 628 (M^+, 5.2%), 341 (18.5%), 339 (17.1%), 317 (base), 152 (14.1%); HRMS calcd for $C_{32}H_{28}NBrO_2$ 627.9471, found *m*/*z* 627.9470.

A solution of **7** (364 mg, 0.58 mmol) and $SOCl_2$ (20 mL) was stirred at room temperature overnight, and the mixture was evaporated under reduced pressure to give (3,5-dibromobiphenyl-4-yl)[3,5-bis(trifluoromethyl)biphenyl-4-yl]chloromethane as a brown viscous oil (375 mg, quantitative yield), which was rather unstable and hence used without further purification: ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 8.13 (s, 2H), 7.82 (s, 2H), 7.69−7.43 (m, 10H), 7.13 (s, 1H). A mixture of silver tetrafluoroborate (321 mg, 1.65 mmol) and ethyl carbamate (7.50 g, 17.7 mmol) was heated at 60 °C. To the mixture was added a solution of the chloromethane (1.07 g, 1.65 mmol) in dioxane (50 mL), and it was heated at 100 °C overnight. The mixture was filtered, and water (50 mL) and $CHCl_3$ (50 mL) were added to the filtrate. The organic layer was washed well with water, dried over anhydrous Na_2SO_4, and the solvent was removed under reduced pressure. The residue was chromatographed on silica gel using *n*-hexane−CH_2Cl_2 (1:1) as an eluent to give ethyl *N*-{(3,5-dibromobiphenyl-4-yl) [3,5-bis(trifluoromethyl)biphenyl-4-yl]methyl}carbamate (**8**) as a yellow semisolid (51 mg, 4.4%): ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 8.12 (s, 2H), 7.80 (s, 2H), 7.70−7.40 (m, 10H), 6.93 (d, *J* = 7.17 Hz, 1H), 5.49 (d, *J* = 7.17 Hz, 1H), 4.16 (q, *J* = 7.17 Hz, 2H), 1.26 (t, *J* = 7.17 Hz, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$, ppm) δ 155.7, 143.0, 142.8, 142.5, 141.6, 141.4, 137.9, 137.3, 136.0, 133.1, 132.1, 131.8 (q, *J* = 31.1 Hz), 129.2, 129.1, 128.6, 127.1, 126.9 (q, *J* = 6.2 Hz), 124.2 (q, *J* = 275.3 Hz), 61.4, 54.9, 14.7; EI-MS (*m*/*z*) 703 (M + 4, 1.8%), 701 (M + 2, 5.8%), 699 (M^+, 3.2%), 621 (42.0%), 619 (40.9%), 576 (base), 504 (16.9%); HRMS calcd for $C_{38}H_{20}FNO_2Br_2$ 698.9844, found *m*/*z* 698.9835.

Into a stirred solution of **8** (67 mg, 0.096 mmol) in anhydrous CCl_4 (5 mL) at 0 °C was bubbled N_2O_4 gas (1.25 g, 13.6 mmol), and AcONa (2.23 g, 27.2 mmol) was added. The mixture was stirred at room temperature overnight, poured onto cold aqueous Na_2CO_3, and extracted with CCl_4. The organic layer was washed with 5% Na_2CO_3 solution and water, dried over anhydrous Na_2SO_4, and evaporated to ethyl *N*-nitroso-*N*-{(3,5-dibromobiphenyl-4-yl)[3,5-bis(trifluoromethyl)biphenyl-4-yl]methyl}carbamate as a yellow oil. To a solution of the nitroso compound in anhydrous THF (10 mL) was added potassium *tert*-butoxide (23.8 mg, 0.21 mmol) at once under an atmosphere of argon. The mixture was stirred at room temperature overnight, poured onto water, and extracted with Et_2O. The ethereal layer was washed with water, dried over anhydrous Na_2SO_4, and evaporated. The reaction mixture was passed through a column (aluminum oxide deactivated with 5% water, *n*-hexane), and the first fraction was further purified by GPC (20 cycles, $CHCl_3$) followed by TLC (*n*-hexane) to give (3,5-dibromobiphenyl-4-yl)[3,5-bis(trifluoromethyl)biphenyl-4-yl]diazomethane (*U*-**1**−N_2) as an orange solid (10 mg, 14.5%): mp 134.4−135.2 °C (dec); ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 8.17 (s, 2H), 7.82 (s, 2H), 7.66−7.38 (m, 10H); ^{13}C NMR (75.5 MHz, $CDCl_3$, ppm) δ 66.0, 124.3, 125.7 (q, *J* = 275.3 Hz), 126.8, 126.9, 127.0, 127.2, 128.7 (q, *J* = 31.5 Hz), 129.1, 129.4, 129.5 (q, *J* = 5.6 Hz), 132.2, 137.4, 137.6, 140.7, 141.3, 142.4, 142.8; IR (KBr, cm^{-1}) 2068 (ν_{CN_2}).

Preparation of Bis(3-bromo-5-trifluoromethyl-1,1′-biphenyl-4-yl)diazomethane (*S*-1−N_2). To a vigorously stirred mixture of 4-amino-3-trifluoromethylbiphenyl (3.68 g, 15.4 mmol)[30] and 47% hydrobromic acid (50 mL) was added dropwise a solution of sodium nitrite (2.12 g, 30.8 mmol) in water (5 mL) at 0 °C. After the mixture was stirred at 0 °C for 1 h, copper powder (2.5 g) was added to the solution and the mixture was stirred at room temperature overnight. The mixture was heated at 60 °C for 2 h, diluted with water (200 mL), and filtered. The filtrate was extracted with ether, washed with water and aqueous Na_2CO_3, and dried over anhydrous Na_2SO_4. The organic layer was

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evaporated to leave crude product, which was chromatographed on silica gel eluted with *n*-hexane to afford 3.39 g of 4-bromo-3-trifluoromethylbiphenyl (**9**) as a colorless liquid in 72% yield: ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 7.89 (d, $J = 2.20$ Hz, 1H), 7.77 (d, $J = 8.27$ Hz, 1H), 7.60−7.40 (m, 6H); ^{13}C NMR (75.5 MHz, $CDCl_3$, ppm) δ 140.7, 138.7, 135.3, 131.4, 130.5 (q, $J = 31.1$ Hz), 129.1, 128.4, 127.0, 126.5 (q, $J = 5.6$ Hz), 123.0 (q, $J = 273.0$ Hz), 118.7; EI-MS (*m*/*z*) 302 (M + 2, 99.3%), 300 (M^+, base), 228 (26.4%), 185 (19.3%); HRMS calcd for $C_{13}H_8F_3Br$ 299.9761, found *m*/*z* 299.9758.

To a solution of tetramethylpiperidine (2.35 g, 16.6 mmol) in dry THF (20 mL) was added *n*-BuLi (2.66 M in hexane, 6.24 mL, 16.6 mmol) at 0 °C. The solution was stirred for 0.5 h, and then a solution of **9** (5.0 g, 16.6 mmol) in THF (20 mL) was added dropwise at −78 °C. After the mixture was stirred for 2 h at this temperature, excess methyl formate was added and stirred overnight at room temperature. The reaction mixture was quenched by addition of saturated aqueous ammonium chloride. The mixture was extracted with ether, washed with water, dried over Na_2SO_4, and the solvent was removed under reduced pressure. The residue was chromatographed on silica gel using *n*-hexane−CH_2Cl_2 (1:1) as an eluent to give 3-bromo-5-trifluoromethylbiphenyl-4-carbaldehyde (**11**) as a light yellow solid (2.50 g, 46%): mp 65.4−66.9 °C; ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 10.42 (s, 1H), 8.06 (d, $J = 2.02$ Hz, 1H), 7.95 (d, $J = 2.02$ Hz, 1H), 7.63−7.48 (m, 5H); ^{13}C NMR (75.5 MHz, $CDCl_3$, ppm) δ 190.2, 146.1, 137.1, 135.6, 131.3 (q, $J = 33.0$ Hz), 129.5, 129.4, 129.3, 129.0, 127.3, 124.8 (q, $J = 5.6$ Hz), 122.8 (q, $J = 275.0$ Hz); EI-MS (*m*/*z*) 330 (M + 2, 97.8%), 328 (M^+, base), 220 (14.3%), 219 (13.0%), 201 (12.4%); HRMS calcd for $C_{14}H_8BrF_3O$ 327.9710, found *m*/*z* 327.9714.

To a solution of tetramethylpiperidine (1.21 g, 8.63 mmol) in dry THF (10 mL) was added ^{n}BuLi (2.66 M in hexane, 3.25 mL, 8.65 mmol) at 0 °C. The solution was stirred for 0.5 h, and then a solution of **9** (2.60 g, 8.63 mmol) in THF (20 mL) was dropwise added at −78 °C. After the mixture was stirred for 2 h at this temperature, **11** (2.84 g, 8.63 mmol) was added and stirred overnight at room temperature. The reaction mixture was quenched by addition of saturated aqueous ammonium chloride. The mixture was extracted with ether, washed with water, dried over Na_2SO_4, and the solvent was removed under reduced pressure. The residue was chromatographed on silica gel using *n*-hexane−CH_2Cl_2 (2:1) as an eluent to give bis(3-bromo-5-trifluoromethylbiphenyl-4-yl)methanol (**12**) as a white solid (2.50 g, 46%): mp 48.0−50.0 °C; ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 8.02 (d, $J = 11.13$ Hz, 2H), 7.68 (d, $J = 11.13$ Hz, 2H), 7.63−7.40 (m, 10H), 6.77 (d, $J = 9.37$ Hz, 1H), 3.12 (d, $J = 9.37$ Hz, 1H); ^{13}C NMR (75.5 Hz, $CDCl_3$, ppm) δ 142.2, 141.7, 138.7, 137.9, 137.6, 136.6, 135.8, 131.7 (q, $J = 31.1$ Hz), 129.2, 128.0, 126.8, 124.0 (q, $J = 274.0$ Hz), 72.8; EI-MS (*m*/*z*) 632 (M + 4, 10.2%), 630 (M + 2, 16.8%), 628 (M^+, 10.4%), 329 (96.7%), 327 (base), 311 (32.4%), 309 (32.2%), 201 (57.9%); HRMS calcd for $C_{27}H_{16}F_6OBr_2$ 627.9471, found *m*/*z* 627.9466.

A solution of **12** (2.23 g, 3.54 mmol) and $SOCl_2$ (20 mL) was stirred at room temperature overnight, and the mixture was evaporated under reduced pressure to give bis(2-bromo-4-phenyl-6-trifluoromethylphenyl)chloromethane as a brown viscous oil (2.30 g, quantitative yield), which was rather unstable and hence used without further purification: ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 6.77 (s, 1H), 7.40−8.05 (m, 14H). A mixture of silver tetrafluoroborate (691 mg, 3.55 mmol) and ethyl carbamate (7.5 g, 35 mmol) was heated at 60 °C. To the mixture was added a solution of the chloromethane (2.30 g, 3.54 mmol) in 1,4-dioxane (50 mL), and it was heated at 100 °C overnight. The mixture was filtered, and water (50 mL) and $CHCl_3$ (50 mL) were added to the filtrate. The organic layer was washed well with water, dried over anhydrous Na_2SO_4, and the solvent was removed under reduced pressure. The residue was chromatographed on silica gel using *n*-hexane−CH_2Cl_2 (1:1) as an eluent to give ethyl *N*-[bis(3-bromo-5-trifluoromethylbiphenyl-4-yl)methyl]carbamate (**13**) as a yellow semisolid (231 mg, 9.3%): ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 7.79 (dd, $J = 7.90$, 2.02 Hz, 2H), 7.75 (dd, $J = 7.90$, 2.02 Hz, 2H), 7.60−7.30 (m, 10H), 7.20 (d, $J = 9.00$, 1H), 5.58 (d, $J = 9.00$ Hz, 1H), 4.19 (q, $J = 7.17$ Hz, 2H), 1.27 (t, $J = 7.17$ Hz, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$, ppm) δ 155.0, 142.0, 137.5, 136.9, 136.3, 136.3, 131.5 (q, $J = 30.5$ Hz), 129.2, 128.8, 127.0, 126.0 (q, $J = 6.3$ Hz), 123.6 (q, $J = 275.3$ Hz), 61.5, 56.8, 14.6; EI-MS (*m*/*z*) 703 (M + 4, 8.5%), 701 (M + 2, 12.9%), 699 (M^+, 7.4%), 671 (29.8%), 622 (base), 620 (96.1%), 576 (28.1%), 453 (20.2%); HRMS calcd for $C_{38}H_{20}FNO_2Br_2$ 698.9844, found *m*/*z* 698.9843.

Into a stirred solution of **13** (230 mg, 0.33 mmol) in anhydrous CCl_4 (5 mL) at 0 °C was bubbled N_2O_4 gas (1.24 g, 13.5 mmol), and AcONa (2.40 g, 29.3 mmol) was added. The mixture was stirred at room temperature overnight, poured onto cold aqueous Na_2CO_3, and extracted with CCl_4. The organic layer was washed with 5% Na_2CO_3 solution and water, dried over anhydrous Na_2SO_4, and evaporated to give *N*-nitroso compound as a yellow oil. To a solution of the nitroso compound in anhydrous THF (10 mL) was added potassium *tert*-butoxide (78 mg, 0.69 mmol) at once under an atmosphere of argon. The mixture was stirred at room temperature overnight, poured onto water, and extracted with Et_2O. The ethereal layer was washed with water, dried over anhydrous Na_2SO_4, and evaporated. The reaction mixture was passed through a column (aluminum oxide deactivated with 5% water, *n*-hexane), and a first fraction was further purified by GPC (15 cycles, $CHCl_3$) followed by TLC (*n*-hexane) to give bis(3-bromo-5-trifluoromethylbiphenyl-4-yl)diazomethane (*S*-**1**−N_2) as an orange solid (26 mg, 12%): mp 148.5−150.2 °C (dec); ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 7.62−7.42 (m, 6H), 7.60 (d, $J = 7.72$ Hz, 4H), 7.94 (d, $J = 2.04$ Hz, 2H), 8.07 (d, $J = 2.04$ Hz, 2H); ^{13}C NMR (300 MHz, $CDCl_3$, ppm) δ 62.0, 125.6 (q, $J = 8.1$ Hz), 126.9 (q, $J = 275.3$ Hz), 126.9, 127.4, 128.4 (q, $J = 30.4$ Hz), 128.8, 129.2, 136.1, 137.5, 141.7; IR (KBr, cm^{-1}) 2068 (ν_{CN_2}).

Product Analysis. Photolysis of *U*- and *S*-**1**−N_2 in degassed benzene gave the following products.

Carbene-dimer from *U*-**1**−N_2: A 6:4 mixture of two isomers, A and B; yellow semisolid (38%); ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 7.81 (d, $J = 1.8$ Hz, 1.2H, A), 7.73 (d, $J = 1.7$ Hz, 1.2H, A), 7.70−7.62 (m, 2.4H, B), 7.60 (s, 2H), 7.57 (s, 2H), 7.50−7.30 (m, 16.4H), 7.07 (s, 0.8H, B), 7.05 (s, 0.8H, B), 6.78 (s, 1.2H, A); MALDI-TOF-MASS calcd for $C_{54}H_{28}Br_4F_{12}$ (carbene dimer) 1219.87, found *m*/*z* 1219.91.

Carbene-dimer from *S*-**1**−N_2: A mixture of rotational isomers; yellow semisolid (52%); ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 8.01 (s, 0.3H), 8.02 (d, $J = 1.7$ Hz, 1.2H), 7.93−7.75 (m, 2H), 7.69 (d, $J = 2.0$ Hz, 1.2H), 7.62−7.21 (m, 20H), 7.12 (s, 0.3H), 7.10 (s, 1.2H), 7.03 (s, 0.3H), 6.72 (s, 1.2H), 6.60 (s, 0.3H); MALDI-TOF-MASS calcd for $C_{54}H_{29}Br_4F_{12}$ (carbene dimmer + H) 1220.88, found *m*/*z* 1220.90.

Photolysis of *U*- and *S*-**1**−N_2 in degassed benzene in the presence of 1,4-cyclobutadiene gave the double-hydrogen abstraction product **1**−H_2.

U-**1**−H_2: White semisolid (59%); ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 8.10 (s, 2H), 7.75 (s, 2H),7.66−7.35 (m, 10H), 4.76 (s, 2H); EI-MS (*m*/*z*) 616 (M + 4, 2.8%), 614 (M + 2, 5.2%), 612 (M^+, 2.7%), 536 (35.0%), 534 (32.0%), 456 (base); HRMS calcd for $C_{27}H_{16}F_6Br_2$ 611.9522, found *m*/*z* 611.9627.

S-**1**−H_2: White solid (32%); mp 121−126 °C; ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 8.08 (s, 1H), 7.96 (s, 1H), 7.92 (s, 2H), 7.64−7.38 (m, 10H), 4.61 (s, 2H); EI-MS (*m*/*z*) 616 (M + 4, 0.6%), 614 (M + 2, 1.2%), 612 (M^+, 0.6%), 536 (77.0%), 534 (82.8%), 456 (base); HRMS calcd for $C_{27}H_{16}F_6Br_2$ 611.9522, found *m*/*z* 611.9557.

Photolysis of *U*- and *S*-**1**−N_2 in nondegassed benzene gave the following ketones **1**−O.

U-**1**−O: White solid (90%); mp 152−154 °C; ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 8.16 (s, 2H), 7.91 (s, 2H), 7.69−7.44 (m, 10H);^{13}C NMR (75.5 MHz, $CDCl_3$, ppm) δ 189.6, 146.2, 143.9, 137.3, 136.7, 136.1, 134.3, 132.8, 130.6 (q, $J = 32.1$ Hz), 129.4, 129.4, 129.2, 128.6 (q, $J = 5.3$ Hz), 127.3, 127.2, 125.9, 125.2, 123.0 (q, $J = 275.1$ Hz); IR (KBr, cm^{-1}) 1684 (ν_{CO}); EI-MS (*m*/*z*) 630 (M + 4, 48.2%), 628

(M + 2, 92.6%), 626 (M^+, 47.0%), 341 (44.7%), 339 (92.6%), 337 (47.3%), 317 (base); HRMS calcd for $C_{27}H_{14}F_6OBr_2$ 625.9315, found *m/z* 625.9313.

S-**1**−O: White solid (80%); mp 76−79 °C; ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 8.05 (d, *J* = 1.70 Hz, 2H), 8.00 (d, *J* = 1.70 Hz, 2H), 7.64−7.46 (m, 10H); ^{13}C NMR (75.5 MHz, $CDCl_3$, ppm) δ 190.5, 145.2, 137.1, 136.1, 135.6, 133.2 (q, *J* = 32.4 Hz), 129.4, 129.3, 127.2, 126.1 (q, *J* = 6.1 Hz), 122.9 (q, *J* = 275.3 Hz), 121.9; IR (KBr, cm^{-1}) 1685 (ν_{CO}); EI-MS (*m/z*) 630 (M + 4, 30.8%), 628 (M + 2, 58.0%), 626 (M^+, 29.7%), 329 (base), 327 (99.6%); HRMS calcd for $C_{27}H_{14}F_6OBr_2$ 625.9315, found *m/z* 625.9315.

EPR Measurements. The diazo compound was dissolved in 2-methyltetrahydrofuran (10^{-3} M), and the solution was degassed in a quartz cell by three freeze−degas−thaw cycles. The sample was cooled in an optical transmission EPR cavity usually at 77 K and irradiated with a Wacom 500 W Xe lamp using a Pyrex filter. EPR spectra were measured on a JEOL JES-TE200 spectrometer (X-band microwave unit, 100 kHz field modulation). The signal positions were read by the use of a gaussmeter. For samples used in the temperature dependence studies, the EPR tube was placed in the spectrometer equipped with a JEOL ES-DVT3 liquid nitrogen transfer system and was irradiated at 77 K. The temperature of the sample was monitored and controlled by a PID controller. The sample temperature was raised in 10 K increments to the desired temperature, allowed to stand for 1 min, and recooled to 77 K to measure the signal. A JEOL liquid helium transfer system was attached for the low-temperature measurement. The temperature was controlled by a 9650 Microprocessor-based Digital Temperature Indicator/Controller, which provided 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. All solvents employed were of spectroscopic grade and purified by distillation just prior to use.

Low-Temperature UV/Vis Spectra. Low-temperature spectra at 77 K were obtained by using an Oxford variable-temperature liquid-nitrogen cryostat (DN 2704) 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 by four freeze−degas−thaw cycles at a pressure near 10^{-5} Torr. The cuvette was flame-sealed, under reduced pressure, placed in the cryostat, and cooled to 77 K. The sample was irradiated for several minutes in the spectrometer with a Halos 500-W high-pressure mercury lamp using a Pyrex filter, and the spectral changes were recorded at appropriate time intervals. The spectral changes upon thawing were also monitored by carefully controlling the matrix temperature with an Oxford Instrument Intelligent Temperature Controller (ITC 4).

Laser Flash Photolysis. All flash photolysis measurements were made on a Unisoku TSP-601 flash spectrometer. The excitation source for the laser flash photolysis was a XeCl excimer laser. A Hamamatsu 150-W xenon short arc lamp (L2195) was used as the probe source, and the monitoring beam guided using an optical fiber scope was arranged in an orientation perpendicular to the excitation source. The probe beam was monitored with a Hamamatsu R2949 photomultiplier tube through a Hamamatsu S3701-512Q linear image sensor (512 photodiodes used). Timing of the laser excitation pulse, the probe beam, and the detection system was achieved through an Iwatsu model DS-8631 digital synchroscope, which was interfaced to a NEC 9801 RX2 computer. This allowed for rapid processing and storage of the data and provided printed graphics capabilities. Each trace was also displayed on a NEC CRT N5913U 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 sealed, and the solution was transferred to the quartz cuvette, which was placed in the sample chamber of the flash spectrometer. The concentration of the sample was adjusted so that it absorbed a significant portion of the laser light.

Crystallographic Data. Crystallographic data were recorded on a Rigaku RAXIS−RAPID imaging plate area detector with graphite-monochromated Mo Kα radiation ($\lambda = 0.71070$ Å) at a temperature of −150 °C. The structure were solved by a direct method with SIR92[33] and refined by the full-matrix least-squares method.[34] All of the non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined by a rigid model. A total of 5339 (for *S*-**1**−N_2) and 5296 (for *U*-**1**−N_2) reflections were collected. The final cycle of full-matrix least-squares refinement on F^2 was based on all reflections and 335 variable parameters and converged with $R = 0.131$ (for *S*-**1**−N_2) and 0.106 (for *U*-**1**−N_2) and $R_w = 0.344$ (for *S*-**1**−N_2) and 0.296 (for *U*-**1**−N_2). All calculations were performed using the CrystalStructure crystallographic software package.[35]

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Supporting Information Available: Transient absorption spectra obtained in LFP of *S*-**1**−N_2 in the presence of oxygen (Figure S1) and 1,4-cyclohexadiene (Figure S2), MALDI-TOF-MASS spectra of carbene dimers from *S*-**1**−N_2 and *U*-**1**−N_2 (Figures S3 and S4), ^{1}H NMR spectra of carbene dimers from *S*-**1**−N_2 and U-**1**−N_2 (Figures S5 and S6), ORTEP drawings of *S*-**1**−N_2 and *U*-**1**−N_2 (Figure S7), selected geometrical parameters for *U*-**1a**−N_2 and *S*-**1a**−N_2 at B3LYP/6-31G* level of theory (Figure S8), Cartesian coordinates, absolute energies of all calculated compounds at the B3LYP/6-31G* level of theory, an X-ray crystallographic file (CIF), and complete ref 23. This material is available free of charge via the Internet at http://pubs.acs.org.

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