

## Di(triptycyl)carbene: A Fairly Persistent Triplet Dialkylcarbene

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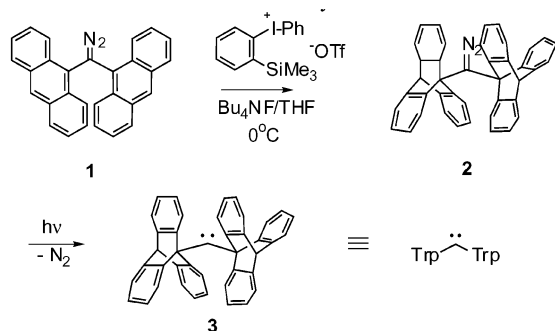
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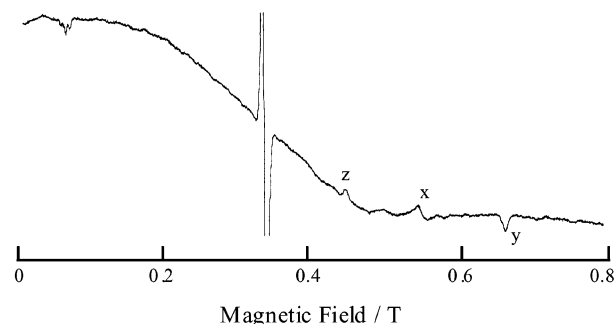
Most diarylcarbenes have triplet ground states that are easily characterized by product analysis or spectroscopy.<sup>1</sup> In marked contrast, most dialkylcarbenes have singlet ground states,<sup>2</sup> and there appear to be very limited data concerning the interception and detection of dialkylcarbenes. This is due to their ability to undergo rapid intramolecular rearrangements.<sup>1–3</sup> As a result, dialkylcarbenes can be intercepted or detected or both by slowing down the rearrangement rate. Thus, dialkylcarbenes that lead to highly strained products as a result of rearrangement can be intercepted and detected.<sup>4,5</sup> Among dialkylcarbenes, diadamantylcarbene (AdCad) is very interesting because it shows persistent triplet ESR signals in matrixes as well as substantial intermolecular triplet reactivity, even in solution at 25 °C.<sup>4</sup> This reactivity contrasts sharply with di(*tert*-butyl)carbene (*t*BuC*t*Bu), which also shows triplet ESR signals in matrixes but produces intramolecular products almost exclusively under identical conditions.<sup>5a</sup> This is obviously because the 1-adamantyl group is not as prone to rearrangement and the elimination process as is the *tert*-butyl (*t*Bu) group. The triptycyl (Trp) group is very interesting in this respect because it is not prone to rearrangement and also contains a repulsive nonbonded interaction when two Trps are attached on one carbon.<sup>6,7</sup>

We generated di(triptycyl)carbene for the first time and fully characterized this exotic dialkylcarbene by product analysis and spectroscopical study along with theoretical calculations.

Di(triptycyl)diazomethane (**2**), a desired precursor for di(triptycyl)carbene (**3**), can be prepared by adding 2 equiv of benzyne to di(9-anthryl)diazomethane (**1**).<sup>8</sup> The reaction was realized only by using (phenyl)[*o*-(trimethylsilyl)phenyl]iodonium triflate,<sup>9</sup> which can generate benzyne under very mild and neutral conditions. Diazomethane (**2**) was obtained as a rather stable yellow solid.<sup>10</sup>



Irradiation of **2** in an degassed 2-methyltetrahydrofuran (2-MTHF) glass at 77 K revealed the characteristic ESR spectrum of a triplet along with a strong signal (333.6 mT) ascribable to a fortuitous double species (Figure 1). The signals at 439, 543, and



**Figure 1.** ESR spectra obtained by photolysis of bis(triptycyl)diazomethane (**2**) in 2-MTHF at 77 K.

659 mT are assigned to a set of the high field *X*, *Y*, and *Z* transitions from which the zero-field splitting parameters were obtained as  $D = 0.720$  and  $E = 0.0263$  cm<sup>-1</sup>. The parameters fully support the assignment of the triplet spectrum as di(triptycyl)carbene (**3**). A comparison of the values with those reported for other sterically congested hydrocarbon dialkylcarbenes suggests that **3** has the largest *D* and the smallest *E* values.<sup>11</sup>

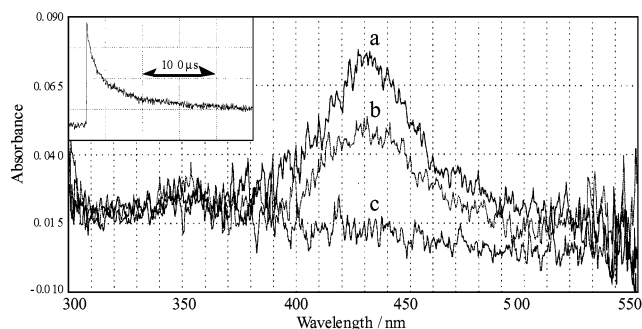
Generally speaking, the *D* value decreases with increasing delocalization of the unpaired electrons, while the *E* value when weighted by *D* decreases upon increasing the bond angle.<sup>12</sup> Thus, the *D* and *E* values observed for **3** can be interpreted as indicating that **3** has a divalent carbon with a large bond angle where the unpaired electrons are tightly held. The nonzero *E* value, however, indicates that this carbene is not completely linear.

The 2-MTHF glass containing **3** was warmed gradually in 10-K increments from 113 K to the desired temperature, allowed to stand for 5 min, and recooled to 113 K to measure the signals due to **3**. The signals due to **3** did not disappear at around 90 K, where the signals of most triplet diarylcarbenes disappeared irreversibly, and they were also observable at around 130 K, where the sample is completely fluid (Figure S1). The thermal stability of **3** is remarkable.

When the irradiation of **2** was monitored by UV/vis spectroscopy, a weak absorption band appeared around 426 nm as the original band due to **2** disappeared (Figure S2). This band disappeared irreversibly when the matrix was warmed to room temperature and recooled to 77 K. Since ESR signals ascribable to a triplet carbene are observed under identical conditions, the band can be assigned to the triplet carbene **3**. When the matrix containing **3** was gradually warmed, the band due to **3** did not disappear appreciably until 120 K, and it then disappeared completely at around 150 K. A remarkable thermal stability was noted again.

Laser flash photolysis (LFP) of **2** in a degassed benzene at room temperature with a 10 ns, 70–90 mJ, 308 nm pulse from a XeCl laser<sup>13</sup> produced a transient species showing an apparent maximum at 430 nm, which coincides with that observed during the photolysis

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**Figure 2.** Transient absorption spectra of the product obtained upon photoexcitation of **2** in a degassed benzene solution recorded after 1 (a), 10 (b) and 100  $\mu$ s (c). Inset shows oscillogram trace monitored at 430 nm.

of **2** in 2-MTHF at 77 K and is hence assignable to  $^3\mathbf{3}$  (Figure 2). The transient band decayed in a second-order kinetics ( $2k/\epsilon l = 5.8 \times 10^5 \text{ s}^{-1}$ ), and the rough first half-life of  $^3\mathbf{3}$  is estimated in the form of the half-life,  $t_{1/2}$ , to be 40  $\mu$ s.

Support is lent to this assignment by trapping experiments using oxygen. When LFP experiments were performed on a nondegassed benzene solution, the half-life of  $^3\mathbf{3}$  decreased dramatically (Figure S3). The spent solution was found to contain di(triptycyl)ketone as the main product. It is well-documented that the carbenes with triplet states are readily trapped by oxygen to generate the corresponding ketone oxides, which eventually lead to ketones.<sup>14</sup> Thus, the observations can be interpreted as indicating that  $^3\mathbf{3}$  is trapped by oxygen to form the ketone, which confirms that the transient absorption quenched by oxygen is due to  $^3\mathbf{3}$ . A quenching rate constant ( $k_{O_2}$ ) of  $^3\mathbf{3}$  by oxygen was determined by monitoring the decay rate of  $^3\mathbf{3}$  as a function of oxygen concentration. From the slope of the plot (Figure S4),  $k_{O_2}$  was estimated to be  $1.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ .

Theoretical studies are expected to give a more quantitative insight into the stability of this unique carbene. The geometries for the lowest singlet and triplet states of **3** were optimized at the B3LYP/6-31G\* level of theories, which indicates that both states have a bevel gear shape, as found in Trp-X-Trp systems.<sup>6</sup> There is a significant difference, however, in the CCC bond angles ( $\theta$ ), which are 129.3 and 153.3° for  $^1\mathbf{3}$  and  $^3\mathbf{3}$ , respectively (Figure S5). As somewhat expected from this difference, the triplet state was found to be a ground state, and the energy gap ( $\Delta G_{ST}$ ) between the two states was estimated to be as high as 14.0 kcal/mol. It is to be noted that not only the bond angle difference ( $\theta_{ST}$ ) but also  $\Delta G_{ST}$  is significantly larger than those estimated for  $^t\text{BuC}^t\text{Bu}$  and AdCad.<sup>15</sup>

Methylene is known to have a triplet ground state with a singlet lying higher in energy by 10 kcal/mol. Compared to methylene, both the singlet and the triplet are stabilized by the alkyl substituent(s) mainly due to hyperconjugation effect, but the magnitude of the effect for the singlets is about twice as large as that for the triplets.<sup>5b</sup> Thus, the S–T gap usually decreases as the alkyl groups are introduced on methylene. However, when bulky groups are introduced, the steric repulsion between the substituents widens the CCC bond angle and influences the S–T splitting, increasing the  $\pi$  character of the doubly occupied  $sp^2$  orbital and destabilizing the singlet. In the case of the triptycyl group, a hyperconjugative effect is considered to be less important as all the C–C bonds are tightly tied back to phenyl rings. Moreover, a repulsive nonbonding

interaction between the Trp groups in **3** must result in a significant widening of the central C–C–C bond angle. This resulted in a larger gap in  $\theta_{ST}$  and  $G_{ST}$  than  $^t\text{BuC}^t\text{Bu}$  and AdCad.

Triplet bis(triptycyl)carbene was thus demonstrated to be the most stable among the triplet dialkylcarbenes thus far generated. This is obviously due to the unique role of the Trp group in the carbene chemistry.

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**Supporting Information Available:** VT-ESR spectra and UV/vis spectra of  $^3\mathbf{3}$  in 2-MTHF at 77K, decay profile of  $^3\mathbf{3}$  in a benzene containing oxygen, plot of the decay rate of  $^3\mathbf{3}$  versus oxygen concentrations and optimized geometries of the singlet and triplet states of **3** at B3LYP/6-31G\* level of theories (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References

- (1) For reviews of general reactions of carbenes, see (a) Kirmse, W. *Carbene Chemistry*, 2nd ed.; Academic Press: New York, 1971. (b) *Carbenes*; Moss, R. A.; Jones, M., Jr., Eds.; Wiley: New York, 1973 and 1975; Vols. 1 and 2. (c) *Carbene(oides)*; Carbene; Regitz, M., Ed.; Thieme: Stuttgart, 1989.
- (2) (a) Bally, T.; Matzinger, S.; Truttmann, L.; Platz, M. S.; Morgan, S. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 19, 1964. (b) Ford, F.; Yuzawa, T.; Platz, M. S.; Matzinger, S. *Fulcher, M. J. Am. Chem. Soc.* **1998**, *120*, 4430.
- (3) (a) Jackson, J. E.; Platz, M. S. In *Advances in Carbene Chemistry*; Brinker, U., Ed.; JAI Press: Greenwich, CT, 1994; Vol. 1, pp 87–160. (b) Platz, M. S. In *Advances in Carbene Chemistry*; Brinker, U., Ed.; JAI Press: Greenwich, CT, 1998; Vol. 2, pp 134–174.
- (4) (a) Myers, D. R.; Senthilnathan, V. P.; Platz, M. S.; Jones, M., Jr. *J. Am. Chem. Soc.* **1986**, *108*, 4232. (b) Morgan, S.; Platz, M. S.; Jones, M., Jr.; Meyers, D. R. *J. Org. Chem.* **1991**, *56*, 1351.
- (5) (a) Gano, J. E.; Wettach, R. H.; Platz, M. S.; Senthilnathan, V. P. *J. Am. Chem. Soc.* **1982**, *104*, 2326. (b) For theoretical calculation of this carbene, see Sulzbach, H. M.; Bolton, E.; Lenoir, D.; Schleyer, P. V. R.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1996**, *118*, 9908.
- (6) (a) Kawada, Y.; Iwamura, H. *J. Am. Chem. Soc.* **1983**, *105*, 1449. (b) Johnson, C. A.; Guenzi, A.; Nachbar, R. B., Jr.; Blount, J. F.; Wennerstrom, O.; Mislow, K. *J. Am. Chem. Soc.* **1982**, *104*, 5163.
- (7) For the role of triptycyl group in carbene chemistry, see: (a) Tomioka, H.; Nakajima, J.; Mizuno, H.; Sone, T.; Hirai, K. *J. Am. Chem. Soc.* **1995**, *117*, 11355. (b) Tomioka, H.; Nakajima, J.; Mizuno, H.; Iiba, E.; Hirai, K. *Can. J. Chem.* **1999**, *77*, 1066.
- (8) Wasserman, E.; Kuck, V. J.; Yager, W. A.; Hutton, R. S.; Greene, F. D.; Abegg, V. P.; Weinshenker, N. M. *J. Am. Chem. Soc.* **1971**, *93*, 6355.
- (9) Kitamura, T.; Yamane, M.; Inoue, K.; Todaka, M.; Fukatsu, N.; Meng, Z.; Fujiwara, Y. *J. Am. Chem. Soc.* **1999**, *121*, 11674.
- (10) Mp 167.3–169.1 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  5.45 (s, 2 H), 6.81 (dt,  $J = 7.63, 7.63 \text{ Hz}$ , 6 H), 7.00 (t,  $J = 7.48 \text{ Hz}$ , 6 H), 7.46 (dd,  $J = 7.33, 7.32 \text{ Hz}$ , 6 H), 7.67 (d,  $J = 7.63 \text{ Hz}$ , 6 H);  $^{13}\text{C}$  NMR (125.65 MHz,  $\text{CDCl}_3$ )  $\delta$  29.7, 55.2, 57.4, 123.7, 124.6, 125.5, 125.8, 144.9, 145.7; IR (KBr)  $\nu$  2042  $\text{cm}^{-1}$ .
- (11) E/D determined for  $^t\text{BuC}^t\text{Bu}$  and AdCad are 0.039/0.689<sup>5a</sup> and 0.038/0.6823,<sup>4a</sup> respectively.
- (12) See for reviews of the EPR 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.
- (13) Details of our LFP equipments are reported elsewhere; see: Tomioka, H.; Okada, H.; Watanabe, T.; Banno, K.; Komatsu, K.; Hirai, K. *J. Am. Chem. Soc.* **1997**, *119*, 1582.
- (14) (a) See, for review: Sander, W. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 344. (b) We are not able to detect the transient band ascribable to the ketone oxide. This is partly due to inefficiency in the decomposition of **2** and weak absorption of this species. It may also be that the major absorption bands of the oxide are overlapping with the precursor diazomethane **2**, and hence, the samples were not sufficiently transparent for adequate monitoring in this region.
- (15) The S–T gap and  $\theta_S/\theta_T$  calculated for  $^t\text{BuC}^t\text{Bu}$  (at B3LYP/TZ2P)<sup>5b</sup> and AdCad (at B3LYP/6-31G\*)<sup>16</sup> are 5.16 and 9.3 kcal/mol, and 125.1/133.9 and 125/149°, respectively.
- (16) Matsuoka, M. Unpublished data.

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