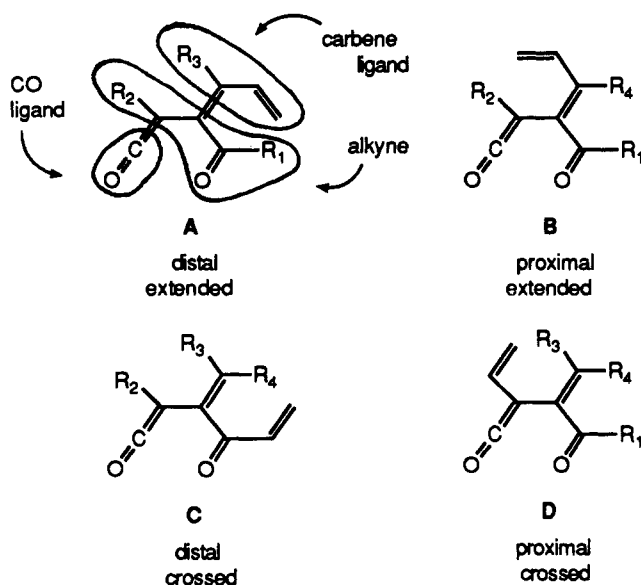


Chart I



the relatively stereochemistry was assigned by X-ray diffraction.⁵ The lactone **6** has the methoxyl group and methine hydrogen *cis* and this requires that the cross-conjugated ketene complex **10-C** cyclizes to **6** via the indicated *Z* isomer. Although the mass balance is not high, the apparent preference for the formation of the *Z* isomer of **10-C** which has the methoxyl anti to the ketone function may be due to an electronic interaction that favors a trans relationship of the methoxyl and the carbonyl.⁶ In support of this idea is the observation that the reaction of the amino complex **1b** with 3-hexyn-2-one shifts the product partition in favor of the lactone product **3** relative to the methoxyl complex **1a**. The formation of **2** requires the intermediacy of a ketoketene complex in which the group XR is *syn* to the keto group of the alkyne, and for the formation of the lactone **3** this relationship must be *anti* as it is for example in **10-C**.² Whether or not the product distribution for these reactions are under stereoelectronic control remains to be established, nonetheless, this result extends the synthetic utility of the lactone-forming reactions in the distal-extended mode in our original observations.²

The reaction of **4** with the alkyne **7** produces two compounds, **8** and **9**, both of which arise from the proximal-crossed configuration. However, these two products are apparently derived from the two stereoisomeric cross-conjugated ketoketene complexes **11-D** and **12-D**. The lactone **8** is thought to arise from the isomer **11-D**, but the monocyclic lactone **9** can only arise from the isomer **12-D**.⁸ The formation of **9** requires a 1,6-hydride shift that involves an unprecedented 10e⁻ reorganization in the overall process. If the product ratio reflects the stereochemistry of the reaction intermediates, then the vinyl ketene complex **11-D** with the methoxyl anti to the ketone carbonyl is preferred by a factor of 2.7:1 over the *syn* isomer **12-D**.

The final example illustrated in Scheme III was examined in an effort to document the fourth cyclization mode for these reactions (proximal-extended). The lactone **14** was the minor

product and arises from the cross-conjugated ketoketene complex **16-A** in which the distal-extended closure wins out over the proximal-crossed closure. A similar competition exists in the intermediate **17-B** where both a proximal-extended and a proximal-crossed closure is possible. However, this intermediate leads to a bicyclization involving an unprecedented 10e⁻ reorganization that produces a seven-membered ring into which both vinyl groups have been incorporated.⁹

That a variety of configurations of cross-conjugated ketoketenes complexes can be easily generated from the reaction of carbene complexes and alkynes should serve to stimulate the general class of 8- and 10e⁻ bicyclization reactions that are inherent to these intermediates.

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Supplementary Material Available: Spectral data for all new compounds (**2b**, **3b**, **5–10**, **14**, and **15**) and X-ray crystallographic data for compound **6** including tables of fractional coordinates, isotropic and anisotropic thermal parameters, bond distances, and bond angles (9 pages); a listing of F_o and F_c for compound **6** (11 pages). Ordering information is given on any current masthead page.

(9) No cyclohexadienone products were observed in this reaction.¹⁰

(10) Tang, P. C.; Wulff, W. D. *J. Am. Chem. Soc.* **1984**, *106*, 1132.

Persistent Triplet Diradicals from the Dimerization of Silacyclobutadienes

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Silacyclobutadiene, SiC₃H₄, is a molecule of great interest because of its unusual electronic structure and novel reaction chemistry.^{1–5} The formal Hückel antiaromaticity of its π system suggests that the HOMO–LUMO gap in this molecule should be small. Ab initio calculations predict a singlet–triplet splitting of only 5 kcal/mol for silacyclobutadiene,⁶ a value significantly less than the 23.0 kcal/mol calculated for cyclobutadiene, C₄H₄.⁷ Due to closely spaced frontier orbitals, diradicaloid behavior should be important in some chemical reactions involving silacyclobutadienes. We now report that persistent triplet diradicals arise from the dimerization of two highly hindered silacyclobutadiene analogues (Scheme I).

When a 3-methylpentane (3-MP) glass containing either 1-Mes or 1-Trip at 77 K is warmed in the cavity of an EPR spectrometer and refrozen at 77 K, strong well-resolved features indicative of triplet species appear (Figure 1). In the case of 1-Mes, two triplets initially appear at ~100 K: a major triplet (A), with $|D|/hc = 0.0243$ cm⁻¹ and $|E|/hc < 0.00001$ cm⁻¹, and a minor triplet (B), with $|D|/hc = 0.0138$ cm⁻¹ and $|E|/hc = 0.00047$ cm⁻¹. If the

(5) See supplementary material for data from the X-ray structural determination.

(6) For examples in alkenes, see: (a) Wasserman, H. H.; Ives, J. L. *J. Org. Chem.* **1985**, *50*, 3573. (b) Schmidt, D. G.; Zimmer, H. J. *Heterocycl. Chem.* **1983**, *20*, 787. (c) Abdulla, R. F.; Fuhr, K. H. *J. Org. Chem.* **1978**, *43*, 4248. (d) Martin, S. F.; Moore, D. R. *Tetrahedron Lett.* **1976**, 4459. (e) Conley, R. A.; Heindel, N. D. *J. Org. Chem.* **1976**, *41*, 3743. (f) Brady, B. A.; Kennedy, J. A.; O'Sullivan, W. I. *Tetrahedron* **1973**, *29*, 359. (g) Kevill, D. P. N.; Weiler, E. D.; Cromwell, N. H. *J. Org. Chem.* **1964**, *29*, 1276. (h) Zimmerman, H. E.; Ahranjian, L. J. *Am. Chem. Soc.* **1959**, *81*, 2086.

(7) Gavrilov, L. D.; Tikhonova, L. G.; Titova, E. I.; Vereshchagin, L. I. *Zh. Org. Khim.* **1976**, *12*, 530.

(8) Compound **9** appears not to be a fragmentation product of **8** as **9** can be recovered in high yield after heating in THF for 105 °C for 15 h with no detectable formation of **8**.

(1) Fink, M. J.; Puranik, D. *Organometallics* **1987**, *6*, 1809–1811.

(2) Fink, M. J.; Puranik, D. B.; Johnson, M. P. *J. Am. Chem. Soc.* **1988**, *110*, 1315–1316.

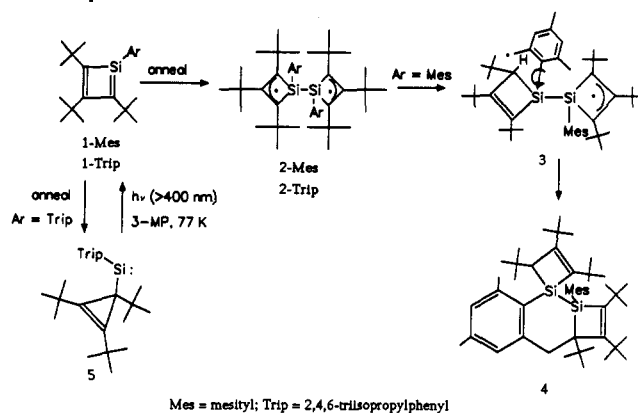
(3) Schriver, G. W.; Fink, M. J.; Gordon, M. S. *Organometallics* **1987**, *6*, 1977–1984.

(4) Puranik, D. B.; Johnson, M. P.; Fink, M. J. *J. Chem. Soc., Chem. Commun.* **1989**, 706–708.

(5) Puranik, D. B.; Fink, M. J. *J. Am. Chem. Soc.* **1989**, *111*, 5951–5952.

(6) Colvin, M. E.; Schaefer, H., III. *Faraday Symp. Chem. Soc.* **1984**, *19*, 39.

(7) Jafri, J. A.; Newton, M. D. *J. Am. Chem. Soc.* **1978**, *100*, 5012–5017.

Scheme 1. Annealing of Silacyclobutadienes in 3-MP Glasses To Give Triplet Diradicals

glass is warmed further, triplet A diminishes with a concomitant increase in the intensity of triplet B, indicating that A is a precursor to B. Above 250 K, both triplets rapidly diminish. In the case of 1-Trip, a single triplet with $|D|/hc = 0.0247 \text{ cm}^{-1}$ and $|E|/hc = 0.00090 \text{ cm}^{-1}$ is observed after warming. This triplet forms at $\sim 200 \text{ K}$ with a lifetime of at least 10 h at 298 K.

These triplets apparently arise from a bimolecular process since no triplet signal appears if a known chemical trap of either 1-Mes or 1-Trip (e.g., EtOH or MeOSiMe_3)^{2,5} is copresent in the 3-MP glass. In addition, the appearance of the triplet signals is correlated with the viscosity of the glass rather than temperature. Thus, triplet signals arise from 1-Mes at 77 K in a "soft" isopentane matrix but not in a "hard" decalin matrix even at 88 K.⁸

Compelling evidence for the identity of these triplet species is provided by the structure of the ultimate dimer which is formed from the thermal decomposition of 1-Mes (Scheme 1). This dimer (4) is formed in near quantitative yield; its X-ray structure has been reported previously.⁴ Spin counting experiments⁹ indicate that triplets A and B are present in sufficient concentration to place these species firmly on the reaction path to 4. The assignment of triplets A and B to the respective diradicals 2-Mes and 3 (Scheme 1) efficiently accounts for the formation of 4. The diradical 2-Mes, formed from the dimerization of 1-Mes, abstracts a hydrogen from an ortho methyl group to give 3, which ring closes to afford 4. The assignment of A as a bisallylic diradical is further supported by the estimation of 0.025 cm^{-1} for $|D|/hc$ using a point dipole model¹⁰ and the AM1 optimized geometry¹¹ for the parent diradical, $\text{Si}_2\text{C}_6\text{H}_8$.

The nearly identical $|D|/hc$ values of A and the triplet arising from 1-Trip suggest the formation of the analogous diradical 2-Trip. This diradical forms only 30% as efficiently as 2-Mes on the basis of spin counting experiments. This result is consistent with previous chemical trapping experiments; 61% of 1-Trip isomerizes to the cyclophenylsilylene 5 (Scheme 1).⁵ The competitive formation of 2-Trip and 5 from 1-Trip is supported by recycling experiments. If 3-MP glasses containing 1-Trip are warmed to 200 K and refrozen to 77 K, the EPR signal of 2-Trip is observed and the glass appears yellow due to 5. Since 5 is a photochemical precursor to 1-Trip,⁵ photolysis of 5 partially regenerates the silacyclobutadiene. Subsequent warming of the glass to 200 K, followed by refreezing to 77 K, results in both an increase

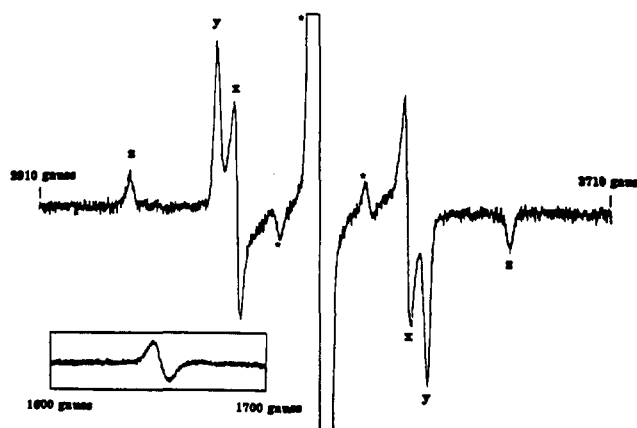
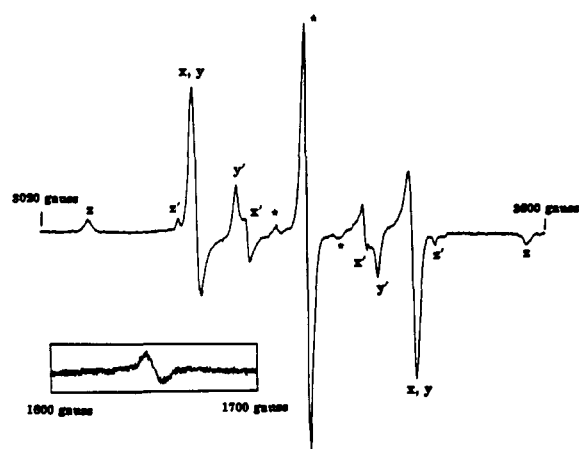


Figure 1. EPR spectra observed after annealing a 3-MP glass containing 1-Mes (top) and 1-Trip (bottom) recorded at 77 K with a spectrometer frequency of 9.28 GHz. In the top spectrum, the features marked by x, y, and z refer to diradical A while those marked by x', y', and z' refer to diradical B. The half-field transitions shown in the insets were recorded with increased spectrometer gain. The doublet features marked by asterisks arise from simple radicals.

in the intensity of the triplet EPR signal and the reappearance of 5 in lesser concentration. Repeating the annealing-photolysis sequence until the formation of 5 is barely detectable gives a doubling of the triplet signal due to 2-Trip.

The dimerization of silacyclobutadiene 1-Mes and 1-Trip may be considered a special case of silene ($\text{Si}=\text{C}$) dimerization. Although the typical course of silene dimerization leads to head-to-tail adducts, highly substituted analogues often give the head-to-head isomers. Brook has proposed that many of these dimerizations proceed via initial formation of a Si-Si bond to give 1,4-diradicals which, in some cases, isomerize by intramolecular hydrogen abstractions.¹² We believe that diradicals 2-Mes and 2-Trip are the first directly observed diradicals of this type. The unusual persistence of these particular diradicals is attributed to allylic delocalization of the radical centers and steric protection of the radical-bearing carbons by *tert*-butyl groups.

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Supplementary Material Available: Details of the point dipole calculations and AM1 calculations for triplet $\text{Si}_2\text{C}_6\text{H}_8$ and doublet SiC_3H_5 (14 pages). Ordering information is given on any current masthead page.

(8) Comparison of viscosities (poise): 3-MP (77 K), 5.4×10^{12} ; 3-MP (88 K), 1.3×10^7 ; isopentane (77 K), 8.9×10^5 ; decalin (88 K), $>1 \times 10^{13}$. (a) Lombardi, J. R.; Raymond, J. W.; Albrecht, A. C. *J. Chem. Phys.* **1964**, *40*, 1148-1156. (b) Ling, A. C.; Willard, J. E. *J. Phys. Chem.* **1968**, *72*, 1918-1923. (c) Fisher, G.; Seger, G.; Muszkat, K. A.; Fischer, E. *J. Chem. Soc., Perkin Trans. 2* **1975**, 1569-1576.

(9) Spin counts were determined by comparing with integrated intensities of the observed triplet spectra with the spectra of known quantities of DPPH or $\text{Cu}(\text{OAc})_2$ using identical instrument conditions and temperature.

(10) (a) McWeeny, R. *J. Chem. Phys.* **1961**, *34*, 399-401. (b) Gordy, W.; Morehouse, R. *Phys. Rev.* **1966**, *151*, 207-210. (c) Rule, M.; Martin, A. R.; Hilinski, E. F.; Dougherty, D. A.; Berson, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 5098-5099.

(11) Dewar, M. J. S.; Jie, C. *Organometallics* **1987**, *6*, 1486-1490.

(12) (a) Brook, A. G.; Baines, K. M. *Adv. Organomet. Chem.* **1986**, *25*, 1-44. (b) Baines, K. M.; Brook, A. G. *Organometallics* **1987**, *6*, 692-696.