

product shown in Figure 1. The molecular structure of its precursor **1**¹⁰ is shown in Figure 2. The initial Fe and S atom positions were determined by using MULTAN-11/82 and the Enraf-Nonius Structure Determination Package. All remaining non-hydrogen atom positions were located by subsequent difference Fourier techniques. Selected bond distances and angles are compared in Table I. The Fe1-Fe2 bond distance in **1** (2.628 (2) Å) is nearly identical with the Fe1-Fe2 distance in Fe₂(CO)₆(μ-PPH₂)₂¹² (2.623 (2) Å).¹² The Fe-P bond lengths observed for **1** are approximately 0.01 Å shorter than the Fe-P values found for the Fe₂(CO)₆(μ-PPH₂)₂¹² dimer (range 2.228 (3)-2.240 (3) Å). In general, the geometry of **1** closely resembles that of Fe₂(CO)₆(μ-PPH₂)₂ dimer.

The molecular structure of **5** shows significant structural changes from **1** although the Fe1-Fe2 bond distance increases by only 0.056 Å upon the substitution of P2 by C in the Fe2 coordination sphere. The Fe-Fe distances in [μ-CH₃C(O)CH₂CHS₂]₂Fe₂(CO)₆¹ and (μ-CH₂S₂)Fe₂(CO)₆¹⁶ are both 2.485 (1) Å. Replacement of a S atom in the Fe₂S₂ core with a C atom (e.g., [μ-CH₃C(O)CH₂SCHS]₂Fe₂(CO)₆) results in an increase of 0.142 Å in the Fe-Fe distance (2.627 Å).

The P1-C38 bond distance of 1.820 (4) Å is not appreciably shorter than a typical P-C single bond (e.g., P2-CMe = 1.845 (4) Å), indicating only nominal multiple-bond character. The Fe2-C38 bond length of 2.139 (3) Å is longer than the Fe-C distances observed¹⁷ in Fe₂(CO)₅(PPh₂Me)(μ-PPH₂)(μ-C(O)Me) (1.962 (7) Å) and the Fe₂(CO)₆ complexes of dithioformic acid esters, HC(S)SR. The Fe-C distances found in [μ-CH₃C(O)CH₂SCHS]₂Fe₂(CO)₆ is 1.998 (4) Å while the same distance¹⁴ in [μ-CH₃SC(C₂H₅)S]₂Fe₂(CO)₆ is 2.007 (3) Å. The Fe-C distance in¹⁵ the structurally similar [μ-SCH₂(C₆H₄)CHS(C₂H₅)]₂Fe₂(CO)₆¹⁶ is 2.072 (a) Å, longer than the distance found in the "unrestrained" dithioformic acid ester iron dimer but shorter than that observed in the phosphido analogue.

The intramolecular attack at a metal atom by carbanions generated in a neutral tertiary phosphine ligand has been reported previously,^{8,9} but, to the best of our knowledge, this is the first case of such a reaction sequence involving a phosphido ligand.

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Registry No. 1-CH₂Cl₂, 90343-31-0; 2, 90343-32-1; 3, 90343-33-2; 4, 90343-34-3; 5, 90343-35-4; (μ-PhPH)₂Fe₂(CO)₆, 39049-79-1; Fe, 7439-89-6; α,α'-dibromo-*o*-xylene, 91-13-4.

Supplementary Material Available: Tables of positional and anisotropic thermal parameters, temperature factor expressions, bond distances, and bond angles for **1** and **5** and a listing of observed and calculated structure factor amplitudes for **1** and **5** (50 pages). Ordering information is given on any current masthead page.

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1,4,5,6-Tetraphenyl-2,3-benzo-7,7-dimethyl-7-silanorbornadiene: A Photochemical Source of Dimethylsilylene¹

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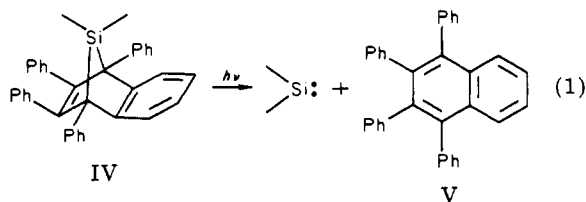
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Summary: 1,4,5,6-Tetraphenyl-2,3-benzo-7,7-dimethyl-7-silanorbornadiene (**IV**) was synthesized in 83% yield by an improved procedure. Photolysis of **IV** at room temperature proved to be an excellent source of dimethylsilylene that could be efficiently scavenged by methanol, 1,2-diphenylacetylene, or benzil to yield the corresponding adducts. Laser flash photolysis experiments showed that the photoexcited state of **IV** decomposed to give dimethylsilylene and triplet 1,4,5,6-tetraphenylnaphthalene within 20-30 ns of the start of the laser pulse.

Photolysis of dodecamethylcyclohexasilane² (**I**) has generally been used to generate dimethylsilylene at room temperature.^{3,4} However, the procedure has a number of disadvantages.

First, photolysis does not lead to a simple distribution of products.³ Decamethylcyclopentasilane (**II**) and dimethylsilylene are formed initially but simply begin the cascade summarized in Scheme I, in which other polysilanes are rapidly formed.³ Of these polysilanes, **III** is rapidly oxidized adding further complexity to product analyses and workup.³ Second, since the detailed photochemistry of the smaller cyclic polysilanes is unknown, it becomes difficult to ascertain whether compounds containing two or more dimethylsilylene moieties arise from repeated insertions of that moiety or whether they derive directly from the photolysis of the cyclic polysilanes themselves.^{3,10}

We have found that photolysis of 1,4,5,6-tetraphenyl-2,3-benzo-7,7-dimethyl-7-silanorbornadiene¹⁴ (**IV**) is an excellent source of dimethylsilylene that obviates many of these problems (eq 1).



The compound was synthesized by a improved method that was similar to that used by Neumann^{15,16} for the preparation of the germanium analogue. Thus, 1,1-di-

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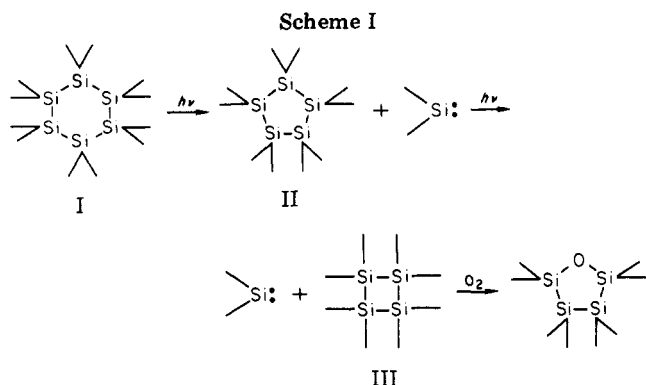
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Table I. Products Derived from Photolysis of 1,4,5,6-Tetraphenyl-2,3-benzo-7,7-dimethyl-7-silanorbornadiene, IV, in Benzene Solutions of Various Substrates at 25 °C

substrate (M)	[IV], M	product	conversion of IV, ^a %	product yield, ^a %
methanol (0.5)	0.20	VI	66	>90
diphenylacetylene (0.05)	0.02	VII	25	~5 ^b
benzil (0.03)	0.02	VIII	57	85

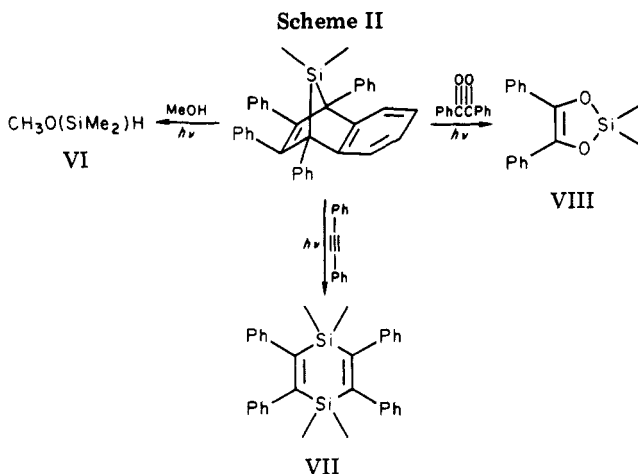
^a By GC analysis and NMR analysis. The samples were all photolyzed under the same conditions. ^b A wide variety of other products were also formed each in low yield and included *cis*- and *trans*-1,2-diphenylethylene.



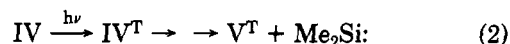
methyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene (1.5 g, 3.6 mmol)¹⁴ was added to magnesium (0.2 g, 8.3 mmol, activated by iodine) in dry tetrahydrofuran (30 mL) under argon. To this mixture was added 2-bromofluorobenzene (1.5 g, 8.6 mmol) dropwise with stirring at 0–5 °C. The mixture was warmed to room temperature after which the stirring was continued for 2 h, and it was finally heated at 40 °C for 30 min. The tetrahydrofuran was evaporated and was replaced by methylene chloride (20 mL). Unreacted magnesium was filtered off, and ethanol (20 mL) was added to the filtrate. Cooling caused IV (1.48 g, 83% yield) to crystallize as a white solid. Further recrystallization from ethanol did not change the melting point (232–233 °C) [lit.¹⁴ 232.5–233.5 °C]: δ (CDCl₃) 0.08 (s, 3 H, SiMe), 0.59 (s, 3 H, SiMe), 7.3–8.7 (m, 24 H, 5Ph). The product was found to be insensitive toward oxygen and moisture.

While thermolysis of IV at 300 °C has been used as a thermal source of dimethylsilylene,¹⁴ its photochemistry does not appear to have been investigated. We used standard scavengers to trap dimethylsilylene and found that photolysis ($\lambda = 250$ nm) of a mixture of IV (10⁻² M) with methanol⁹ (0.5 M), diphenylacetylene¹⁴ (0.05 M), or benzil⁵ (0.03 M) at 37 °C gave the corresponding adducts VI, VII, and VIII, respectively, as shown in Scheme II. Further details are given in Table I. Compounds V, VI, VII, and VIII were identified by their ¹H NMR and from parent ions in their GC/mass spectra or by comparison with authentic samples.

Photolysis of IV in an isopentane glass at -196 °C gave rise to the uv-visible absorption spectrum of V, indicating that decomposition had occurred but it did not give rise to a band at 450 nm that has previously been associated with dimethylsilylene.⁶ Laser flash photolysis of IV in cyclopentane solvent at room temperature gave a transient spectrum similar to that obtained by photolyzing the naphthalene V alone under the same conditions.¹⁷ The transient, which had absorption maxima at 470 and 350 nm, had a lifetime of 2.5 μ s and was quenched by oxygen. We therefore assign it to triplet V. The quantum yield for



its formation was independent of the flow rate used to sweep products formed from sample cell and was directly proportional to the laser power. We therefore conclude that triplet V is formed directly from photoexcited IV within 20–30 ns of the start of laser pulse (eq 2). Moreover, since dimethylsilylene was presumably formed in its singlet ground state,⁷ spin conservation dictates that the photoexcited state of IV that leads to these products must itself be a triplet.



In conclusion 1,4,5,6-tetraphenyl-2,3-benzo-7,7-dimethyl-7-silanorbornadiene can be easily synthesized in high yield as stable, white crystalline solid that is an excellent photochemical source of dimethylsilylene at room temperature.

Acknowledgment. We thank Dr. J. C. Scaiano for the use of the laser flash photolysis equipment and Dr. J. Luszyk for help in its operation. Thanks are also due to Drs. W. P. Neumann and W. P. Weber for helpful discussions.

Registry No. IV, 18816-24-5; V, 751-38-2; VI, 18033-75-5; VII, 751-37-1; VIII, 55629-19-1; dimethylsilylene, 6376-86-9; 1,1-dimethyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene, 7641-40-9; 2-bromofluorobenzene, 1072-85-1.

Synthesis of an η^2 -CH(SMe) Carbene Ligand by Protonation of the Carbyne in [HB(pz)₃](CO)₂W(≡CSMe). A Possible Model Step in CO Hydrogenation

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Summary: Protonation of [HB(pz)₃](CO)₂W(≡CSMe) with strong acids gives [HB(pz)₃](CO)₂W[η^2 -CH(SMe)]⁺ in

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(17) In fact, the ratio of optical densities for the 350- and 470-nm bands was 3.1 for the photolysis of IV vs. 2.1 for V. This implies the presence of a second transient in the photolysis of IV which absorbs at 350 nm and has a lifetime of ~2.5 μ s. It is possible that this additional absorption is due to dimethylsilylene.