disproportionation of the radical pair to give tri-*tert*-butylcyclopropene, 8, and ethoxymesitylsilylene. The silylene subsequently reacts with the ethanol which is present to give the diethoxysilane, 10.[13] Similarly, we believe that the formation of the monoethoxysilane, 11, results from homolytic cleavage of the starting trisilane to give tri-*tert*-butylcyclopropenyl and mesityl(trimethylsilyl)silyl radicals. Since these radicals cannot undergo the same disproportionation reaction as does the previously discussed radical pair, each of the radicals probably abstracts a hydrogen atom from the solvent system to give 8 and mesitylbis(trimethylsilyl)silane. The silane may then photolyze to give mesitylsilylene which reacts with ethanol to give 11. Although we do not detect the mesityltrisilane in our photolysis mixtures, we have independently shown that this compound photolyzes much more efficiently than our starting trisilane. Considering the small amounts of 11 actually formed in this photolysis (vide infra, minor pathway), it is possible that the steady state concentration of this intermediate would be too small to be detected in our experiment.

Interestingly, we see little evidence for the trapping of valence isomers of the silylene 12. Only when **4b** was photolyzed at near ambient temperatures and at low concentrations of ethanol (0.25% v/v) can several isomers of the silylene-trapped product be detected. The overall yield of these products is less than 1%. We believe that these products arise from the trapping of small amounts of valence isomers, and attempts to characterize these compounds are presently underway.

In conclusion, the cyclopropenylsilylene 12 does not appear to undergo facile isomerization under conditions which would be favorable for the isomerization of the analogous carbenes and nitrenes. The origin of this difference may lie in the relative stability of the silylene in respect to its closed-shell valence partners. Results of a recent ab initio molecular orbital calculation indeed suggest that cyclopropenylsilylene is nearly thermoneutral with silacyclobutadiene and over 30 kcal mol^{-1} more stable than silatetrahedrane.[14] The presence of a significant activation barrier for the isomerization of the silylene would thus account for the apparent thermal stability of 12.

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Supplementary Material Available: Complete listings of atomic coordinates and bond lengths and angles (24 pages); a listing of structure factor amplitudes (23 pages). Ordering information is given on any current masthead page.

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(13) A similar disproportionation of silyl radicals to form silylene and silane has been observed in the gas phase. Reimann, B.; Matten, A.; Lavpert, R.; Potzinger, P. *Ber. Bunsenges. Phys. Chem.* 1977, *81*, 500–504. We favor the radical disproportionation mechanism in our system on the basis of deuterium-labeling experiments. For instance, the photolysis of the Si–D isotopomer of 9 in EtOH gives mostly the C–D isotopomer of 8. Complete details of these labeling experiments will be described in a future paper.

(14) Schriver, G. W.; Fink, M. J.; Gordon, M. S., submitted for publication in *Organometallics*.

Characterization of Bis(2,4,6-tri-*tert*-butylphenyl)germanium(II) Using Extended X-ray Absorption Fine Structure

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Summary: Bis(2,4,6-tri-*tert*-butylphenyl)germanium(II) was characterized by extended X-ray absorption fine structure (EXAFS).

Although germylenes R_2Ge have received attention as reactive intermediates in synthetic chemistry and reaction mechanism,[1] there is no report on the direct observation of germylenes in solution. The technique of the direct observation of germylenes has been limited to the matrix isolation until now.[2] In this communication, we report the first direct observation of germylene, bis(2,4,6-tri-*tert*-butylphenyl)germanium(II), in solution by extended X-ray absorption fine structure (EXAFS).

The synthesis of bis(2,4,6-tri-*tert*-butylphenyl)germanium(II) (1) was carried out similarly as described in literatures.[3,4] Thus, after the addition of germanium(II) iodide (0.82 g, 2.5 mmol) to a solution of 2,4,6-tri-*tert*-butylphenyl bromide (1.63 g, 5.0 mmol) in tetrahydrofuran (THF) (20 mL) and *n*-butyllithium (5.0 mmol) in hexane at −78 °C, the resulting mixture was stirred at the same temperature for 2 h and then warmed to room temperature.[4]

EXAFS measurements were performed by using the laboratory EXAFS spectrometer reported elsewhere.[5] The sample was transferred from a reacting vessel to a Pyrex flat cell (path length ≈ 2 mm) in an argon atmosphere in order to avoid decomposition by moisture, and the cell was sealed after the sample was degassed.

EXAFS is the most suitable method because it can tell the kinds of interatomic distances in the first several coordination shells surrounding the absorbing atom in a multicomponent system.[6]

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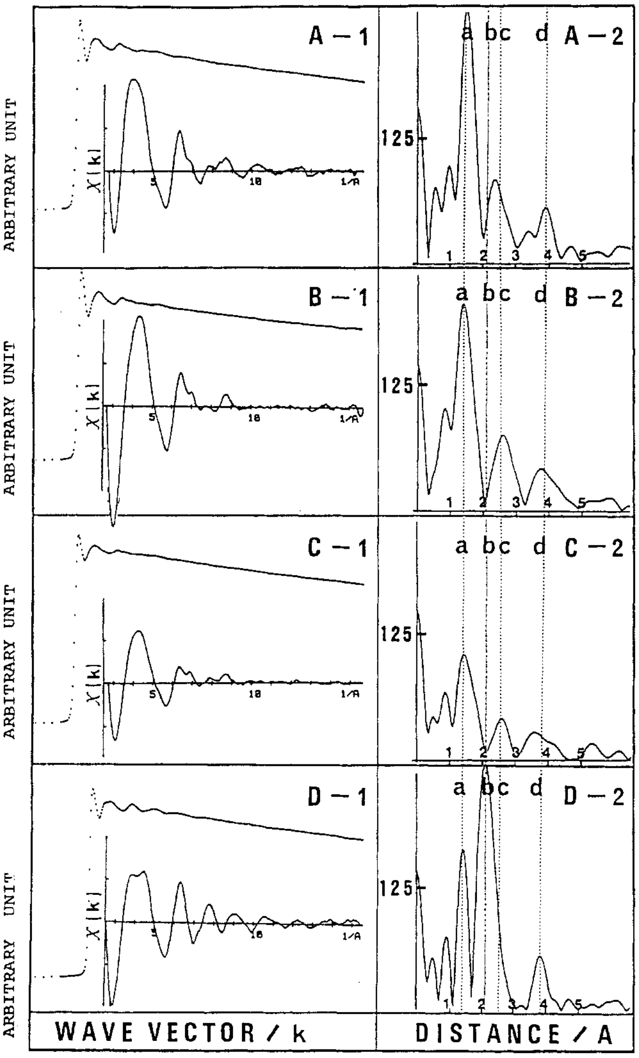

Figure 1. EXAFS spectra and the associated Fourier transforms of Ph_4Ge (A), Ph_3GeH (B), Ph_2GeH_2 (C), and $Ph_3Ge-GePh_3$ (D).

The effect of the number of phenyl rings and that of the Ge–Ge bond on the EXAFS spectra were studied for four reference materials: Ph_4Ge, Ph_3GeH, Ph_2GeH_2, and $Ph_3Ge-GePh_3$. EXAFS spectra and the associated Fourier transforms of the reference materials are shown in Figure 1A–D. Extracted oscillations used to Fourier transform were taken over the same wave vector range of $2.8 < k < 11$ Å^{-1}. Therefore, the comparison of the coordination number of each Fourier transform can be done precisely. The peaks a, c, and d in Figure 1 correspond to the interatomic distances of Ge and the first, second, and third nearest carbon of the aryl ring, respectively. Indeed, a calculation including the phase factor shows that the peaks are at representive interatomic distances of 1.94–1.97 Å, which agree well with the known Ge–C bond distance.[7] The heights of the peaks on the line change with the increasing number of aryl rings and serve as a ring number marker. The peak b is observed only for $Ph_3Ge-GePh_3$. It is certain that this peak at around 2.2 Å corresponds to the Ge–Ge bond,[7-9] since after the correction for the phase factor, the interatomic distance is determined to be 2.43 Å, which coincides with the reported value of 2.44 Å for a similar molecule. This peak is the strongest one in Figure 1D, since the Ge atom has much stronger back-scattering amplitude than carbon. Therefore, if Ge=Ge bond exists in the product, the corresponding peak should appear prominently at around 2.2 Å, in addition to those corresponding to Ge—C bonds. The number of aryl rings should be determined from the intensities of Ge–C peaks.

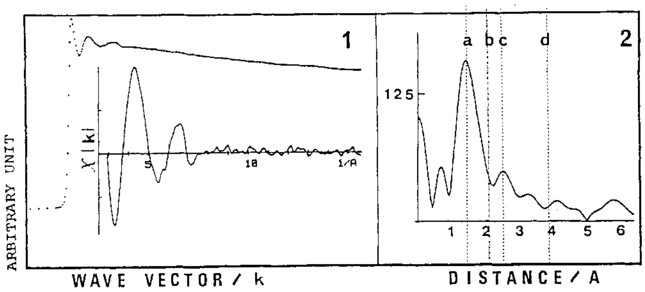

Figure 2. EXAFS spectrum and the associated Fourier transform of 1.

Extracted oscillation and the associated Fourier transform of the EXAFS of the product is shown in Figure 2. From a comparison of extracted oscillation, the product is similar to that of Ph_2GeH_2; on the Fourier transform, the bond length and the intensity of the first and the second nearest peaks agree with those of Ph_2GeH_2. In addition, no peak is observed around 2.2 Å, where the Ge–Ge bond is expected if it exists at all. Therefore, EXAFS results clearly show that the local structure around Ge atoms in the product has only two aryl groups and does not have Ge=Ge bond. Therefore, the structure of the product is concluded to be a carbene structure.

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Synthesis and Structure of $[(NMe_2)_3TiFe(CO)_2(Cp)]$: A Stable Iron–Titanium Bond

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Summary: $[Ti(NMe_2)_4]$ reacts with $[FeH(CO)_2(Cp)]$ to form $[(NMe_2)_3TiFe(CO)_2(Cp)]$ (**1**), by the elimination of 1 equiv of $HNMe_2$. This compound was spectroscopically characterized, and its structure was determined by single-crystal X-ray diffraction ($R = 4.0\%$, $R_w = 4.4\%$). There is a direct, unsupported bond between iron and titanium in **1**, with bond lengths of 2.567 (1) and 2.569 (1) Å in two independent molecules. The relative orientation of the ligands on iron and titanium suggests that there may be a π-component of the metal–metal bond. Amide methyl groups distal to iron show unusually obtuse Ti–N–C angles of about 130°. Analogous complexes with alkoxide ligands on titanium are more labile than **1**.