Silylfullerenes

Takeshi Akasaka,^{*a} Takatsugu Wakahara,^a Shigeru Nagase,^{*b} and Kaoru Kobayashi^b

^aGraduate School of Science and Technology, Niigata University,

^bDepartment of Chemistry, Graduate School of Science, Tokyo Metropolitan University,

Received July 4, 2000

Abstract: Novel chemical derivatizations of C₆₀, higher fullerenes and endohedral metallofullerenes with activated organosilicon compounds have been made to afford the mono- and bis-silylated fullerenes (silylfullerenes) in order to understand the basic chemical properties of fullerenes and to obtain new derivatives with interesting physical and chemical properties.

1. Introduction

Since the isolation of C₆₀ in preparatively useful quantities, much attention has been devoted to chemical derivatization of this new allotropic form of carbon, which continuously yields fascinating results.¹ Exohedrally derivatized fullerenes have been extensively developed to explore their potential usefulness as novel materials. In principle, there are three types of fullerene chemistry: i) exohedral chemistry, in which chemical functionalization has been studied, ii) endohedral chemistry, in which encapsulated metal,² nitrogen³ and noble gas⁴ atom dopings have been investigated and iii) framework chemistry, in which heterofullerenes⁵ such as C₅₉N and endohedrally metal-doped heterofullerenes⁶ have recently been found.

Meanwhile, organosilicon compounds such as disilanes and polysilanes represent a unique feature of materials.⁷ The combination of these two different classes of interesting molecules reveals exciting possibilities for the creation of new types of materials. In this context, we carried out photolytic reactions of fullerenes and endohedral metallofullerenes with activated organosilicon compounds such as silylene, disilane, disilane and polysilane. Upon photo-irradiation, they act not only as an attractive synthetic reagent but also as a mechanistic probe to clarify the chemical and electronic properties of fullerenes and endohedral metallofullerenes.

In this account, we would like to briefly summarize our recent results on novel photochemical derivatization of fullerenes with organosilicon compounds to afford the corresponding silylated fullerenes (silylfullerenes), which open new routes to synthetically useful bis-silylation and fullerene chemistry.

2. Mono- and Bis-silylation of C₆₀

2.1 1,2-Cycloaddition with Silylene

The addition of bis(2,6-diisopropylphenyl)silylene⁸ (**1a**) to C₆₀ furnishes the first silylated adduct (**2a**) as the ring-closed 1,2-bridged isomer.⁹ A typical reaction was as follows. Trisilane **3a**, a silylene precursor, was photolyzed with a low-pressure mercury lamp in a toluene solution of C₆₀. Purification by chromatography led to thermally stable mono-adduct **2a** (58%) and bis-adduct **4a** (27%) together with a trace of tris-adduct **5a** (Scheme 1).

Scheme 1

Fast atom bombardment (FAB) mass (pos) spectrometry (*m*-nitrobenzylalcohol was used as the matrix solvent) of **2a** displays a peak for **2a** as well as for C₆₀ which arises from loss of **1a**.⁹ The UV-vis absorption spectrum of **2a** is typical of most monoaddition derivatives of C₆₀. Several IR bands are observed, including four bands which correspond to those in the C₆₀ spectrum.⁹ The FAB mass, UV-vis and FTIR spectra of **2a** suggest that this new derivative retains the essential electronic and structural character of C₆₀. The ¹³C NMR spectrum of **2a** shows a total of 17 signals (4 × 2; 13 × 4) for the C₆₀ skeleton, suggesting that **2a** has C_{2v} symmetry (Figure 1).⁹ The ¹³C NMR signal at δ = 71.12, which is ascribed to the sp³ carbons of the silirane ring, strongly sup-

Figure 1. Optimized structures of **2a**, **10f**, **16** and **22g** at the AM1 level.

ports **2a** rather than silamethano[10]annulene **6a'**; an sp^2 C-Si should give rise to a signal below $\delta = 130$. This is confirmed by the ^{29}Si NMR peak at $\delta = -72.74$, since a typical chemical shift for a silicon atom in a silirane ring appears at high field ranging from $\delta = -50$ to $\delta = -85$.¹⁰

The experimental finding for **2a** was confirmed by AM1 molecular orbital calculations¹¹ on the reaction of C_{60} and silylenes $\text{Ph}_2\text{Si:}$ and $\text{H}_2\text{Si:}$ (Table 1).⁹ $\text{Ph}_2\text{Si:}$ and $\text{H}_2\text{Si:}$ add across the junction of two six-membered rings in C_{60} to give siliranes **2d** and **2e** (1,2-adducts), with an exothermicity of 61.3 and 78.0 kcal/mol, respectively. The isomeric **2d'** and **2e'** were not found to be minima on the potential energy surface. The 1,2-adduct **2d** was 19.4 and 10.7 kcal/mol more stable than the 1,2-adducts **6d** and **6d'**, respectively. **2e** was 19.0 and 6.2 kcal/mol more stable than **6e** and **6e'**, respectively. The less stable **6d** and **6e** isomerize to **6d'** and **6e'** with small barriers of 2.0 and 1.0 kcal/mol, respectively. This is in interesting contrast with the addition of diphenylmethylene for which the 1,2-adduct at the 6,6-junction was calculated to be only 1.2 kcal/mol more stable than the 1,2-adduct at the 5,6-junction.

Table 1. Relative energies (kcal/mol) of isomers of C_{60} /silylene adduct at the AM1 level

	1,2-adduct at the 6,6-junction		1,2-adduct at the 5,6-junction

2		2'	6	6'
d: R=Ph	0.0	no minimum	19.4	10.7
e: R=H	0.0	no minimum	19.0	6.2

For the silylene addition an interesting feature supporting the formation of several multiple-addition products has been observed in the FAB mass spectra of the reaction mixtures. The product composition of silylene-addition reactions varies with the amount of trisilane used.^{9b} When an excess of trisilane was used, four **1a** molecules bonded on the surface of C_{60} affording **7a**. The NMR spectra of each of the isolated multiple-addition products, $\text{C}_{60}(\text{Dip}_2\text{Si})_2$, $\text{C}_{60}(\text{Dip}_2\text{Si})_3$ and $\text{C}_{60}(\text{Dip}_2\text{Si})_4$, reveal a mixture of several regioisomeric adducts. In the cases of bis(2,6-diethylphenyl)- (**1b**) and bis(2,6-dimethylphenyl)silylene (**1c**), the corresponding five silylene adducts (**8b** and **8c**) were also obtained as confirmed by FAB mass analysis. A reason why several silylenes so easily add onto C_{60} is explained by means of AM1 calculations.^{9b} Table 2 reveals that there is no significant difference in the heat of reaction for the first, second, third, or even sixth addition of silylene. This result is also confirmed by the charge densities on the diphenyl silylene adduct (**2d**), in which calculated negative charge densities are mainly localized on the sp^3 carbons with only negligible change at other carbon atoms. Meanwhile, almost one electron flows into C_{60} , indicating that **2a** has higher reduction and lower oxidation potentials than C_{60} .⁹ In fact, reduction potentials (oxidation potentials) of C_{60} and **2a** are $-1.13(1.26)$ and $-1.26(0.65)$ V vs Fc/Fc^+ couple, respectively, as discussed in Section 2.2.

Table 2. AM1 calculations of C_{60} /silylene adduct

	$\text{C}_{60}(\text{SiH}_2)_n$			
	n=1	n=2	n=3	n=6
ΔH per SiH_2 (kcal/mol)	78.0	77.8 (C _S) 77.7 (D _{2h})	77.5 (C _{2v} -A) 77.5 (C _{2v} -B) 77.6 (C ₁)	76.9

It is known experimentally and theoretically that the reaction of a silylene with olefin is initiated by a π -electrophilic approach of the silylene.¹² However, in the present case it was found that silylene nucleophilically attacks C_{60} via σ -approach. This might be attributable to the stronger electron-accepting ability of C_{60} . Similarly, the HOMO(silylene)-LUMO(C_{70}) interaction plays an important role in the reactivity of C_{70} .¹³

2.2 1,2- and 1,4-Cycloaddition with Disilirane

It is well known that strained Si-Si δ bonds can act as an electron donor.^{14,15} Therefore, the chemical derivatization of C_{60} by 1,1,2,2-tetramesityl-1,2-disilirane¹⁴ (**9f**) was investigated.¹⁶ When a toluene solution of C_{60} and **9f** was subjected to thermal reaction, however, no addition reaction occurred. This indicates that the nucleophilicity of the disilirane is too small to permit the reaction with the ground state C_{60} . One promising approach in this direction is the photochemical activation of C_{60} .¹⁶ Since photoexcited C_{60} is a stronger electron acceptor than C_{60} in its ground state, the excited state of C_{60} is of particular interest under laboratory conditions without acid or base catalysts. Although photo-induced charge-transfer between C_{60} and various electron donors such as aromatic amines, semiconductor colloids, porphyrins, and photoconducting polymers¹⁷ can occur, there has so far been no example of formation of a photoadduct. Here we report the first photochemical reaction of C_{60} with a disilirane to produce a cycloadduct, via a charge-transfer interaction.¹⁶ This is noteworthy since bisilylation of an unsaturated carbon-carbon bond with disilane has been successful only in the presence of a metal catalyst¹⁸; no non-metal catalyzed bisilylation has been reported yet.

Photolysis (>300 nm) of a toluene solution of disilirane **9f** and C_{60} led to the facile formation of the 1,1,3,3-tetramesityl-1,3-disilolane **10f** in 82% yield as the first doubly silylated fullerene, together with a small quantity of bis-adduct **11f**¹⁶ (Scheme 2). The adduct **10f** can be readily isolated by preparative HPLC. Very similar results were obtained with 1,1,2,2-tetrakis(2,6-dimethylphenyl)-1,2-disilirane (**9c**). Both disiliranes were thermally unreactive toward C_{60} at 90 °C.

Scheme 2

Interestingly, the UV-vis spectrum of **10f** has absorption features comparable to those of the carbon and oxygen analogs of **10f**, and the related carbene, silylene, and oxygen adduct, as one would expect from the similarity of the chromophore in these compounds.¹⁶

NMR investigations as well as AM1 calculations¹¹ reveal that **10** has a 6-6 ring bridged structure. The ¹H NMR spectrum of **10f** displays six methyl signals and four meta-proton signals from the mesityl groups. An AB quartet for the two methylene protons is also observed. The ¹³C NMR spectrum of **10f** shows 32 (28 × 2; 4 × 1) signals for the C₆₀ skeleton. Twelve signals for 4 tertiary and 8 quaternary aromatic carbon atoms, and 1 signal for the methylene carbon atom of the disilirane component are also observed. These spectral data suggest that **10f** has C_s symmetry. Analysis of the C-H 3-bond coupling in the H-C COLOC NMR spectrum gave crucial evidence for the identification of the 1,3-disilolane structure in **10f**. A cross-peak corresponding to a proton of the methylene group and two sp³ carbon atoms of C₆₀ at 73.36 ppm was observed. The ²⁹Si NMR spectrum of **10f** shows a peak at 9.81 ppm.

Symmetry arguments support several possibilities shown in Figure 2. To obtain further information on the structure of **10f**, variable-temperature ¹H NMR measurements were made. Coalescence of the para-methyl signals at 2.06 and 1.96 ppm at 44 °C reflecting conformational change of the molecule was observed, yielding a free energy of activation of ΔG[‡] = 17.0 kcal/mol. The two pairs of four resonances between 6.7 and 6.3 ppm, and 3.3 and 2.3 ppm also coalesce at 60 and 80 °C, respectively. The ΔG[‡] for both the meta-proton and ortho-methyl groups at the coalescence temperatures is 16.2 kcal/mol. These results reveal that the methylene, methyl and aromatic protons are equivalent above the coalescence temperature and give strong support to hypothesis (iii).

Figure 2. Possible structures of **10f** with C_s symmetry.

Hypothesis (iii) was also supported by AM1¹¹ and *ab initio* 3-21G¹⁹ calculations which show that the 1,2-adduct at the 6,6-junction is 16.9 (AM1) and 26.5 (3-21G//AM1) kcal/mol more stable than the 1,2-adduct at the 5,6-junction of C₆₀ and disilirane **9e** (Figure 2). The 1,2-adduct at the 6,6-junction is 3.3(AM1) and 3.7(AM1) kcal/mol more stable than the 1,4-adduct **III** and **IV** on the reaction with **9f**, respectively (Table 3). The experimental finding of a C_s structure for **10f** (1,2-adduct at the 6,6-junction) was confirmed by full geometry optimization at the AM1 level; its C_s structure corresponds to an energy minimum and is the most stable. As the optimized structure in Figure 1 shows, four bulky mesityl groups are beautifully spaced in C_s symmetry with the

Table 3. Relative energies (kcal/mol) of isomers of C₆₀/disilirane adducts at the AM1 level

	1,2-addition		1,4-addition		
	envelope	twist	5-membered envelope	6-membered envelope	twist
	I (C _s)	II (C ₂)	III (C _s)	IV (C _s)	V (C ₁)
R=Mes, X=CH ₂	0.0	3.8	3.3	3.7	1.2
R=Dep, X=CH ₂	1.0	-	3.8	3.9	-1.7
	0.0 (C ₁)				
R=Mes, X=O	0.0	8.7	1.8	2.7	-2.9

observed equivalency. The high barrier observed is ascribed to the fact that the space between C₆₀ and mesityl groups, as well as between the mesityl groups, becomes filled upon transformation from one envelope-conformer to the other. Such steric effects were also reflected in the fact that the exothermicity (34.1 kcal/mol) for the addition of **9f** to C₆₀ is 43.2 kcal/mol smaller than that (77.3 kcal/mol) of **9e** at the AM1 level.

A characteristic feature is that **10f** has both a higher reduction (−1.29 V vs Fc/Fc⁺ couple) and a lower oxidation (0.60 V) potential than C₆₀, as does **2a**.¹⁶

The free energy change (ΔG)²⁰ for electron transfer reaction from disilirane to the triplet state of C₆₀ is 8.1 kcal/mol, indicative of endothermic electron transfer.¹⁶ The rate of disappearance of C₆₀ during the photoreaction with disilirane was suppressed by addition of 1,4-diazabicyclo[2.2.2]octane and 1,2,4,5-tetramethoxybenzene, each of which has a lower oxidation potential and is photochemically unreactive toward C₆₀. The reaction was completely inhibited by addition of rubrene as a triplet quencher. Although no absorption of disilirane is observed at >400 nm, the photocycloaddition proceeds smoothly upon irradiation (>400 nm). These observations were interpreted as a possible exciplex formation between the disilirane and a triplet state of C₆₀, prior to production of the adduct. Actually, very efficient C₆₀ triplet quenching by disilirane **9f** has been observed supporting the above mechanism. Laser flash photolysis technique has been used to confirm the reaction mechanism.²¹ 532 nm laser photolysis was carried out to observe transient absorption bands in the near-IR region, as mentioned in Section 5. In benzene, the absorption band of C₆₀[−] was not observed at all. However, the decay of ³C₆₀^{*} was accelerated, probably due to the generation of an exciplex intermediate followed by the formation of the adduct of **9f** and C₆₀.

In the case of 1,1,2,2-tetrakis(2,6-diethylphenyl)-1,2-disilirane (**9b**), both 1,2- and 1,4-cycloadducts were isolated and characterized by means of the NMR measurement.²² Irradiation (>300 nm) of a toluene solution of **9b** and C₆₀ resulted in formation of 1,3-disilolane (**13b**, 1,2-adduct at the 6,6-junction) and 1,3-disilepane (**13b'**, 1,4-adduct). A sample of **13b** and **13b'** can be separated and purified by preparative HPLC.

The structure of **13b** was determined by means of ¹H, ¹³C, ²⁹Si and ¹³C INADEQUATE (Incredible Natural Abundance Double Quantum Experiment) NMR measurements.²² Spectroscopic analysis and theoretical investigation confirm that

the 1,3-disilepane structure for **13b'** has C_1 symmetry because of the 1,4-addition. The ^1H NMR spectrum of **13b'** reveals that all methyl and methylene protons on the ethyl groups, and both methylene protons are inequivalent. The resolved ^{13}C NMR spectrum showed the C_{60} adduct resonances expected for a C_1 -symmetrical compound. In INADEQUATE NMR measurements of **13b'**, a cross-peak corresponding to two bridgehead sp^3 carbon atoms of the fullerene skeleton was not observed, indicating no connectivity between them (Figure 3). Each of these sp^3 carbon atoms, however, has three cross-peaks associated with sp^2 carbon atoms in the fullerene. These results confirm the 1,4-addition product.

Figure 3. ^{13}C INADEQUATE NMR spectrum of **13b'**.

As Table 3 shows,²² full geometry optimization was carried out for the 1,2-cycloadducts (**I** and **II**) and 1,4-cycloadducts (**III**, **IV** and **V**) at the AM1 level.¹¹ 1,2-Adduct **13b** is less stable than 1,4-adduct **13b'**. It is notable that the most stable structure **V** resulting from 1,4-cycloaddition has C_1 symmetry in the twisted form. This agrees with the experimental finding from spectroscopic data. The optimized structures of **13b** and **13b'** are shown in Figure 4.

Figure 4. Optimized structures of **13b** and **13b'** at the AM1 level.

Analysis of the HC 3-bond coupling in the gradient HMBC NMR spectrum, which is associated with the dihedral angles between the methylene protons and the sp^3 carbon atoms, gave crucial evidence for the twisted form, as shown in Figure 5.²² For **V**, one proton of the methylene group couples with one sp^3 carbon atom and another proton couples to the other sp^3 carbon atom, whereas, for **III** and **IV**, one proton of a methylene group couples with both sp^3 carbon atoms of the fullerene skeleton, while the other proton does not couple with any sp^3 carbon atom. In Figure 5,

Figure 5. HMBC spectrum of **13b'**.

two cross-peaks were actually observed, corresponding to one proton of the methylene group and one sp^3 carbon atom, and another proton and another carbon atom, respectively.

Coalescence of the methyl signals occurs at 75 $^{\circ}\text{C}$, reflecting conformational change of the molecule with a free energy of activation of $\Delta G^{\ddagger} = 17.8$ kcal/mol. This high barrier is ascribed to the fact that the space between C_{60} and the 2,6-diethylphenyl groups as well as between the 2,6-diethylphenyl groups is limited during the transformation from one twist-conformer to the other.

A most interesting finding is that the 1,2-adduct **13b** thermally isomerize to the 1,4-one **13b'**.²² This preferential isomerization is ascribable to the fact that the 2,6-diethylphenyl group (Dep) is bulkier than the mesityl group, and hence steric repulsions between C_{60} and Dep groups as well as between Dep groups are larger in the 1,2-adduct.

The oxadisilirane **14** also reacts with C_{60} to give a mixture of 1,2-adduct at the 6,6-junction and 1,4-adduct.²³ The relative stabilities of the possible products were calculated by the AM1 method¹¹ and found to be fully consistent with the experimental results. (Table 3) A thermal rearrangement of the 1,2-adduct to the 1,4-adduct was also observed by monitoring the ^1H NMR spectral changes with time.

Photochemical bis-silylation of C_{70} with disilirane **9f** was also accomplished to afford the 1,4-adduct having an equatorial bonding structure.²⁴

On the other hand, the digermirane **15** reacts with C_{60} to afford the 1,4-adduct (**16**, twist form) selectively, as the first example of photochemical bis-germylation (Figure 1).²⁵ The structure of the 1,4-adduct was also confirmed by ^{13}C INADEQUATE NMR measurement.

To design new organofullerenes for applications in material science and biochemistry, one should know how the substituents on C_{60} affect its electronic properties. Namely, an interesting point is how the silicon groups on C_{60} affect its

redox properties. The relationship between the structures and redox properties was investigated by a comparative electrochemical study of various organofullerenes derivatized with oxygen-, carbon-, and silicon containing groups at a 6,6-ring junction.²⁶

A characteristic feature of the mono-silylated and bis-silylated fullerenes is their higher reduction and lower oxidation potentials than that of C_{60} itself and analogous carbon substituted derivatives, due to the electron-releasing nature of silicon relative to carbon.²⁶ AM1 molecular orbital calculations¹¹ were carried out on selected organofullerenes to examine the linear correlations of the redox potentials with MO energy levels. The first and second reduction potentials correlate well with the LUMO energy levels, while the third reduction potentials correlate better with the LUMO+1 energy levels. The oxidation potentials also show good linear correlation with the HOMO energy levels. Silicon derivatives **2a** and **10f** are even more electropositive than their carbon analogs **17** and (diphenylmethano)fullerene **19**. The reduction potentials depend on the electronegativities of the attached atoms. Electron-donating groups, such as alkyl and silyl, significantly lower the oxidation potential of C_{60} . This is in agreement with the calculations which indicate that almost one electron is transferred onto C_{60} from the silicon substituent.

Table 4 shows the redox potentials of carbon (**17**),²⁶ silicon (**10f**),¹⁶ and germanium (**16**)²⁵-containing organofullerenes. The electron affinities of these organofullerenes decrease in the order **17** > **16** > **10f**, which is in accord with the electronegativity order of the attached atoms. This is in agreement with the calculations which indicate that the LUMO levels increase in the order **17** (−2.80 eV) < **16** (−2.59 eV) < **10f** (−2.49 eV). The salient feature in Table 4 is that **16** has a remarkably low oxidation potential (+0.59 V vs Fc/Fc⁺ couple), as does **10f** (+0.60 V), compared with the value of **17** (+1.03 V). This result is in agreement with the fact that the HOMO levels of **16** (−8.73 eV) and **10f** (−8.68 eV) are higher than that of **17** (−9.24 eV). It may thus be assumed that partial charge transfer into C₆₀ from the germanium group in **16** occurs, as is the case for **10f**.

The multiple addition product ratios in the reaction of **C₆₀** with silylene **1a** and disilirane **9f** are significantly different. When equimolar amounts of **C₆₀** and a silicon reagent were

Table 4. Redox potentials of C₆₀ and organofullerenes by cyclic voltammetry (V)

Compound	oxE_1	redE_1	redE_2	redE_3
C₆₀	+1.21	-1.12	-1.50	-1.95
17		-1.23	-1.58	-2.11
18		-1.13	-1.50	-1.99
10f	+0.60	-1.29	-1.67	-2.18
16	+0.59	-1.24	-1.63	-2.15
19		-1.18	-1.56	-2.03
20		-1.08	-1.48	-1.93
2a	+0.65	-1.26	-1.63	-2.18

17

18

19

20

used, in the silylene case, the ratio of the mono- and di-adduct is 2 to 1.^{9a} However, in the case of disilirane, the ratio goes up 10 to 1.¹⁶ As mentioned before, almost one electron flows onto C₆₀ from the silicon substituent in disilirane and silylene adducts, and hence their redox potentials are almost the same. This means that electronically there is little difference between the silylene- and disilirane-adducts. It might be considered that steric effects play an important role in this addition reaction. In the silylene-adduct, some space remains for a second attack by silylene. In the case of the disilirane-adduct, however, the second attack is very difficult, because of bulkiness of the disilirane moiety.

2.3 1,6-Addition with Disilane

The bisilylated C₆₀ obtained by the photochemical reaction of C₆₀ with a disilane has a strikingly low oxidation potential.²⁷ Irradiation of a benzene solution of 1,1,2,2-tetraphenyl-1,2-di-*tert*-butyl-1,2-disilane (**21g**) and C₆₀ (1:1) with a low-pressure mercury-arc lamp in a quartz tube resulted in formation of the adduct **22g** in 58% yield²⁷ (Scheme 3). The adduct **22g** can be readily isolated by preparative HPLC. Similar results were also obtained with hexaphenyldisilane (**21h**) and 1,1,2,2-tetraphenyldisilane (**21i**).

Scheme 3

The ^1H , ^{13}C and ^{29}Si NMR, and ^{13}C 2D NMR spectral data clearly indicate C_2 symmetry for **22g**. AM1 molecular orbital calculations¹¹ confirm the 1,6-adduct structure with C_2 symmetry for **22g** (1,16- or 1,29-addition product represented by the Schlegel diagram is named 1,6-adduct for convenience). The optimized structure of 1,6-($^t\text{BuPh}_2\text{Si}$) $_2\text{C}_{60}$ at the AM1 level is shown in Figure 1.²⁸

As mentioned in Section 2.2, the photochemical bis-silylation of C_{60} via its excited state has been found.¹⁶ In order to shed light on the mechanism of the reaction of **21g** with C_{60} , 532 nm laser photolysis with observation of transient absorption bands in the near-IR region was carried out. The absorption band of ${}^3C_{60}^*$ at 740 nm was observed immediately after laser exposure. The decay of ${}^3C_{60}^*$ was not accelerated by addition of disilane **21g**. The absorption band of $C_{60}^{\cdot-}$, which would be anticipated to appear at 1070 nm, was not observed at all. Thus, it is evident that ${}^3C_{60}^*$ and $C_{60}^{\cdot-}$ do not play an important role in these reactions. These results indicate that the formation of **22g** might be rationalized in terms of the intermediacy of a ${}^tBuPh_2Si\cdot$ radical generated by photochemical Si-Si cleavage of **21g**. In fact, no **22g** was produced upon irradiation at > 300 nm where cleavage of **21g** does not occur. This radical mechanism²⁹ is further substantiated by control experiments in the presence of a radical scavenger (cumene and CCl_4). In contrast, no silylated C_{60} product was obtained in the photolysis of C_{60} with $(MePh_2Si)_2$ (**21j**), $(Me_2PhSi)_2$ (**21k**), and $({}^iPrPh_2Si)_2$ (**21l**). These results of **21j-l** might be attributable to inhibition of silyl radical addition to C_{60} caused by the concomitant reactions such as disproportionation of silyl radicals and intramolecular 1,3-silyl

migration.

As shown in Table 5, **22g** and the related bissilylated compounds **10f** (1,2-adduct), **13b'** (1,4-adduct) showed three reversible reductions and two irreversible oxidations in 1,2-dichlorobenzene.²⁷ The salient feature is that 1,6-adduct **22g** has a remarkably low oxidation potential (+0.33 V) compared with **10f** (+0.77 V) and **13b'** (+0.73 V). The theoretical calculation (3-21G//AM1)³⁰ is in agreement with this result; the ionization potentials of (H₃Si)₂C₆₀ decrease in the order 1,2-adduct **23** (7.26 eV) > 1,4-adduct **23'** (7.09 eV) > 1,6-adduct **23''** (6.40 eV) as shown in Table 6. This dramatic result for the electrochemical properties can be explained by the unique structure of the 1,6-adduct; the 1,6-adduct has two short bonds between a pentagon and a hexagon, which gives more strain to the carbon framework (Figure 6).²⁷ This strain energy may be released in the cationic form where

Table 5. Redox potentials (V), and HOMO and LUMO levels (eV) of **10f**, **13b'**, and **22g**

Compound	oxE ₂ ^b	oxE ₁ ^b	redE ₁	redE ₂	redE ₃	HOMO ^c	LUMO ^c
C ₆₀		+1.21	-1.12	-1.50	-1.95	-9.64	-2.95
1,2-adduct 10f ^a	+1.22	+0.60	-1.29	-1.67	-2.18	-8.68	-2.49
1,4-adduct 13b'	+1.26	+0.73	-1.22	-1.61	-2.12	-8.66	-2.52
1,6-adduct 22g	+1.20	+0.33	-1.19	-1.59	-2.18	-8.35	-2.66

^a Ref. 2. ^b Irreversible. ^c Calculated at AM1 level.

Table 6. The relative energies (kcal/mol) of **23**, **23'**, **23''** and their cation radicals, and ionization potentials (IP, eV)^a

Isomer	Neutral	Cation radical	IP
1,2-adduct 23	3.4	7.4	7.26
1,4-adduct 23'	0	0	7.09
1,6-adduct 23''	14.5	-1.4	6.40

^a Calculated at the HF/3-21G//AM1 level.

Figure 6. Neutral and cationic forms of **23**, **23'** and **23''**.

these bonds (1.450 Å by AM1) are much longer than those in the neutral form (1.387 Å by AM1). Consequently, it has been demonstrated that bissilylation of C₆₀ takes place readily *via* silyl radicals generated photochemically from some simple disilanes. Experimental data and theoretical calculations suggest that the redox properties of fullerenes are controlled not only by the electronegativity of the substituents, but also by the regiochemistry of the functionality and its effect on their network. It is expected that these derivatized fullerenes, which display strikingly low oxidation potentials, will open up new applications of C₆₀ as electron-donors. In this context, we recently obtained tetrakis-silylated C₆₀ derivatives in a regioisomeric mixture.³⁰

3. Bis-silylation of Endohedral Metallofullerenes

The successful construction of silicon derivatives of C₆₀ and C₇₀ has prompted us to investigate the addition of disilane to endohedral metallofullerenes (fullerenes encapsulating metals inside the carbon cage) and higher fullerenes. Endohedral metallofullerenes have long attracted special interest in the fullerene science as new species or materials with novel properties.² Extensive efforts have been made for their production and characterization. Up to now, it has been demonstrated that group 3 metals (Sc, Y, La) and most lanthanides can be trapped inside the higher fullerenes such as C₈₂ and C₈₄ (much less abundant than C₆₀ and C₇₀) to form soluble and relatively stable metallofullerenes. Recent important progress includes the successful isolation and purification of Sc@C₈₂, Y@C₈₂, La@C₈₂, Pr@C₈₂, Gd@C₈₂, La₂@C₈₀, Sc₂@C₈₄, and Sc₃@C₈₂ in macroscopic quantities, and some of their physical properties have been reported. (Figure 7) However, little is known about their interesting electronic properties and chemical reactivities. It is a challenge to learn how the properties of empty fullerenes are modified by endohedral metal-doping. Recently, we have clarified the electronic structures and properties of endohedral metallofullerenes based on theoretical calculations.² Here, we summarize the first exohedral functionalization of metallofullerenes with organosilicon compounds, which can act as a mechanistic probe to clarify the electronic and chemical characters of fullerenes. Although it is still difficult to obtain pure endohedral metallofullerene in large amount, exohedral functionalization of endohedral metallofullerenes should trigger much more work of this kind and further develop their synthetic application.

The first exohedral functionalization of La@C₈₂ with disilane (**9f**) was undertaken, initially by a photochemical reaction. (Scheme 4)³¹ It was verified from LD-TOF and FAB mass spectra that the reaction leads to the formation of the 1:1 adduct (**24**); no molecular ion peaks ascribable to multi-

Figure 7. Optimized structures of La@C₈₂, La₂@C₈₀ and Sc₂@C₈₄ calculated with the *ab initio* method.

Scheme 4

ple-addition products were observed. A more remarkable finding is that La@C_{82} reacts thermally with **9f**. This is in sharp contrast with the fact that empty fullerenes react with **9f** only photochemically. This is the first reported thermal bisilylation of an olefin by disilane without a metal catalyst or irradiation. The facile thermal addition of **9f** to La@C_{82} can be rationalized by the stronger electron-acceptor as well as the stronger electron donor properties as shown in Table 7. The EPR spectra measured during the reaction reveal the formation of, at most, two regioisomers with different La isotopic splittings.

In an attempt to see how the reactivity changes when a different metal is inside the cage, the reactions of Gd@C_{82} ³² and Pr@C_{82} ³³ with **9f** were also carried out. It is found that both Gd@C_{82} and Pr@C_{82} are functionalized both photochemically and thermally, as in the case of La@C_{82} . (Table 7) This is not surprising since the IP (ionization potential) and EA (electron affinity), and redox potentials of Gd@C_{82} and Pr@C_{82} are comparable to those of La@C_{82} . Very similar results were also obtained in the reaction of La@C_{82} with digermirane.³⁴ EPR spectra show that the adducts of La@C_{82} and diphenylmethylene³⁵ have the same hyperfine coupling constants and g values as those of La@C_{82} . The much larger hyperfine coupling constants for the disilirane and digermirane adducts indicate that important electron donation from the silicon and germanium atoms to C_{82} occurs.

Table 7. Reactivities, oxidation (^{ox}E) and reduction (^{red}E) potentials, HOMO–LUMO levels, and the calculated ionization potentials (IP) and electron affinities (EA) of metallofullerenes and empty fullerenes.

Compd	Reactivity		^{ox} E ₁	^{red} E ₁	HOMO	LUMO	IP/eV	EA/eV
	hv	heat	/V	/V	/eV	/eV		
La@C_{82}	yes	yes	+0.07	-0.42			6.19	3.22
Pr@C_{82}	yes	yes	+0.07	-0.39				
Gd@C_{82}	yes	yes	+0.09	-0.39			6.25	3.20
$\text{La}_2\text{@C}_{80}$	yes	yes	+0.56	-0.31	-7.18	-2.55		
$\text{Sc}_2\text{@C}_{84}$	yes	no	+1.21	-0.97	-6.77	-1.38		
C_{60}	yes	no	+1.21	-1.12	-8.33	-0.63	7.78	2.57
C_{70}	yes	no	+1.19	-1.09	-7.97	-0.84	7.64	2.69
C_{76}	yes	no	+0.81	-0.94	-7.42	-1.13	7.14	3.17
C_{78}	yes	no	+0.85	-0.73	-7.44	-1.49		
C_{82}	yes	no	+0.72	-0.69	-7.36	-1.52	6.96	3.37
C_{84}	yes	no	+0.73	-0.58	-7.79	-1.34		

It is of great interest to investigate the reactivities when two metals are encapsulated inside the fullerene cage. As summarized in Table 7, it is found that both $\text{La}_2\text{@C}_{80}$ and $\text{Sc}_2\text{@C}_{84}$ can be functionalized by the photochemical addition of disilirane **9f**.^{36,37} These are the first examples of the functionalization of dimetallofullerenes. The empty higher

fullerenes C_{76} , C_{78} , C_{82} , and C_{84} as well as C_{60} and C_{70} do not react thermally with **9f**. Remarkably, $\text{La}_2\text{@C}_{80}$ reacts thermally with **9f** to afford a 1:1 adduct. This is due to the low-lying LUMO level of $\text{La}_2\text{@C}_{80}$ which is 1–2 eV lower than those of the empty fullerenes, consistent with the fact that $\text{La}_2\text{@C}_{80}$ has a lower reduction potential. On the other hand, the thermal addition of **9f** to $\text{Sc}_2\text{@C}_{84}$ is suppressed, as in empty fullerenes, because of its higher-lying LUMO level and its higher reduction potential. These strongly suggest that the thermal additions are initiated by electron transfer from **9f** to any endohedral metallofullerene with a large electron-accepting power, regardless of the number of metals.

It is expected that these successful exohedral derivatizations constitute an important stepping-stone on the way to new practical applications as precursors of additional new compounds. In this context, an important point to be emphasized is that the present case differs significantly from those of endohedral noble gas fullerenes such as He@C_{60} and He@C_{70} ⁴ (which allow the trapped atom to penetrate through the fullerene cage). In the chemical derivatizations of La@C_{82} and Gd@C_{82} , the degree of the electron transfer from the electropositive metal to the fullerene cage plays a crucial role in tuning the electronic properties of the fullerene cage, unlike the noble gas case.

4. C_{60} Main Chain Polysilane

Polysilanes, in which extensive delocalization of σ -electrons takes place along the silicon chain, have many interesting electronic properties and represent a unique class of materials.⁷ It is well known that photolysis of polysilane with UV radiation leads to facile bond cleavage of the Si–Si bonds to afford the corresponding silyl radicals.^{7a} To extend the silylation reactions of C_{60} , we have carried out the photoreaction of polysilane with C_{60} to obtain a novel silicon polymer, which incorporates C_{60} into the polysilane chain.³⁸

A mixture of C_{60} and polysilanes **25–27** in benzene in a degassed quartz tube was photo-irradiated with a low-pressure mercury-arc lamp (Scheme 5).³⁸ The reaction mixture was separated by gel permeation column chromatography to collect a high molecular weight polymer with absorption band above 400 nm (Figure 8). This result suggests the incorporation of C_{60} in the polysilane chain, because the original polysilanes **25–27** have no absorption in this wavelength region. The molecular-weight of the adducts is higher than the those of irradiated polysilanes, indicating that C_{60} might act as a linker.

Scheme 5

The mass spectrum of C_{60} /polysilane adducts analyzed by FAB mass spectroscopy shows a C_{60} signal, which also confirms that C_{60} is incorporated in the polysilane chain.³⁸ Elemental analysis of the C_{60} /polysilane **25** adduct reveals that about 14% by weight of C_{60} is incorporated into the polysi-

Figure 8. UV-Vis spectra of $C_{60}/25$, **25** (after photolysis) and its difference spectrum.

lane chain. Definitive evidence for a direct connection of the C_{60} and polysilane chain was gained from ^{13}C -NMR measurements of the adduct obtained from ^{13}C -enriched C_{60} and polysilane. A broad signal between 130 and 150 ppm from the sp^2 carbons of the C_{60} skeleton reveals that C_{60} actually attaches to the polysilane chain. The ^{29}Si NMR of $C_{60}/$ polysilane **25** adduct indicates the existence of polysilane units in the $C_{60}/$ polysilane **25** adduct.

The incorporation of C_{60} into polysilane was not observed upon irradiation at >300 nm, where the cleavage of Si-Si bond does not take place.³⁸ Formation of $C_{60}/$ polysilane adduct was also suppressed by addition of CCl_4 , which is known as a good silyl-radical scavenger. These results indicate that the formation of $C_{60}/$ polysilane adduct can be rationalized in terms of the intermediacy of a silyl radical generated by photochemical Si-Si cleavage of polysilane.

In order to control the polysilane chain-length in $C_{60}/$ polysilane adducts, the photoreaction of cyclic oligosilanes with C_{60} was carried out. (Scheme 6)³⁸ A polymer obtained from C_{60} and cyclopentasilane **28** was separated. Elemental analysis shows about 38 wt% of C_{60} is incorporated into the polysilane chain. In the photoreaction of cyclohexasilane **29** and cyclopentasilane **30** with C_{60} , the high molecular weight fraction could not be collected, but $C_{60}(\text{SiR}_2)_4$ **31** ($\text{R}=\text{Me}$) and **32** ($\text{R}=\text{Et}$) were obtained after HPLC separation.³⁹ From the ^1H -, ^{13}C -NMR and UV-Vis spectra, $C_{60}(\text{SiR}_2)_4$ has C_s symmetry and is a 1,4- addition product after fast ring inversion. It was reported that cyclohexasilane **29** formed $(\text{SiMe}_2)_4$

Scheme 6

after extrusion of two silylenes (Me_2Si) during UV irradiation, followed by a ring-opening reaction that results in for-

mation of a 1,4-diradical⁴⁰. The 1,4-diradicals reacted with C_{60} to give the adducts. These adducts may be good precursors for opening polymerization to produce new silicon/ C_{60} polymers.

To learn the electronic properties of a $C_{60}/$ polysilane adduct, its redox potentials were measured and compared with those of C_{60} and polysilane itself.³⁸ The $C_{60}/25$ adduct has a lower oxidation potential ($+0.77$ V vs. Fc/Fc^+ couple) than C_{60} ($+1.21$ V) and a lower reduction potential (-1.24 V) than polysilane (> -2 V). These data indicate that a $C_{60}/$ polysilane adduct has unique electronic property.

It has been reported that C_{60} acts as a good dopant for photoconductive polymers.¹⁷ Wang *et al.* reported that C_{60} -doped polysilane is a good photoconductor.¹⁷ Electric conductivity of iodine-doped $C_{60}/25$ ($5 \times 10^{-6} \text{ S} \cdot \text{cm}^{-1}$) is similar to that of the iodine-doped mixture of C_{60} and **25** ($6 \times 10^{-6} \text{ S} \cdot \text{cm}^{-1}$). The electric conductivity of the iodine-doped polysilane is $1 \times 10^{-6} \text{ S} \cdot \text{cm}^{-1}$. These data reveal that C_{60} main chain polysilane has higher electric conductivity than the original polysilane. The photoconductivity measurement of the $C_{60}/$ polysilane adduct is in progress.

The photochemical reaction of polysilanes and cyclic oligosilanes with C_{60} afforded $C_{60}/$ polysilane adducts in which C_{60} was incorporated into a polysilane chain. The incorporation of C_{60} into polysilane could promise to open further extension of its application to new types of material.

5. C_{60} -Sensitized Bis-silylation of Unsaturated Compounds

As mentioned in Section 2.2, the first photochemical bis-silylation of C_{60} with disilirane **9** affords the 1:1 adduct in a nonpolar solvent. This section reports novel metal-free bis-silylations of nitrile, ketone and aldehyde by the photoreaction of C_{60} with **9** via a photoinduced electron transfer in a polar solvent, which promises to be a new route to synthetically useful bis-silylation chemistry.^{21a,c,41}

Bis-silylation of unsaturated organic compounds has long attracted special interest in the area of organic synthesis because it introduces two silicon groups in one molecule simultaneously. Up to now, successful bis-silylation has been limited to transition metal complex-mediated systems.^{21a,c}

Irradiation of a benzonitrile solution of disilirane **9f** and C_{60} (1:1) with a Tungsten-halogen lamp (cutoff < 400 nm) resulted in formation of the 1:1 (**33f**) and 1:2 adduct (**34f**) of **9f** with benzonitrile in good yields (Scheme 7).^{21a} The 1:1 adduct **33m** and **33n** of oxadisilirane **35**^{21c} and digermirane **15**⁴¹ with benzonitrile, respectively, were also obtained under similar reaction conditions. FAB mass analysis shows the formation of the 1:1 adduct of **9f** with acetonitrile used as solvent.^{21c} The structures of **33f**, **33m** and **34f** were character-

Scheme 7

ized by the spectroscopic data and those for **33m** and **34f** were finally determined by X-ray crystallographic analysis^{21a}. Similar results were also obtained by using a catalytic amount of C₆₀, C₇₀, 9,10-dicyano-anthracene, and 2,4,6-triphenylpyriliun tetrafluoroborate. It is noteworthy that C₆₀ can act as a photosensitizer.^{21a}

The 1:1 adducts of acetophenone and phenylacetaldehyde with **9f** were obtained in 54% and 30% yield, respectively.^{21c} The bis-silylated products of **9f** with acetone and benzaldehyde were also obtained, but no adduct of **9f** with benzophenone or dipropylketone was detected by means of FABMS spectra. These results reveal that bis-silylation is prevented by steric hindrance on a carbonyl moiety.

Disilirane **9f** has no absorption above 350 nm, which allows irradiation to produce excited C₆₀ only at wavelengths longer than 400 nm.^{9a} The free energy change (ΔG)²⁰ for electron transfer from **9f** to the triplet state of C₆₀ in benzonitrile is -7.8 kcal/mol. The formation of **33f** and **34f** was suppressed by addition of 1,4-diazabicyclo[2.2.2]octane or 1,2,4,5-tetramethoxybenzene. These results suggest one plausible rationale for formation of cycloadducts, **33f** and **34f**, in which an electron transfer from **9f** to ³C₆₀* takes place. Photochemically generated reactive cation radical **9f**^{•+} could be efficiently captured with benzonitrile acting as a nucleophile to afford intermediate **A**, followed by addition of benzonitrile to produce **B**. Then, **33f** and **34f** are formed by coupling of the resulting diradical intermediate via a back electron transfer process (Scheme 8).

AM1 MO calculations¹¹ show that **9f**^{•+} corresponds to a local minimum on the potential energy surface (Figure. 9).^{21a} This is also confirmed by non-local hybrid density functional calculations at the B3LYP/6-311G(d,p) level for its parent

Scheme 8

Figure 9. Charge and spin (in parentheses) densities of **9f**^{•+} at the HF/3-21G//AM1 level.

radical cation **9e**^{•+} (R = H, X = CH₂).

A remarkable solvent effect observed in the photoinduced electron transfer reaction of disilirane **9** with C₆₀ differentiates the product formation.^{9a,21a} To clarify the mechanism of the reaction of **9f** with C₆₀, 532 nm laser photolysis was carried out to observe transient absorption bands in the near-IR region.^{21a} In benzene, the absorption band of C₆₀^{•-} at 1070 nm was not observed at all, although the decay of ³C₆₀* at 740 nm was accelerated, probably due to the generation of an exciplex intermediate followed by the formation of the adduct of **9f** and C₆₀ (Fig. 10a). In benzonitrile, the absorption band of ³C₆₀* at 740 nm, which was observed immediately after laser exposure, began to decay in the presence of **9f** (Fig. 10b). Accompanying the decay of ³C₆₀* at 740 nm, the absorption intensity of C₆₀^{•-} at 1070 nm increased, reaching a saturated intensity after about 500 ns. In a solution of **9f** and C₆₀ in acetophenone, similar results were obtained. Thus, it is evident that ³C₆₀* plays an important role in these reactions by generating C₆₀^{•-} via electron transfer from **9f**. These results support the mechanism shown in Scheme 8.

In order to shed light on the intermediacy of **9f**^{•+}, the electrochemical generation of **9f**^{•+} was carried out.⁴² Electrolysis of **9f** in benzonitrile using Bu₄NPF₆ as the supporting electrolyte under argon atmosphere resulted in formation of **33f** in 47% yield. By electrolysis of **9c**, **33c** was also obtained under similar reaction conditions. These results confirm that the reactive cation radical **9f**^{•+} can act as an important intermediate in bis-silylation of benzonitrile. Its C₆₀-mediated

Figure 10. Transient absorption spectra obtained by 532-nm-laser flash photolysis of C₆₀ (0.1 mM) in the presence of disilirane **9f** (5 mM) (a) in deaerated benzene. (•) 50 ns and (○) 500 ns. Insert: Time profiles at 740 and 1070 nm and pseudo-first-order plots for the decay of ³C₆₀* at 740 nm in the presence of **9f**. (b) in deaerated benzonitrile. (•) 100 ns and (○) 1 ms. Insert: Time profiles at 740 and 1070 nm.

production permits photoinduced electron transfer bis-silylation to proceed under mild conditions without a metal catalyst.

6. Conclusion

Derivatization of fullerenes and endohedral metallofullerenes by the addition of silicon compounds has been developed. It is expected that these silicon derivatives will constitute an important stepping-stone on the way to material, catalytic, and biological applications. The chemical derivatization of endohedral metallofullerenes is especially interesting, since it could lead to new physical and chemical properties which the fullerene derivatives do not have, and provides a new stage in the chemistry of endohedral metallofullerenes.

Acknowledgment We are particularly thankful to Drs. M. Kako, Y. Nakadaira, W. Ando, K. Yamamoto, T. Kato, T. Suzuki, O. Ito, M. Fujitsuka, M. Wälchli, K. Kikuchi and Y. Achiba for their collaboration. We are also thankful to Dr. M. W. Schmidt for a critical reading of this manuscript. This work was partly supported by grants from the Asahi Glass Foundation, the Uchida Energy Science Promotion Foundation, the Iketani Science and Technology Foundation, the Shourai Science and Technology Foundation, the REIMEI Research Resources of Japan Atomic Energy Research Institute, and the Ministry of Education, Science, Sports, and Culture of Japan.

References and Notes

- (a) Hirsch, A. *Fullerenes and Related Structures*, Springer, Berlin, 1998. (b) Taylor, R. *The Chemistry of Fullerenes*, World Scientific, 1995. (c) Hirsch, A. *The Chemistry of the Fullerenes*, Thime Verlag, Stuttgart, 1994.
- (a) Nagase, S.; Kobayashi, K.; Akasaka, T. *Bull. Chem. Soc. Jpn.*, **1996**, 69, 2131. (b) Nagase, S.; Kobayashi, K.; Akasaka, T. *J. Mol. Struct. (Theochem)*, **1997**, 398, 221. (c) Nagase, S.; Kobayashi, K.; Akasaka, T. *J. Comput. Chem.*, **1998**, 19, 232. (d) Nagase, S.; Kobayashi, K.; Akasaka, T. *J. Mol. Struct. (Theochem)*, **1999**, 461/462, 97. (e) Nagase, S.; Kobayashi, K.; Akasaka, T.; Wakahara, T. In *Fullerenes: Chemistry, Physics and Technology*, Kadish, K., Ruoff, R. S., Eds.; John Wiley & Sons; New York, 2000; pp395-436.
- Hirsch, A. in ref. 1a, pp49-57.
- (a) Saunders, M.; Jimenez-Vazquez, H. A.; Cross, R. J.; Mroczkowski, S.; Freedberg, D. I.; Anet, F. A. L. *Nature*, **1994**, 367, 256. (b) Saunders, M.; Cross, R. J.; Jimenez-Vazquez, H. A.; Shimshi, R.; Khong, A. *Science*, **1996**, 271, 1693.
- Hummelen, J. C.; Bellavia-Lund, C.; Wudl, F. in ref. 1a, pp93-134.
- Akasaka, T.; Okubo, S.; Wakahara, T.; Kobayashi, K.; Nagase, S.; Kako, M.; Nakadaira, Y.; Kato, T.; Yamamoto, K.; Funasaka, H.; Kitayama, Y.; Matsuura, K. *Chem. Lett.*, **1999**, 945.
- (a) West, R. In *The Chemistry of Organic Silicon Compounds*, Patai, S., Rappoport, Z., Eds.; John Wiley & Sons: Chichester, England, 1989; Part 2, pp1207-1240. (b) Miller, R. D.; Michl, J. *Chem. Rev.* **1989**, 89, 1359.
- For a recent review of silylenes, see: Gasper, P. P.; West, R. In *The Chemistry of Organic Silicon Compounds*, 2nd ed.; Rappoport, Z., Apeloig, Y., Eds.; John Wiley & Sons: New York, 1999; Part 3, pp2463-2568.
- (a) Akasaka, T.; Ando, W.; Kobayashi, K.; Nagase, S. *J. Am. Chem. Soc.* **1993**, 115, 1605. (b) Akasaka, T.; Kobayashi, K.; Nagase, S. unpublished results.
- Ando, W.; Fujita, M.; Yoshida, H.; Sekiguchi, A. *J. Am. Chem. Soc.* **1988**, 110, 3310 and references cited therein.
- Dewar, M. J.; Jie, C. X. *Organometallics*, **1987**, 6, 1486.
- Weidenbruch, M. *Coord. Chem. Rev.* **1994**, 130, 275.
- Akasaka, T.; Mitsuhide, E.; Ando, W.; Kobayashi, K.; Nagase, S. *J. Chem., Chem. Commun.* **1995**, 1529.
- (a) Ando, W.; Kako, M.; Akasaka, T.; Nagase, S. *Organometallics*, **1993**, 12, 1514 and references cited therein. (b) Ando, W.; Kako, M.; Akasaka, T. *J. Am. Chem. Soc.* **1991**, 113, 6286.
- (a) Traven, Y. F.; West, R. *J. Am. Chem. Soc.* **1973**, 95, 6824. (b) Sakurai, H.; Kira, M.; Uchida, T. *J. Am. Chem. Soc.* **1973**, 95, 6826.
- Akasaka, T.; Ando, W.; Kobayashi, K.; Nagase, S. *J. Am. Chem. Soc.* **1993**, 115, 10366.
- Wang, Y.; West, R.; Yuan, C. -H.; *J. Am. Chem. Soc.* **1993**, 115, 3844 and references cited therein.
- (a) Sharma, H. K.; Pannell, K. H. *Chem. Rev.* **1995**, 95, 1351. (b) Ito, Y. *J. Organomet. Chem.* **1999**, 576, 300. (c) Tanaka, Y.; Yamashita, H.; Tanaka, M. *Organometallics*, **1995**, 11, 530.
- Gordon, M. S.; Bunkley, J. S.; Pople, J. A.; Pietro, W. J.; Hehre, W. J. *J. Am. Chem. Soc.* **1982**, 104, 2797.
- Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, 8, 259.
- (a) Akasaka, T.; Maeda, Y.; Wakahara, T.; Okamura, M.; Fujitsuka, M.; Ito, O.; Kobayashi, K.; Nagase, S.; Kako, M.; Nakadaira, Y.; Horn, E. *Org. Lett.*, **1999**, 1, 1509. (b) Fujitsuka, M.; Ito, O.; Maeda, Y.; Kako, M.; Wakahara, T.; Akasaka, T. *Phys. Chem. Chem. Phys.* **1999**, 1, 3527. (c) Maeda, Y.; Sato, R.; Wakahara, T.; Okamura, M.; Akasaka, T.; Fujitsuka, M.; Ito, O.; Kobayashi, K.; Nagase, S.; Kako, M.; Nakadaira, Y.; Horn, E. *J. Organomet. Chem.* in press. references cited therein.
- Akasaka, T.; Ito, M.; Maeda, Y.; Wakahara, T.; Mizushima, T.; Ando, W.; Kako, M.; Nakadaira, Y.; Waelchli, M.; Kobayashi, K.; Nagase, S. unpublished results.
- Akasaka, T.; Wakahara, T.; Mitsuhide, E.; Ando, W.; Kako, M.; Nakadaira, Y.; Waelchli, M.; Kobayashi, K.; Nagase, S. unpublished results.
- Akasaka, T.; Mitsuhide, E.; Ando, W.; Kobayashi, K.; Nagase, S. *J. Am. Chem. Soc.* **1994**, 116, 2627.
- Akasaka, T.; Maeda, Y.; Wakahara, T.; Mizushima, T.; Ando, W.; Waelchli, M.; Suzuki, T.; Kobayashi, K.; Nagase, S.; Kako, M.; Nakadaira, Y.; Fujitsuka, M.; Ito, O.; Sasaki, Y.; Yamamoto, K.; Erata, T. *Org. Lett.* **2000**, 2, 2671.
- Suzuki, T.; Maruyama, Y.; Akasaka, T.; Ando, W.; Kobayashi, K.; Nagase, S. *J. Am. Chem. Soc.* **1994**, 116, 1359.
- Akasaka, T.; Suzuki, T.; Maeda, Y.; Ara, M.; Wakahara, T.; Kobayashi, K.; Nagase, S.; Kako, M.; Nakadaira, Y.; Fujitsuka, M.; Ito, O. *J. Org. Chem.*, **1999**, 64, 566.
- Kusukawa, T.; Ando, W.; *Angew. Chem., Int. Ed. Engl.* **1996**, 35, 1315.
- (a) Kusukawa, T.; Shike, A.; Ando, W. *Tetrahedron*, **1996**, 52, 4995. (b) Kusukawa, T.; Ando, W. *Organometallics*, **1997**, 16, 4027. (c) Kusukawa, T.; Ando, W. *J. Organomet. Chem.* **1998**, 559, 11.
- Akasaka, T.; Rahman, G. M. A.; Maeda, Y.; Wakahara, T.; Kobayashi, K.; Nagase, S. unpublished results.
- Akasaka, T.; Kato, T.; Kobayashi, K.; Nagase, S.; Yamamoto, K.; Funasaka, H.; Takahashi, T. *Nature*, **1995**, 374, 600.
- Akasaka, T.; Nagase, S.; Kobayashi, K.; Suzuki, T.; Kato, T.; Yamamoto, K.; Funasaka, H.; Takahashi, T. *J. Chem. Soc., Chem. Commun.* **1995**, 1343.
- Akasaka, T.; Okubo, S.; Kondo, M.; Maeda, Y.; Wakahara, T.; Kato, T.; Suzuki, T.; Yamamoto, K.; Kobayashi, K.; Nagase, S. *Chem. Phys. Lett.*, **2000**, 319, 153.
- Akasaka, T.; Kato, T.; Nagase, S.; Kobayashi, K.; Yamamoto, K.; Funasaka, H.; Takahashi, T. *Tetrahedron*, **1996**, 52, 5015.
- Suzuki, T.; Maruyama, Y.; Kato, T.; Akasaka, T.; Kobayashi, K.; Nagase, S.; Yamamoto, K.; Funasaka, H.; Takahashi, T. *J. Am. Chem. Soc.* **1995**, 117, 9606.
- Akasaka, T.; Nagase, S.; Kobayashi, K.; Suzuki, T.; Kato, T.; Kikuchi, K.; Achiba, Y.; Yamamoto, K.; Funasaka, H.; Takahashi, T. *Angew. Chem., Int. Ed. Engl.* **1995**, 34, 2141.
- Kobayashi, K.; Nagase, S.; Akasaka, T. *Chem. Phys. Lett.* **1995**, 245, 230.
- Wakahara, T.; Kondo, T.; Okamura, M.; Akasaka, T.; Hamada, Y.; Suzuki, T.; Kako, M.; Nakadaira, Y. *J. Organomet. Chem.*, in press.
- Kusukawa, T.; Kabe, Y.; Ando, W. *Organometallics*, **1995**, 14, 2142.
- Ishikawa, M.; Kumada, M. *Adv. Organomet. Chem.* **1981**, 19, 51.
- Maeda, Y.; Takahashi, S.; Wakahara, T.; Akasaka, T.; Sasaki, Y.; Fujitsuka, M.; Ito, O.; Kobayashi, K.; Nagase, S.; Kako, M.; Nakadaira, Y. *ITE Lett. on Battery, New Technology & Medicine*, **2000**, 1, 408.
- Maeda, Y.; Wakahara, T.; Akasaka, T. unpublished results.

Takeshi Akasaka is Professor of Organic Chemistry at Niigata University. He was born in 1948 in Kyoto and grew up in Osaka. He received his Ph. D. degree from University of Tsukuba in 1979. He did postdoctoral work at Brookhaven National Laboratory. In 1981 he joined the Chemistry Department at University of Tsukuba. Since 1996, he has been a professor of Graduate School of Science and Technology, Niigata University. His current research interests include the chemistry of fullerenes, metallofullerenes and carbon nanotubes.

Takatsugu Wakahara is a Research Associate of Niigata University. He was born in Nagoya in 1970 and received his B. Sc. (1992) and Ph. D. degree (1998) from Tsukuba University. He was appointed Research Associate of Graduate School of Science and Technology, Niigata University, in 1998. His research interests are in the areas of fullerene chemistry and organometallic chemistry.

Shigeru Nagase is Professor of Theoretical Chemistry at Tokyo Metropolitan University. He was born in Osaka in 1946 and received his Ph. D. degree (1975) from Osaka University. After working as a postdoctoral fellow (1976-1979) at the University of Rochester and Ohio State University, he returned to the Institute of Molecular Science in 1979. In 1980 he moved to Yokohama National University as associate professor and was promoted to professor in 1991. He moved in 1995 to the Department of Chemistry at Tokyo Metropolitan University. He has great interest in developing new molecules and reactions through a close interplay between theoretical predictions and experimental tests.

Kaoru Kobayashi is an Assistant Professor of Tokyo Metropolitan University. She received her M. Sc. degree (1994) from Yokohama National University and Ph. D. degree (1997) from Tokyo Metropolitan University. In 1995 she became a JSPS research fellow. In 1996, she was appointed Assistant Professor of the Department of Chemistry, Tokyo Metropolitan University. She organizes the assembly for young fullerene scientists. She is interested in the application of quantum chemistry to chemically interesting problems. Her current research interests include the theoretical study of the properties and growth mechanism of silicon clusters, fullerenes, and endohedral metallofullerenes.