Structure of (tropolonato)$_4$M-Type Compounds (M = Si, Ge, Sn)

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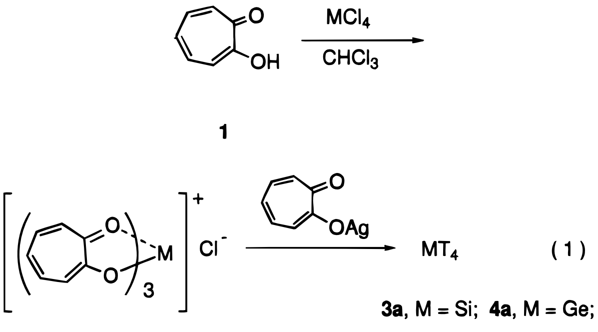
Received October 27, 1997

T_4M (M = Si, Ge, Sn; T = tropolonato)-type compounds were synthesized by reactions of tropolone with tetramethoxysilane, tetramethoxygermane, and tetrachlorostannane, respectively. X-ray and NMR analyses have shown that, both in the solid state and in solution, T_4Si exists as an ion pair of a hexacoordinate silicocation (T_3Si^+) with an associated tropolone anion (T^-), while T_4Sn has an octacoordinate structure. The geometry around the tin atom is best described as a bicapped trigonal prism distorted toward a dodecahedron, in which the eight oxygen atoms of four tropolonato ligands are coordinated to a tin atom with an average Sn−O bond distance of 2.168 Å. Features of NMR and UV−vis spectra of T_4Ge are similar to those of T_4Si, indicating ion pairing between T_3Ge^+ and T^- in solution; the black color of the solid of T_4Ge is suggestive of the ion pairing in the solid-state as well, whereas single crystals suitable for X-ray analysis have not been obtained.

Introduction

Recently, there has been a great deal of interest in the structural properties and mechanistic significance of the hypercoordinate compounds of group 14 elements that have coordination numbers greater than 6.[1,2] Such compounds may offer a very wide range of geometries and also could be of considerable value in understanding a variety of group 14 organometallic reactions.

The chelating behavior of tropolone (**1**) was first recognized by Nozoe in 1936.[3] In the 1960s, on the basis of extensive studies of metal complexes with tropolonato ligand, Muetterties et al. suggested that the tropolonato ligand is an ideal ligand for the formation of complexes having high coordination numbers due to the rigidity and planarity of the ligand.[4] They reported the preparation of an interesting class of compounds with the composition of T_4M (T = tropolonato; M = Si (**3a**), Ge (**4a**), Sn (**5a**)) as shown in eq 1.



3a, M = Si; **4a**, M = Ge; **5a**, M = Sn.

On the basis of a few physical measurements made on these compounds, it was proposed that the structure of SiT_4 and GeT_4 was largely in the form of salts or ion pairs, i.e., $T_3Si^+T^-$ and $T_3Ge^+T^-$, in solution and in the solid state, while SnT_4 was octacoordinated.[4a] However, the definitive structure, such as the coordination number at the central atoms and other structural details, remains unexplored. If all four of the tropolonato ligands are coordinated to the central atom, these complexes form hypercoordinate compounds with coordination numbers greater than 6. Renewed interest in the chemistry of hypervalent compounds of the Si, Ge, and Sn elements has led us to explore the structure of these species, utilizing NMR, UV, and IR spectroscopy and X-ray crystallography.

Results and Discussion

Synthesis of T_4M-Type Compounds. Muetterties et al. reported that the chloride salts of chelated silicon and germanium cations T_3Si^+ and T_3Ge^+ react with silver tropolonate to give T_4Si or T_4Ge in 75% yield in acetonitrile−water solution, as shown in eq 1.[4] We have found that **3a** and **4a** are simply obtained by the reaction of tropolone with the corresponding silicon and germanium tetramethoxides without solvent, as shown in eq 2. T'_4M [T′ = 5-isopropyltropolonato, M = Si (**3b**) and Ge (**4b**)] species are prepared similarly.

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[1] For recent reviews of hypercoordinate group 14 metal compounds, see: (a) Chuit, C.; Corriu, R. J. P.; Reye, C.; Yong, J. C. *Chem. Rev. (Washington, D.C.)* **1993**, *93*, 1371. (b) Jastrzebski, J. T. B. H.; van Koten, G. *Adv. Organomet. Chem.* **1993**, *35*, 241. (c) Tandura, S. N.; Voronkov, M. G.; Alekseev, N. V. *Top. Curr. Chem.* **1986**, *131*, 99.

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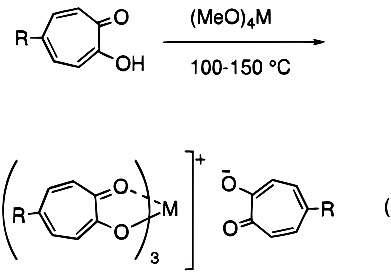
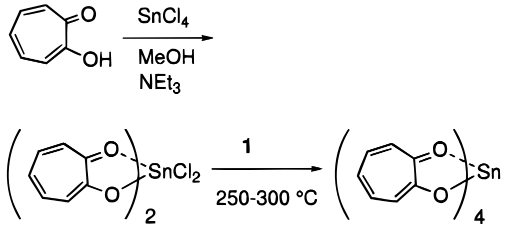


(2)

3a, M = Si, R = H (80 %); **3b**, M = Si, R = i-Pr (75 %);
4a, M = Ge, R = H (60 %); **4b**, M = Ge, R = i-Pr (55 %).

Although T_4Sn^{IV} was reported by Muetterties and Wright in 1965,[4a] in later papers,[5] numerous unsuccessful attempts were made to synthesize the octacoordinate tetrakis(tropolonato)tin(IV), giving instead other products such as T_2SnCl_2 and T_3SnCl. We have successfully synthesized T_4Sn by the reaction of tropolone with T_2SnCl_2, which was obtained from the reaction of tin tetrachloride with tropolone in a methanol solution in the presence of triethylamine, without solvent at 250−300 °C for 1 h (eq 3).



(3)

5a (50 %)

Structure of T_4M-Type Compounds in Solution. NMR spectra of the silicon (**3a**,**b**), germanium (**4a**,**b**), and tin (**5a**) compounds were measured, to determine the coordination number at the metal center and structural characteristics of the tropolonato ligands in these T_4M-type compounds in solution. In the ^1H NMR spectrum of **3b** in CD_2Cl_2, two sets of ^1H resonances for two types of 5-isopropyltropolone rings were found with an integration ratio of 3:1. Similarly, ^1H NMR spectra of **3a**, **4a**, and **4b** showed the existence of two types of tropolone rings with an integration ratio of 3:1. However, the four tropolonato rings were found to be equivalent in the ^1H NMR spectrum of **5a** in $CDCl_3$. No temperature dependence of the spectra of these T_4M compounds (M = Si, Ge, Sn) was observed between −30 and 40 °C.

These results reveal that, in the T_4Si and T_4Ge compounds, three tropolonato ligands chelate to the central silicon or germanium to form cationic hexacoordinate metal species and one tropolonato ligand exists as a separated counteranion. On the other hand, in the case of T_4Sn, four tropolonato ligands are equivalently coordinated to the Sn atom, forming an 8-coordinate compound, at least in solution.

While the UV−vis spectrum of **3a** in CH_2Cl_2 is very similar to that of $T_3Si^+Cl^-$ in the range 200−380 nm, there are extra bands at 412 and 581 nm for **3a**, which can be assigned to the n−π^* transition of the tropolonato anion, T^-, and a CT transition between T_3Si^+ and T^-, respectively. Since considerable positive charge is present on the ligands of T_3Si^+, ion pairing in solution should provide sufficient close approach for charge transfer. The 581 nm band in **3a** shifted to 492 nm in **3b**, suggesting that the accepting ability of T'_3Si^+ is poorer than that of T_3Si^+ due to the electron-donating effects of the isopropyl group. The UV spectrum of T_4-Sn in CH_2Cl_2 showed no absorption band in the of wavelength longer than 412 nm, indicating the absence of ion pairing in T_4Sn. The behavior is consistent with the results of the ^1H NMR spectral analysis and X-ray analysis.

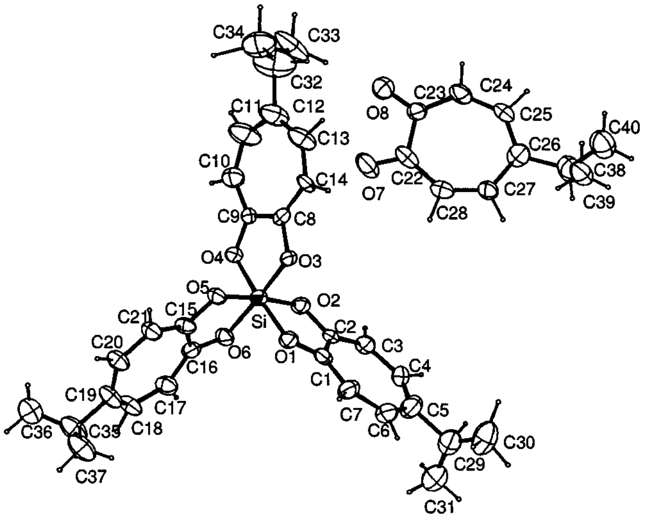


Figure 1. ORTEP drawing of $T'_3Si^+T'^-$ (**3b**; T′ = 5-isopropyltropolonato) showing the atom-numbering scheme. Thermal ellipsoids are drawn at the 30% probability level. Selected bond distances (Å): Si−O1 = 1.785(9), Si−O2 = 1.752(8), Si−O3 = 1.772(8), Si−O4 = 1.765(8), O1−C1 = 1.306(14), O2−C2 = 1.300(14), O3−C8 = 1.284(14), O4−C9 = 1.301(13), O5−C15 = 1.289(14), O7−C22 = 1.208(18), O8−C23 = 1.228(16), C1−C2 = 1.414(16), C1−C7 = 1.376(18), C3−C2 = 1.342(17), C4−C3 = 1.411(18), C5−C4 = 1.329(19), C7−C6 = 1.402(20), C6−C5 = 1.405(21), C22−C23 = 1.445(19), C23−C24 = 1.426(20), C24−C25 = 1.380(21), C25−C26 = 1.356(20), C26−C27 = 1.373(20), C27−C28 = 1.341(19), C22−C28 = 1.442(20). Selected bond angles (deg): O1−Si−O2 = 85.8(3), O1−Si−O3 = 87.4(3), O1−Si−O4 = 174.3(4), O1−C1−C2 = 112.2(10), C2−C1−C7 = 128.2(11), C1−C2−C3 = 125.8(11), O7−C22−C23 = 116.0(13), O8−C23−C22 = 118.3(11), C22−C23−C24 = 119.6(12), C23−C22−C28 = 123.9(12).

Structure of T_4M-Type Compounds in the Solid State. Single crystals of **3b** were obtained by recrystallization from a mixture of CH_2Cl_2 and ether, while **3a** did not give a suitable single crystal for X-ray analysis. Single crystals of **5a** were obtained as the CH_2Cl_2 solvate by recrystallization from CH_2Cl_2. Molecular structures of **3b** and **5a** determined by X-ray crystallography are quite different from each other, as shown in Figures 1 and 2. Thus, **3b** exists as an ion pair of the hexacoordinate tris(tropolonato)silicon cation (T_3Si^+) with an associated tropolone anion (T^-), while T_4Sn has an octacoordinate structure with four tropolonato ligands. The X-ray analysis of the germanium analogue could not be performed because neither **4a** nor **4b** gave single crystals suitable for X-ray analysis. The molecular structure of T_4Ge in the solid state would be similar to that of **3b**, as suggested by the color; crystals of **3a** and **4a** are black and those of the isopropyl

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(5) Rein, A. J.; Herber, R. H. *J. Chem. Phys.* **1975**, *63*, 1021.

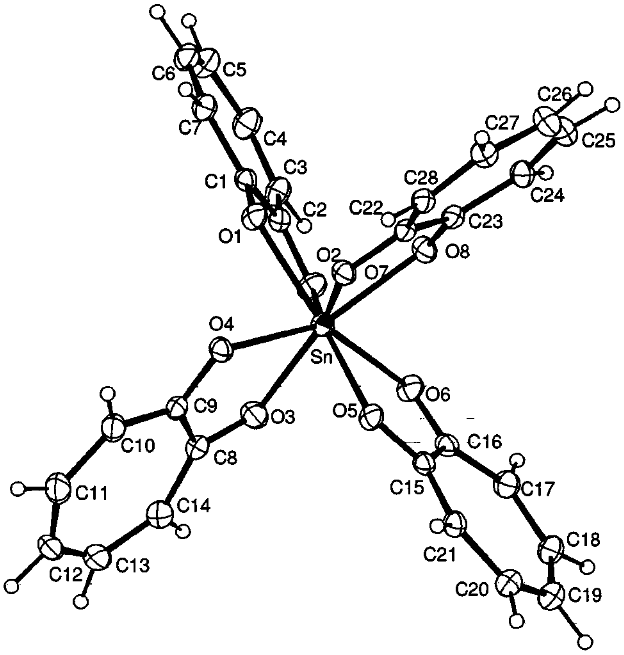

Figure 2. ORTEP drawing of T$_4$Sn (**5a**), showing the atom-numbering scheme. Thermal ellipsoids are drawn at the 30% probability level. Selected bond distances (Å): Sn−O1 = 2.165(4), Sn−O2 = 2.173(4), O1−C1 = 1.286(6), O2−C2 = 1.283(6), O3−C8 = 1.282(7), O4−C9 = 1.279(7), O5−C15 = 1.293(6), O6−C16 = 1.273(7), O7−C22 = 1.273(6), O8−C23 = 1.298(6), C1−C2 = 1.462(7), C1−C7 = 1.403(8), C3−C2 = 1.404(8), C4−C3 = 1.378(9), C5−C4 = 1.386(9), C5−C6 = 1.390(9), C6−C7 = 1.380(8). Selected bond angles (deg): O1−Sn−O2 = 71.7(1), O1−Sn−O3 = 108.4(1), O1−Sn−O4 = 76.0(1), O1−Sn−O5 = 146.8(1), O1−Sn−O6 = 139.9(1), O1−Sn−O7 = 76.4(1), O1−Sn−O8 = 85.5(1), O1−C1−C2 = 114.7(4), C2−C1−C7 = 126.3(4), C1−C2−C3 = 125.5(4), O7−C22−C23 = 115.7(4), O8−C23−C22 =114.3(4), C22−C23−C24 = 127.0(4), C23−C22−C28 = 125.4(4).

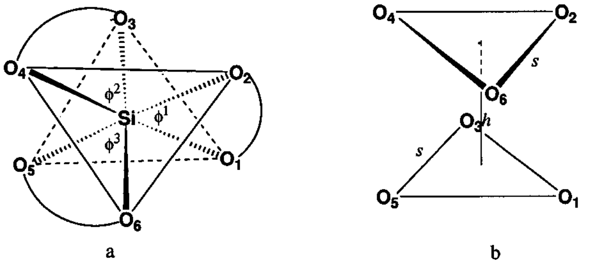

Figure 3. (a) Projected view of the silicon−oxygen coordination sphere illustrating the twist angles (*φ*). (b) View of the octahedron illustrating the intertriangle distance *h* and the triangle side length *s*.

derivatives **3b** and **4b** are orange to red, while **5a** is pale yellow in the solid state.

It is clear that the three tropolonato ligands of **3b** chelate to the central silicon atom, forming a hexacoordinate structure around the silicon, as shown in Figure 1. The other tropolonato group is located far from the central silicon atom. The results eliminate the possibility that T$_4$Si exists in a hepta- or octacoordinate structure in the solid state.

A projected view of the silicon−oxygen hexacoordination sphere in SiO6 is shown in Figure 3. The two planes formed by O1O3O5 and O2O4O6 are nearly parallel to each other (the dihedral angle 0.75°), and the three planes formed by O1MO2, O3MO4, and O5MO6 are arranged nearly perpendicular to each other (the average dihedral angle is 85°). The values of Si−O bond distances are in the range 1.753−1.785 Å, which are comparable with those found for the hexacoordinate tris(*o*-phenylenedioxy)silicate (1.78 ± 0.025 Å);[6] no significant difference among the six Si−O bond distances are found within the estimated experimental error.

Table 1. Twist Angles and Compression Ratios for T′$_3$Si$^+$ and Related Tris-Chelate Complexes

complex[a]	*s* (Å)	*h* (Å)	*s*/*h*	*φ* (deg)	ref
regular octahedron			1.22	60	7
trigonal prism			1.00	0	7
Si(opd)$_3^{2-}$	2.54	2.02	1.26	59	6
SiT′$_3$	2.53	2.02	1.25	54	this work
AlT$_3$	2.70	1.88	1.27	48	9

[a] Abbreviations used: opd = *o*-phenylenedioxy; T = tropolonato; T′ = 5- isopropyltropolonato.

Previously Stiefel and Brown identified octahedral geometry in complexes by using the two parameters *φ* and *s*/*h*.[7] As a measure of the twisting is taken the angle *φ*, which is set equal to 60° for the undistorted octahedron by definition (Figure 3a). The compression ratio is *s*/*h*, where *s* is a polyhedral edge length and *h* is the distance between the parallel equilateral triangles, as shown in Figure 3b.

To describe the octahedron formed by six oxygen atoms, we have calculated the values of *φ* and *s*/*h* for T′$_3$Si$^+$, which are listed in Table 1 with those of related compounds. These values show that the SiO6 sphere in the T′$_3$Si$^+$ cation ($\phi = 54°$, $s/h = 1.25$) is quite close to a regular octahedral geometry, where $\phi = 60°$ and $s/h = 1.22$ Å. The coordination nature of bidentate tropolonato ligands is quite similar to that found in diphenylbis(tropolonato)silicon,[8] while two different types of Si−O bond distances are observed in the latter.

Consistent with our expectation, in **5a**, four tropolonato ligands chelate to the central tin atom to give an octacoordinate tin structure (Figure 2). Only three tin(IV) complexes with octacoordinated tin atoms have been analyzed so far by X-ray crystallography: tin tetranitrate,[10a] tin tetraacetate,[10b] and stannic phthalocyanine.[10c]

A configuration diagram of oxygen atoms around tin is given in Figure 4. The tin atom is coordinated by the eight oxygen atoms of four bidentate tropolonate ligands. The Sn−O distances (Sn−O1 = 2.141−2.201 Å) are similar to those of the Sn−O distances in the heptacoordinate tin compounds T$_3$SnCl and T$_3$SnOH (Sn−O = 2.13, 2.16).[11] To describe the octahedron formed by the eight oxygen donor atoms, we have used

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(11) Park, J. J.; Collins, D. M.; Hoard, J. L. *J. Am. Chem. Soc.* **1970**, *92*, 3636.

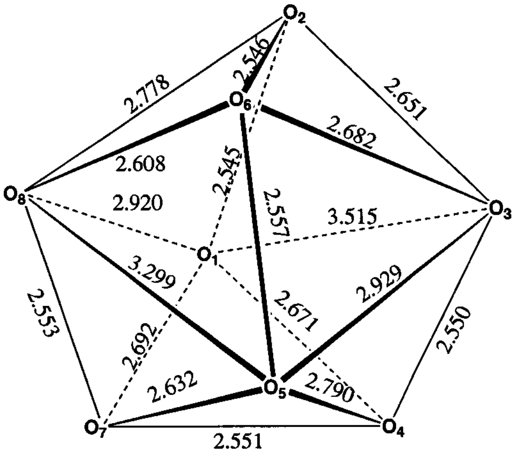

Figure 4. Perspective view of the irregular bicapped trigonal prism formed by the eight O donor atoms in SnT_4.

Table 2. Comparison of δ (deg) and φ (deg) among Various Tetrakis(tropolonato)metal Complexes

complex	δ (deg)				φ (deg)	
dodecahedron	29.5	29.5	29.5	29.5	0	0
bicapped trigonal prism	0	21.7	48.2	48.2	16.1	16.1
square antiprism	0	0	52.5	52.5	24.5	24.5
T_4Sc^- [a]	13.4	29.0	42.3	43.0	10.8	10.8
T_4Zr[a]	22.9	31.8	32.4	40.1	6.6	1.9
T_4Nb^+ [a]	19.4	21.0	42.9	45.1	11.5	13.9
T_4Sn[b]	13.4	22.3	43.9	44.0	22.3	22.1

[a] Reference 14. [b] This work.

the criteria that were originally established by Porai-Koshits and Aslanov[12] and extended by Muetterties and Guggenberger.[13]

The dodecahedron is described by four δ values, which are the angles between pairs of faces which intersect along edges connecting vertexes at which five edges are joined. These vertexes are seen in Figure 4 as O1, O3, O5, and O8. The angle (φ), which represents the twist that occurs in the diagonal trapezoids of a regular dodecahedron as a result of distortion, is also important. The φ values for the trapezoids defined by O1, O6, O5, O2 and O3, O4, O7, O8 as well as the four δ values of **5a** are compared with those of T_4Zr, T_4Nb^+, T_4Sc^-,[14] and an idealized octahedron in Table 2. The $[SnO_8]$ dodecahedron is best described as an irregular bicapped trigonal prism distorted toward the regular dodecahedron.

Structure of Tropolonato Ligands in $T'_3Si^+T'^-$ and T_4Sn. Selected bond lengths and angles in the tropolonato ligands in T'_3Si^+ and T_4Sn are given in Figures 1 and 3. The dimensions of the bond lengths and angles within the tropolonato ligands in T'_3Si^+ and T_4Sn do not differ significantly from those obtained in previous structural studies of the hexacoordinate silicon, germanium, and tin compounds[8] and also of the transition-metal tropolonates T_3Fe,[6] T_3Al,[7] and T_4M (M = Sc, Zr, Nb).[14]

Each seven-membered ring of T'_3Si^+ and T_4Sn is nearly planar. The dihedral angles between the least-mean-squares planes of seven-membered rings and the planes defined by a central metal and the two oxygens connected to the ring are 1.6, 2.7, and 11.9° for T'_3Si^+ and 4.9, 8.2, 2.2, and 4.3° for T_4Sn. The deviation of the tin atom in **5a** from each least-mean-squares plane defined by C1−C7, two O's, and Sn is small (0−0.0013 Å), though a larger deviation of the corresponding oxygen atoms from the planes (0.024−0.1779 Å) is observed. The origin of the deviation is probably packing effects, as is often observed in other tropolonato complexes.[15]

A T'_3Si^+ cation is connected with a tropolonato anion (T'^-) in the crystal structure. Although the tropolonato anions in T'_4Si are far from the silicon atom, it is noted that an anionic oxygen of T'^- is in close proximity to hydrogens of a tropolonato ring (O---H = 2.0−2.2 Å) which is coordinated to the silicon atom, seeming to form a weak hydrogen bond. This interaction may be related to the effective charge-transfer interaction between T'_3Si^+ and a tropolonato counteranion, as detected by UV spectroscopy. The bond distances and angles of the tropolonato anion are very different from those found in sodium tropolonate.[16] In particular, the deviation of the corresponding oxygen atoms from the least-mean-squares plane defined by seven ring carbons and two oxygens (0.2465 and −0.2155 Å) is much larger than that of sodium tropolonate (0.017 and −0.005 Å). The considerable twisting of the two oxygens of T'^- may be also due to the hydrogen bonding in part.

Conclusion

In this paper, the structure of T_4M-type compounds (M = Si, Ge, Sn) is discussed in detail on the basis of NMR, UV, and X-ray analysis. Both in solution and in the solid state, T_4Si species have a $T_3Si^+T^-$ ion-pair structure with weak hydrogen bonding between hydrogens of tropolonato ligands on a metal and an oxygen of the tropolonato counteranion, while T_4Sn has an octacoordinate structure. The structure of T_4Ge is similar to that of T_4Si in solution, as evidenced by NMR and UV spectroscopy, while the solid-state structure was not determined. These results can be rationalized by the fact that the radii of group 14 elements increase in the order Si < Ge ≪ Sn and therefore Si and Ge atoms, in contrast to Sn, have difficulty maintaining a coordination number greater than 6.

Experimental Section

General Methods. ^1H (300 MHz), ^{13}C (75.4 MHz), and ^{29}Si (59.6 MHz) NMR spectra were measured on a Bruker AC300P NMR spectrometer. ^1H (600 MHz) and ^{13}C (150 MHz) NMR spectra were measured on a Bruker AM600P NMR spectrometer. ^1H and ^{13}C NMR chemical shifts were referenced to internal residual protons and carbons in chloroform-*d* (^1H, δ 7.24; ^{13}C, δ 77.0) or CD_2Cl_2 (^1H, δ 5.26; ^{13}C, δ 53.1). ^{29}Si NMR chemical shifts, in ppm, are relative to Me_4Si. Mass spectra and high-resolution mass spectra were obtained on a JEOL JMS D-300 mass spectrometer. Electronic spectra were recorded on a Shimadzu UV2000 and a Milton Roy SP-3000 spectrometer. GLC analysis was conducted by using a Shimadzu 8A gas chromatograph.

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Table 3. Crystal Data for 3b and 5a

	3b	5a
formula	$C_{40}H_{44}O_8Si$	$C_{28}H_{20}O_8Sn/CH_2Cl_2$
mol wt	680.8	688.08
cryst color, habit	red, prism	pale yellow, prism
cryst size, mm	0.20 × 0.20 × 0.30	0.20 × 0.20 × 0.30 mm
cryst syst	monoclinic	triclinic
space group	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)
a, Å	14.176(3)	10.488(6)
b, Å	12.379(2)	13.487(2)
c, Å	21.943(4)	10.081(2)
α, deg	90	97.86(1)
β, deg	109.86(2)	94.68(2)
γ, deg	90	103.53(3)
V, Å^3	3621.6(9)	1363.7(9)
Z	4	2
D_{calc}, g cm^{-3}	1.25	1.68
radiation; λ, Å	Mo Kα; 0.710 69	Mo Kα; 0.710 69
temp, K	150	150
scan type	$\omega-2\theta$	$\omega-2\theta$
scan speed, deg/min	8	8
scan width	$1.20 + 0.30 \tan\theta$	$1.20 + 0.30 \tan\theta$
$2\theta_{max}$, deg	58	55
no. of rflns measd	6735	5667
no. of rflns used	2786 ($F_o > 2\sigma(F_o)$)	5235 ($F_o > 3\sigma(F_o)$)
function minimized	$\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2$	$\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2$
temp factors	anisotropic for Si, C, O	anisotropic for Sn, C, O, Cl
final R factor ($\sum\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\sum\lvert F_o\rvert$)	0.088	0.047
$R_w = [(\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\sum wF_o^2)]^{1/2}$	0.087	0.054

All reactions were conducted in oven-dried or flame-dried glassware under atmospheres of dry argon or nitrogen. All solvents were purified before use.

Preparation of T$_4$M (M = Si, Ge). A mixture of the tropolone (12.3 mmol) and tetramethoxysilane (3 mmol) or tetramethoxygermane (3 mmol) was heated at 100−150 °C for 4−5 h under an inert atmosphere. To the reaction mixture was added toluene (5 mL), and this mixture was then stirred for 5 min. The resultant precipitate was collected, washed with dry ether, and recrystallized from a CH_2Cl_2−ether mixture to give the desired compound.

T$_3$Si$^+$T$^-$ (3a; T = Tropolonato): black crystals; mp 130−131 °C; yield 80%; ^{1}H NMR (300 MHz, CD_2Cl_2) δ 6.12 (td, J = 9.3, 1.0 Hz, 1 H), 6.59 (dd, J = 11.4, 1.0 Hz, 1 H), 6.78 (dd, J = 11.3, 9.3 Hz, 2 H), 7.80 (t, J = 9.7, 1.0 Hz, 3 H), 7.94 (dd, J = 10.8, 1.0 Hz, 6 H), 8.10 (dd, J = 9.7, 10.8 Hz, 6 H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 123.0, 128.3, 128.6, 135.5, 136.0, 145.1, 171.4, 172.3; ^{29}Si NMR (CP mass) δ −139.6; MS m/z (FAB, %) 512 (M$^+$, 1.23), 391 (M, 100), 270 (M, 7.6); UV (CH_2Cl_2) λ_{max}/nm (ϵ) 243 (71 600), 312 (22 400), 354 (16 000), 367 (13 900), 412 (7100), 581 (1200); IR (KBr) ν_{max}/cm^{-1} 1610, 1591, 1545, 1516, 1227. Anal. Calcd for $C_{28}H_{20}O_8Si$: C, 65.52; H, 3.93. Found: C, 65.50; H, 3.91.

T′$_3$Si$^+$T′$^-$ (3b, T′ = 5-Isopropyltropolonato): orange crystals; mp 194−195 °C; yield 75%; ^{1}H NMR (300 MHz, CD_2Cl_2) δ 1.07 (d, J = 6.8 Hz, 6 H), 1.25 (d, J = 6.4 Hz, 18 H), 2.57 (sept, J = 6.8 Hz, 1 H), 3.07 (sept, J = 6.4 Hz, 3 H), 6.57 (dd, J = 12.1 Hz, 2 H), 6.70 (d, J = 12.1 Hz, 2 H), 7.77 (d, J = 11.6 Hz, 6 H), 7.95 (d, J = 11.6 Hz, 6 H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 24.0, 24.4, 37.0, 39.1, 123.1, 127.8, 128.1, 133.2, 143.8, 158.2, 169.8, 170.3; ^{29}Si NMR (CP, mass) δ −139.3; MS m/z (FAB, %) 517 (100), 339 (10.1); UV (CH_2Cl_2) λ_{max}/nm (ϵ) 247 (122 500), 320 (43 300), 423 (7700), 492 (460); IR (KBr) ν_{max}/cm^{-1} 1599, 1554, 1529, 1443. Anal. Calcd for $C_{40}H_{44}O_8Si$: C, 70.56; H, 6.51. Found: C, 70.53; H, 6.50.

T$_3$Ge$^+$T$^-$ (4a): black crystals; mp 180 °C dec; yield 60%; ^{1}H NMR (300 MHz, CD_2Cl_2) δ 6.42 (td, J = 9.3, 1.0 Hz, 1 H), 6.47 (d, J = 11.3, 1.0 Hz, 1 H), 6.98 (dd, J = 11.3, 9.3 Hz, 2 H), 7.80 (t, J = 9.7, 1.0 Hz, 3 H), 7.95 (dd, J = 10.8, 1.0 Hz, 6 H), 8.10 (dd, J = 9.7, 10.8 Hz, 6 H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 122.2, 127.5, 129.2, 134.7, 136.0, 144.3, 170.6, 171.9; MS m/z (FAB, %) 558 (M$^+$, 2.5), 557 (M$^+$, 3.7), 437 (M$^+$ − 121, 89.1), 316 (6.1), 195 (83.4), 154 (100); UV (CH_2Cl_2) λ_{max}/nm (ϵ) 247 (107 400), 314 (35 300), 356 (21 500), 413 (4570), 571 (840); IR (KBr) ν_{max}/cm^{-1} 1609, 1593, 1533, 1520, 1230, 1261. Anal. Calcd for $C_{28}H_{20}O_8Ge$: C, 60.37; H, 3.62. Found: C, 60.34; H, 3.66.

T′$_3$Ge$^+$T′$^-$ (4b): red crystals; mp 190−191 °C; yield 55%; ^{1}H NMR (300 MHz, CD_2Cl_2) δ 1.09 (d, J = 7.0 Hz, 6 H), 1.27 (d, J = 6.7 Hz, 18 H), 2.59 (sept, J = 7.0 Hz, 1 H), 3.08 (sept, J = 6.7 Hz, 3 H), 6.6 (d, J = 12.1 Hz, 2 H), 6.72 (d, J = 12.1 Hz, 2 H), 7.87 (d, J = 11.7 Hz, 6 H), 7.94 (d, J = 11.7 Hz, 6 H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 24.0, 24.2, 37.4, 38.9, 123.4, 127.9, 129.3, 134.4, 142.9, 158.7, 169.2, 170.3. MS m/z (FAB, %) 724 (M$^+$, 0.2), 563 (M$^+$ − 163, 100), 400 (2.5), 237 (83.4); UV (CD_2Cl_2) λ_{max}/nm (ϵ) 248 (114 300), 321 (44 200), 408 (4820), 499 (510); IR (KBr) ν_{max}/cm^{-1} 1599, 1541, 1534. Anal. Calcd for $C_{40}H_{44}O_8Ge$: C, 66.23; H, 6.11. Found: C, 66.01; H, 6.30.

Preparation of T$_4$Sn (5a). A solution of tropolone (**1**; 1 g, 8.2 mmol) and triethylamine (1 g, 10 mmol) in methanol (20 mL) was added to tin tetrachloride (534 mg, 2 mmol) and then heated at 60 °C for 40 h under an argon atmosphere. A precipitate was collected and then treated with tropolone (1 g, 8.2 mmol) without solvent at 250−300 °C for 1 h. Recrystallization from CH_2Cl_2 gave the corresponding product **5a**: pale yellow crystals; yield 50%; mp 356−357 °C (lit.[4] mp 354−356 °C); ^{1}H NMR (300 MHz, $CDCl_3$, δ) 6.96 (t, J = 9.4 Hz, 4 H), 7.40 (dd, J = 9.4, 11.0 Hz, 8 H), 7.54 (d, J = 11.0 Hz, 8 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 124.8, 126.8, 138.9, 173.7; ^{119}Sn NMR (111.9 MHz, $CDCl_3$) δ −793.10; m/z MS (FAB, %) 514 (33), 483 (M$^+$ − 121, 100), 481 (72.4), 242 (6.8); UV λ_{max}/nm (CH_2Cl_2, ϵ) 239 (135 400), 325 (54 300), 366 (30 600); IR ν_{max}/cm^{-1} (KBr) 1593, 1520, 1230, 1261. Anal. Calcd for $C_{28}H_{20}O_8Sn$: C, 55.75; H, 3.34. Found: C, 55.54; H, 3.35.

X-ray Crystallography. Crystal data and numerical details of the structure determination are given in Table 3. A crystal suitable for X-ray structure determination was mounted on a Rigaku AFC5R (graphite monochromator, rotating anode) and irradiated with graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å) for data collection. All data were corrected for absorption (ψ-scan method) and Lorenz and polarization effects. The structures were solved by a heavy-atom method and successive difference Fourier method. Refinement on F was carried out by a full-matrix least-squares method for **3b** and by a block-diagonal least-squares method for **5a**. All non-hydrogen atoms were refined with anisotropic thermal parameters. Atomic scattering factors were applied from ref 17. All calculations were performed on a MICRO VAX II computer using the Rigaku "TEXSAN" Package Program System (1985) and on an ACOS3000 computer at Tohoku University using the UNICSIII Package System.[18]

Acknowledgment. We thank Dr. Jerome P. Lillis, Photodynamics Research Center, The Institute of Physical and Chemical Research, for his helpful discussion.

Supporting Information Available: Crystallographic data with complete tables of bond lengths, bond angles, and thermal and positional parameters for **3b** and **5a** and figures giving ^{1}H NMR spectra of **3b**, **4a**, and **5a** and UV−vis spectra of **3a** and **5a** (27 pages). Ordering information is given on any current masthead page.

OM970937H

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(18) Sakurai, T.; Kobayashi, K. *Rikagaku Kenkyusho Hokoku* **1979**, *55*, 69.