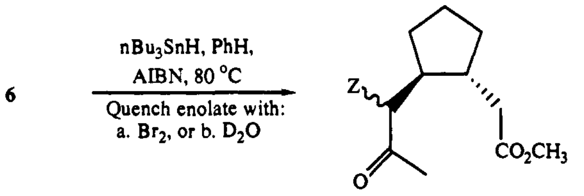
Table II. Dilution Experiments with Methyl (2*E*,7*E*)-9-Oxo-2,7-decadienoate (**6**)

$$\mathbf{6} \xrightarrow{n\text{-Bu}_3\text{SnH (1.1 equiv)}} \mathbf{7} + \mathbf{8}$$

	reaction conditions	7:8 (% yield)
1.	1.00 M **6** in benzene	9:1 (75)
2.	0.10 M **6** in benzene	25:1 (82)
3.	0.01 M **6** in benzene	>50:1 (82)

Scheme IV



17a Z = Br (86%)
17b Z = D (87%)

electron cyclizations promoted by tributyltin hydride. In addition, excellent anti stereoselectivities (>50:1) with the ring appendages are achievable in this reversible 5-*exo-trig* free-radical cyclization.

We have initially examined three substrates, shown in Table I, which successfully underwent free-radical cyclization to produce a cyclopentane ring with anti-disposed appendages as the major product in each case. Variation of the electron-withdrawing group in each example did not appear to alter the ratios to any significant extent. The major and minor products were both formed by an initial one-electron cyclization to give the cyclopentane ring. The minor product, produced from syn-disposed appendages, underwent a second cyclization to render bicyclo[3.3.0] ring systems, not possible with the major anti isomers because of ring strain. These tandem ring cyclizations likely arise from the *O*-stannyl enolate reacting in a two-electron aldol-type condensation to afford the second ring. It is also interesting to note that in one minor product, compound **14**, four stereogenic centers were created; however, only the single diastereomer shown was observed. The stereochemistry was confirmed by difference NOE studies.[7]

The activated alkene acceptor appears to be a prerequisite for success in these reactions. When we attempted the cyclization with **15**,[8] shown in Scheme III, only reduction of the olefin portion of the enone was observed.[9] It would appear that intermolecular hydrogen atom transfer from tributyltin hydride is more rapid to radical species **3** when compared to the slower rate of cyclization with an unactivated alkene.

When the cyclization of **6** was examined at greater dilution, we were delighted to obtain much higher levels of stereoselectivity; note Table II. A ratio of >50:1 for the anti:syn products could be achieved at 0.01 M in benzene. The increase in stereoselectivity can likely be attributed to the reversibility of the cyclization and the decreased availability of *n*-Bu_3SnH.

Two additional experiments were performed which clearly establish the presence of the stannyl enolate. In each, the one-electron or radical reactivity of the allylic *O*-stannyl ketyl from **6** was induced to cyclize under the anti-selective dilute reaction conditions in experiment 3 shown in Table II. The resultant stannyl enolate was then immediately quenched with either Br_2 or D_2O[12] to produce a ca. 2:1 mixture of **17** as shown in Scheme IV. These results indicate that the one-electron reactivity in the allylic *O*-stannyl ketyl can be isolated from the two-electron reactivity by sequential transformations; moreover, by the correct choice of experiment, both types of reactivity can be achieved.

In summary, these studies illustrate that an α,β-unsaturated ketone can function as a precursor to an allylic *O*-stannyl ketyl which permits anti-selective β-coupling cyclizations with a tethered activated alkene. The intermediates in the reaction display a dichotomy of one- and two-electron reactivity.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research (Grant ACS-PRF 23356-AC4). We also gratefully acknowledge support by the National Science Foundation (Grant CHE-9013121) for this work.

Supplementary Material Available: General procedure for the intramolecular β-coupling of activated olefins, spectral data for compounds **6**–**17**, and difference NOE data for **14** (4 pages). Ordering information is given on any current masthead page.

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(7) A summary of the difference NOE experiments is provided in the "Supplementary Material" section.

(8) **15** was prepared from 2-hydroxytetrahydropyran by treatment with (a) $Ph_3P{=}CHC_5H_{11}$, THF, 0 °C; (b) PDC, CH_2Cl_2 HOAc (cat.), 4-Å sieves; (c) $Ph_3P{=}CHCOCH_3$, CH_2Cl_2.

(9) We have also examined the cyclization of these substrates with SmI_2, which should produce the allylic *O*-samarium ketyl analogues of **2** and **3**. Unfortunately, treatment of **6** with 2 equiv of SmI_2 in THF–methanol at −78 °C led to a low yield of an acyclic product by simple reduction of the enone alkene (as in **16**) along with several unidentified minor products.

(10) The diene starting materials were prepared in good yields in two ways. In the first method, freshly distilled glutaric dialdehyde was treated sequentially with (a) $Ph_3P{=}CHCOCH_3$, CH_2Cl_2; (b) $Ph_3P{=}CH\text{-EWG}$, CH_2Cl_2. In the second method, 2-hydroxytetrahydropyran was treated sequentially with (a) $Ph_3P{=}CHCOCH_3$, CH_2Cl_2; (b) PDC, CH_2Cl_2, HOAc (cat.), 4-Å sieves; (c) $Ph_3P{=}CH\text{-EWG}$, CH_2Cl_2.

(11) General procedure: A solution of the ketone in benzene (0.10 M) with AIBN (0.1 equiv) and tributyltin hydride (3.0 equiv) was carefully degassed with argon and heated to 80 °C (bath temperature). After 5–8 h, thin-layer chromatography indicated that starting diene had been consumed. The reaction was quenched with water and extracted with ether. The organic layers were dried and concentrated, and the crude oil was subjected to flash chromatography with ether–hexanes to remove the tin byproducts and isolate the desired cyclic products.

(12) Deuterium incorporation was >85% as calculated by ^1H NMR integration of the methylene protons.

Synthesis and X-ray Structure of the First Dicoordinate Dialkylstannylene That Is Monomeric in the Solid State[1]

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Synthesis and characterization of stable organostannylenes have presented a fascinating challenge in the chemistry of low-valent group 14 organometallic compounds.[2] Whereas, very recently, the first monomeric dialkyl- and diarylstannylenes, 2-pyridylbis(trimethylsilyl)methyl-substituted stannylenes[3] and bis[2,4,6-tris(trifluoromethyl)phenyl]stannylene,[4] have been synthesized and characterized by X-ray crystallography, these stannylenes are stabilized by intramolecular contacts between the tin atom and neighboring nitrogen or fluorine atoms.[5] We report herein

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(1) Chemistry of Organosilicon Compounds. 287.

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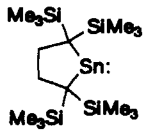
(5) Several amino-,[6a] alkoxy-,[6b,c] and arylthio-substituted[6d] stannylenes have been revealed by X-ray crystallography to be monomeric in crystals in which the tin has the coordination number of 2. The divalent tin would be stabilized by the effects of electronegativity of the ligand atoms and by the donation of the lone-pair electrons to the vacant 5pπ orbital of the tin.

the synthesis and characterization of the *first monomeric dialkylstannylene with coordination number 2 in the solid state*: 2,2,5,5-tetrakis(trimethylsilyl)-1-stannacyclopentane-1,1-diyl (**1**). In contrast to **1**, the structurally similar bis[bis(trimethylsilyl)methyl]stannylene (**2**) is known to be dimeric in the solid state, while monomeric in diluted solution as well as in the gas phase.[7]



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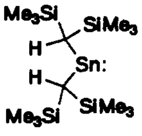

2

1,4-Dilithio-1,1,4,4-tetrakis(trimethylsilyl)butane, prepared in THF by the reaction of 1,1-bis(trimethylsilyl)ethylene with excess lithium,[8] was added to a suspension of anhydrous tin dichloride in ether in a Schlenk tube at −100 °C and then stirred for 1 h at 0 °C. After additional stirring for 20 min at room temperature, the solvent was substituted for hexane. Filtration of the suspension gave a dark-red solution. Recrystallization from hexane at −20 °C afforded **1** as air- and moisture-sensitive dark-red crystals in ca. 30% yield.[9]

The ^{119}Sn signal of **1** appeared at 2323 ppm as a sharp singlet in benzene-d_6 even at room temperature, which is the lowest ^{119}Sn chemical shift found until now. The band width and the chemical shift were almost unchanged between −40 and 80 °C in toluene-d_8. Thus, **1** exists as a monomer even at −40 °C at relatively high concentrations. In contrast, the variable-temperature ^{119}Sn NMR spectrum[10] of **2** in toluene-d_8 has been reported to show a large downfield resonance at 2315 ppm at 102 °C attributable to the monomer. At −108 °C, however, two signals are seen at 740 and 725 ppm, which have been assigned to different conformations of the dimeric species. The ^{119}Sn signal disappears at around room temperature due to the rapid equilibrium between the monomeric and the dimeric forms. The ^{13}C chemical shift of 69.5 ppm for the quaternary carbons is also indicative of the monomeric structure of **1** in solution; the corresponding ^{13}C chemical shift for **2** is severely temperature dependent between 28.7 and 60.0 ppm, the latter of which is assigned to the shift for the monomeric form.[10]

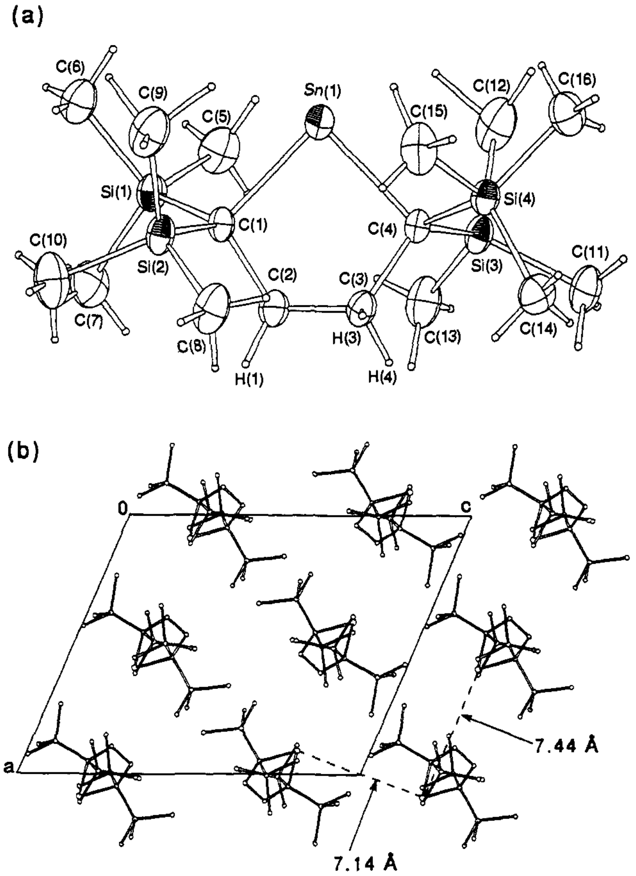

Figure 1. (a) Molecular structure of **1** showing atom-labeling scheme. The thermal ellipsoids are shown at the 30% level. Selected bond distances (Å) and angles (deg) are as follows: Sn–C(1), 2.218 (7); Sn–C(4), 2.223 (7); Si(1)–C(1), 1.869 (7); Si(1)–C(5), 1.887 (12); Si(2)–C(1), 1.898 (7); C(1)–C(2), 1.583 (10); C(2)–C(3), 1.482 (10); C(1)–Sn–C(4), 86.7 (2); C(1)–Si(1)–C(5), 110.0 (4); C(5)–Si(1)–C(6), 104.5 (4); Sn–C(1)–C(2), 103.7 (4); Sn–C(1)–Si(1), 102.0 (3); C(1)–C(2)–C(3), 113.5 (6); C(2)–C(3)–C(4), 115.8 (6). (b) Packing diagram for **1** along the *b* axis, showing the shortest distances between two tin atoms.

The solid-state structure of **1**, determined by a single-crystal X-ray diffraction study,[11] is shown with selected bond lengths and angles in Figure 1. The stannylene **1** was monomeric in the solid state with the shortest Sn- - -Sn distance of 7.14 Å. No intramolecular contacts with the divalent tin atom were observed.[12] Whereas no other crystal structural data is available for monomeric dialkylstannylene, the C–Sn bond length of 2.22 Å and the C–Sn–C angle of 86.7° in **1** can be compared with the gas-phase structural data for **2** (Sn–C = 2.22 (2) Å and C–Sn–C = 97°).[7i]

All the reported monomeric stannylenes include possible interaction between lone-pair orbitals and the vacant Sn 5pπ orbital,[3-6] showing yellow to orange color in solution. The dark-red color of **1** would be a good indication of the absence of any intramolecular dative bonds. The broad absorption band at 484

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(9) **1**: mp 93–95 °C; ^1H NMR (C_6D_6) δ 0.17 (s, 36 H), 2.94 (s, 4 H); ^{13}C NMR (C_6D_6) δ 2.43, 41.41, 69.53 [$^1J(^{119}Sn-^{13}C)$ = 359 Hz]; ^{29}Si NMR (C_6D_6) δ −3.98; ^{119}Sn NMR (C_6D_6) δ 2323; MS (EI, 12 eV) *m/z* (rel intensity) 464 [M(^{120}Sn), 19], 292 [M(^{120}Sn) − 172, 100], 172 (44), 157 (46), correct isotope distribution for M^+; HRMS calcd for $C_{16}H_{40}Si_4{}^{120}Sn$ 464.1229, found 464.1211; UV (hexane) λ_{max} (nm) (ε) 247 (9700), 285 (sh, 770), 370 (90), 484 (400).

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(11) Crystal data for **1** are as follows: monoclinic, space group $P2_1/a$ (No. 14), $a = 13.800$ (1) Å, $b = 11.526$ (2) Å, $c = 16.741$ (5) Å, $\beta = 113.03$ (3)°, $V = 2450.6$ (20) $Å^3$, $Z = 4$, $d_{calcd} = 1.256$ g/cm^3, $\mu = 12.34$ cm^{-1}. A total of 6446 reflections were collected on a Rigaku Denki AFC-5PR diffractometer (Mo, $\lambda = 0.71069$ Å, 13 °C, $2\theta/\theta$ scan technique). Of these, 4359 reflections [$F > 3\sigma(F)$] were used in refinement. $R = 0.058$, $R_w = 0.064$ (Sn, Si, and C were refined anisotropically, and H was refined isotropically). The crystal is very unstable at ambient conditions. Therefore, the sample should be mounted in a glass capillary under a nitrogen atmosphere in a glove box.

(12) The largest residual electron density in the final difference Fourier map was located around the Sn atom with two peaks of 0.60 and 0.50 e/Å^3. However, the distances of the peak positions (A and B) from Sn (ca. 1.0 Å) and the angles [C(1)–Sn–A = 55° and C(4)–Sn–B = 75°] are incompatible with the existence of hydrogens or the lone-pair electrons. The residual peaks would be due to the extinction effects. The detailed structural features will be discussed elsewhere.

nm (ϵ 400) for **1** is assigned to the n(Sn)-5pπ(Sn) transition,[13] since the spectral feature is similar to those of dimethylsilylene[14a] and dimethylgermylene,[14b] which show the n(metal)-pπ(metal) transition band at around 450 nm with relatively low absorption coefficients.

Whereas both **1** and **2** involve two bulky bis(trimethylsilyl)alkyl substituents as the ligands on tin, the cyclic ligand in **1** works like a helmet, protecting the central tin atom much more effectively than the two Lappert's Januslike ligands[15] in **2**. Additionally, the smaller C-Sn-C angle of **1** than that of **2** may partly be responsible for the stabilization of the monomeric structure due to enhancement of the singlet-triplet energy separation.[16]

Although the structural arrangement of several sterically protected low-valent organometallic compounds in the solid state can be provided by the ligand-ligand interactions or packing effects,[17] weak but significant Sn-Sn bonding would be principally responsible for determining the solid-state structure of **2**, where the bonding between the tin atoms may be best described by the double dative bond as originally proposed by Lappert et al.[7b,j]

Acknowledgment. We are grateful for the financial support of the Ministry of Education, Science, and Culture of Japan (Specially Promoted Research No. 02102004).

Supplementary Material Available: X-ray experimental details for **1**, tables of positional parameters, thermal parameters, bond lengths, and bond angles for **1**, and ^{1}H and ^{13}C NMR spectra of **1** (11 pages); listing of observed and calculated structure factors for **1** (22 pages). Ordering information is given on any current masthead page.

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[13] The relative intensities of the 370- and 484-nm bands for **1** did not depend on the concentration. In addition, the two bands decayed rapidly with the same rate when the sample was aerated. Therefore, the weak 370-nm band is not caused by artifacts but by the intrinsic electronic transition of **1**, whereas the nature of the transition remains open.

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Preparation and Reactivity of the Aquachromium(IV) Ion

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High-valent metal ions are postulated intermediates in biological[1a] and synthetic organic[1b] oxidations. Chromium(IV) is an elusive species, detected in a complex with 2-ethyl-2-hydroxybutyrate,[2] but definitively characterized only with the tetraphenylporphyrin ligand.[3] The latter species contains an oxo ligand similar to the ferryl porphyrins[4] known in oxidation of organic substrates. Despite several decades of interest,[5] aquachromium(IV) has never been directly observed. This communication describes four methods for its preparation. In the absence of reducing agents, this species is surprisingly long-lived, with a half-life of 0.75 min at 0.10 M ionic strength at room temperature.

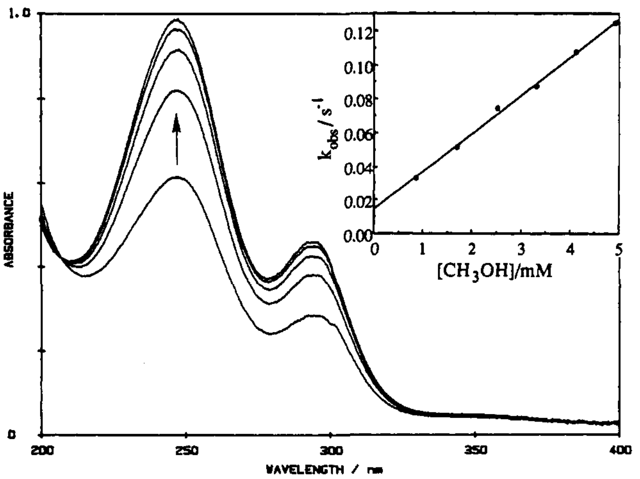

Figure 1. Development of the CrO_2^{2+} spectrum in the reaction between 0.1 mM CrO^{2+} and 1.0 mM CH_3OH, in the presence of 1 mM O_2. The time interval between spectra is 7 s. The inset shows the dependence of the pseudo-first-order rate constants on [CH_3OH] at 25 °C in 0.10 M $HClO_4$. Slope = 22.7 L mol^{-1} s^{-1}; intercept = 0.014 s^{-1}.

Generation of the new chromium species was accomplished anaerobically by stopped-flow mixing of superoxochromium(III), CrO_2^{2+}(aq),[6] or (μ-peroxo)dichromium(III), $CrOOCr^{4+}$(aq),[7] or Tl^{III}(aq) with an equal concentration of Cr^{2+}(aq), 0.1-0.5 mM, in acidic (0.1-1.0 M $HClO_4$) aqueous solution. Also, mixing Cr^{2+}(aq) and oxygen, in a 1:1 ratio with stopped-flow mixing or a 1:5 ratio by syringe injection into a spectrophotometer cell, yields chromium(IV). Yields are low (15-50% based on total chromium) because of the competing oxidation of Cr^{2+} by Cr(IV). The low concentration of Cr(IV) available by these methods, its lack of significant absorbance in the visible region, and its relatively short lifetime preclude direct characterization of Cr(IV), which explains why this species has been overlooked despite numerous studies of chromium redox reactions. Therefore, we studied the reactivity of this species in order to identify it (and quantify its yield) and establish its properties.

The chromium(IV) species formed by syringe injection or stopped-flow mixing of Cr^{2+} and O_2 reacts readily with 0.01-0.04 M Ph_3P with rate constant $k = (2.1 \pm 0.2) \times 10^3$ L mol^{-1} s^{-1} in 0.10 M $HClO_4$/85% CH_3CN at room temperature.[8] Under these conditions, reaction 1 is complete in less than 0.2 s; therefore the decomposition of Cr(IV) does not contribute to the kinetics. The product Ph_3PO is formed quantitatively and was identified by comparison of its UV spectrum with that of an authentic sample. We infer from this that the chromium(IV) exists as an oxo complex, as in the porphyrin complex.[3]

$$Cr{=}O^{2+}(aq) + PPh_3 \rightarrow Cr^{2+}(aq) + O{=}PPh_3 \qquad (1)$$

The immediate addition of millimolar quantities of methanol to oxygenated solutions containing ca. 0.1 mM CrO^{2+}, prepared by mixing Cr^{2+} with O_2, causes the spectrum of CrO_2^{2+} to develop, Figure 1. The equation for this reaction requires O_2 on the reactant side for mass balance, eq 2. The increase in absorbance

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[6] When Cr^{2+}(aq) (from Zn/Hg reduction of $Cr(H_2O)_6^{3+}$) is injected into an acidic aqueous solution containing oxygen at very low Cr:O_2 ratios, <0.05:1, the adduct CrO_2^{2+} is formed quantitatively (Brynildson, M. E.; Bakac, A.; Espenson, J. H. *J. Am. Chem. Soc.* **1987**, *109*, 4579) with rate constant 1.6 × 10^8 L mol^{-1} s^{-1} (Sellers, R. M.; Simic, M. G. *J. Am. Chem. Soc.* **1976**, *98*, 6145). The CrO_2^{2+} was identified and quantified by its intense and characteristic UV spectrum, ϵ_{290nm} = 3100 L mol^{-1} cm^{-1}, ϵ_{245nm} = 7000 L mol^{-1} cm^{-1} (Ilan, Y. A.; Czapski, G.; Ardon, M. *Isr. J. Chem.* **1975**, *13*, 15).

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[8] The reaction was monitored via the loss of absorbance at 256 nm, a maximum in the spectrum of PPh_3, or competition with $ABTS^{2-}$ ((2,2'-azinobis(3-ethylbenzothiazoline-6-sulfonic acid)). The latter is oxidized to an intensely absorbing radical anion by CrO^{2+}.

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