(η^4-Butadiene)Sn(0) Complexes: A New Approach for Zero-Valent p-Block Elements Utilizing a Butadiene as a 4π-Electron Donor
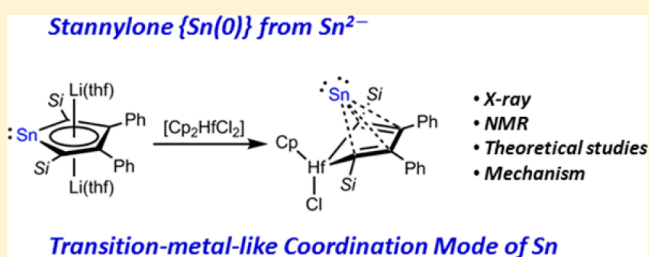
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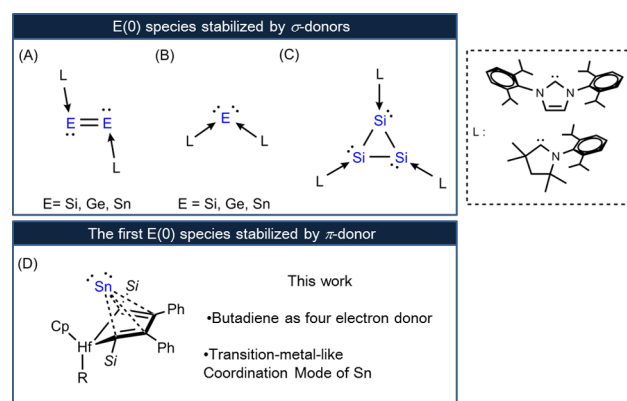
(S) Supporting Information

ABSTRACT: Research on zero-valent p-block elements is a recent hot topic in synthetic and theoretical chemistry because of their novel electronic states having two lone pairs in both the s- and p-orbitals. It is considered that σ-donating ligands bearing large substituents are essential to stabilize these species. Herein, we propose a new approach using butadiene as a 4π-electron donor to stabilize zero-valent group 14 elements. During our study to explore the coordination chemistry of stannacyclopentadienyl ligands, unexpected products, in which the tin atom is coordinated by a butadiene in a η^4-fashion, were obtained. Because butadiene is a neutral 4π-electron donating ligand, the formal oxidation number of the tin atoms of the products should be zero, which is supported by X-ray diffraction analysis and theoretical calculations. A mechanism for the formation of the products is also described.

Stannylone {Sn(0)} from Sn²⁻

• X-ray
• NMR
• Theoretical studies
• Mechanism

Transition-metal-like Coordination Mode of Sn

■ INTRODUCTION

The concept of oxidation number and valence electrons is a fundamental issue to understand the chemical bonding, properties, and reactivities of various compounds. In particular, compounds with zero-valent atoms of the relevant elements stabilized by suitable ligands are of significant importance because they can be regarded as compounds bearing the simplest electronic state without covalent bonds. Zero-valent transition metals (M(0)) play important roles in a large number of useful catalytic reactions such as Nobel-Prize-winning Suzuki coupling,[1] Heck reaction,[2] and Negishi coupling.[3] In contrast, research on zero-valent s- and p-block elements (E(0), where E = p-block elements) was much less explored and is now recognized as a hot topic for synthetic and theoretical chemists because of their new bonding modes, causing new reactivities and properties.[4] In 2008, the diatomic Si(0) was synthesized for the first time by using bulky N-heterocyclic carbenes (NHCs) as ligands (Chart 1A).[5] After the pioneering work by Robinson, various types of formal E(0) species such as diatomic (Chart 1A)[6] and monoatomic (Chart 1B)[7] derivatives were reported one after another. Recent theoretical calculations revealed that trisila- and tristannaallenes can be regarded as Si(0) (silylone) and Sn(0) (stannylone) species stabilized by two tetrylenes, respectively.[8] The synthesis of triatomic silicon(0) was also achieved by Roesky's group (Chart 1C).[9] These E(0) species, called ylidones,[8] are of great interest because of their nonclassical electronic states bearing two lone pairs in their s- and p-orbitals as well as their characteristics as soluble allotropes of main group elements.[10] It is believed that σ-

Chart 1. Representative Drawings of E(0) Species: (A) Diatomic E(0) Species, (B) Monoatomic E(0) Species, (C) Triatomic E(0) Species, and (D, This Work) Sn(0) Species Utilizing a Butadiene as a 4π-Electron Donor

E(0) species stabilized by σ-donors

(A)   (B)   (C)

E= Si, Ge, Sn   E = Si, Ge, Sn

The first E(0) species stabilized by π-donor

(D)

This work
• Butadiene as four electron donor
• Transition-metal-like Coordination Mode of Sn

donating ligands, such as carbenes,[11] and tetrylenes, are indispensable to isolate such highly reactive E(0) species. In fact, all of the E(0) species isolated to date are stabilized by two lone pairs of the ligands to meet the octet rule. However, E(0) species stabilized by this method have sterically protected E(0) metal centers, which suppress further investigation on their reactivity. Indeed, reports on the reactivities of E(0) species are

still limited to oxidation,[12] the addition of electrophiles,[7c,13] and complexation with main group and transition metals.[14,15] Herein we propose a new strategy to stabilize E(0) species utilizing a butadiene as a 4π-electron donor (Chart 1D), which was discovered during the course of our study on the reactivities of dilithiostannoles toward transition metal reagents.[16] In this report, the structures of the first butadiene complexes bearing Sn(0) states, NMR analysis, and theoretical studies as well as a mechanism for the formation of the complexes are described.

■ RESULTS AND DISCUSSION

To synthesize the stannylene-hafnium complex, reactions of dilithiostannole 1[17] with hafnocene dichloride in tetrahydrofuran were investigated (Scheme 1). The color of the solution

Scheme 1. Reactions of Dilithiostannole 1 with Hafnocene Dichloride
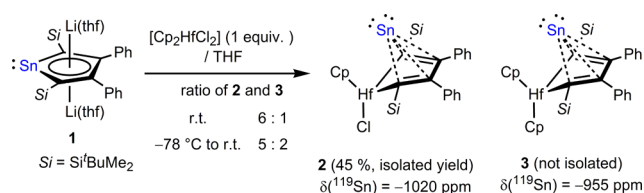
changed from red to dark brown via deep green, which occurred within 10 s when the two reagents were mixed at room temperature. In contrast, when the reaction was monitored from −78 to −40 °C, no color change was observed. However, the color of the solution gradually changed from red to deep green at around −30 °C. Finally, the color became dark brown upon warming up to room temperature. Notably, the deep green color was maintained as long as the reaction solution was kept under −30 °C. In the ^{119}Sn NMR of the crude product, a main signal was observed at −1020 ppm, accompanied by weak signals at −987 and −955 ppm, suggesting the generation of three products whose tin atoms are highly shielded (Figure S6). The single-crystal X-ray diffraction analysis revealed that the major product is the unexpected pyramid-like molecule 2 with an exotic structure, bearing Cp and Cl groups on the hafnium atom. One of the byproducts (−955 ppm in the ^{119}Sn NMR) was another pyramid-like molecule 3, which has a similar structure to 2 with two Cp ligands on the hafnium atom, as characterized by X-ray diffraction analysis and the ^{1}H, ^{13}C, and ^{119}Sn NMR data (Figures S7−S9). Thus, the remaining byproduct (−987 ppm in the ^{119}Sn NMR) might be an isomer of 2 whose Cp and Cl groups are situated opposite those of 2. The generation ratio of 2 to 3 is dependent on the reaction temperature: 2:3 = 6:1 and 5:2 at room temperature and lower temperature, respectively (Figures S4 and S5). Compound 2 is unstable both in the solid state and in solution at room temperature, and it decomposed even in a glovebox to give insoluble gray powder, which may be elemental tin.[18]

The molecular structures and selected geometric parameters of 2 and 3 are shown in Figure 1 and Table 1. The tin atoms in 2 and 3 are drastically deviated from the C_4 plane of the butadiene moieties, leading to the pyramid-like structures. As a consequence, the tin atoms appear to have interactions with not only C_α but also C_β. The Sn−C_α and Sn−C_β bond lengths are 2.300(5)−2.341(5) and 2.419(6)−2.451(4) Å, respectively, making them 5−12% longer than the original Sn−C_α bonds in

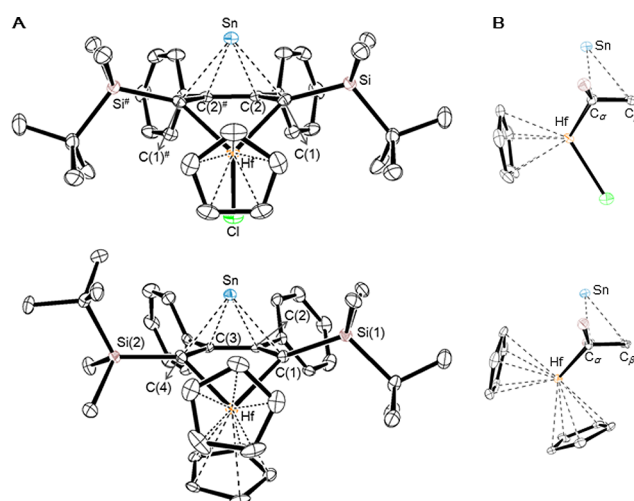**Figure 1.** (A) ORTEP drawings of 2 (upper) and 3 (lower) with 50% probability. All hydrogen atoms and cocrystallized solvents (a toluene and a THF molecules for 2 and 3, respectively) were omitted for clarity. (B) Side views of 2 and 3 without the selected substituents for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) of Compounds 2, 3, and 1

	2	3	1
Sn−C_α	2.314(4)	2.341(5), 2.300(5)	2.185(3), 2.196(3)
Sn−C_β	2.451(4)	2.447(5), 2.419(6)	
C_α−C_β	1.484(5)	1.515(7), 1.475(7)	1.431(3), 1.425(4)
C_β−C_β	1.450(7)	1.423(6)	1.440(3)
Hf−C_α	2.144(4)	2.209(5), 2.229(5)	
Hf⋯C_β	2.565(4)	2.823(4), 2.830(5)	
bent angles for HfC$_4$ ring[a]	60.4	47.1	

[a]The bent angles were defined as 180° − {Hf − (midpoint of C_α) − (midpoint of C_β)}.

1 (approximately 2.19 Å). Such long Sn−C bonds were also found in [(Ar′Sn)$_2$(μ_2-η^2:η^3-cot)] (2.364−2.590 Å),[19] the stannapyramidane Sn[η^4-C$_4$(SiMe$_3$)$_4$] (2.339−2.343 Å),[20] and (η^3-allyl)Sn(II) complexes (2.380−2.418 Å),[21] implying that the Sn−C bonds in 2 and 3 are considered π-bonds rather than σ-bonds. Thus, they can be regarded as (η^4-butadiene)Sn(0) complexes. Main group metals coordinated by butadiene ligands in a η^4-fashion are still rare, although butadienes are widely used as ligands for transition metals. To the best of our knowledge, such an example has only been reported in the boron-butadiene complex,[22] and our compounds 2 and 3 are noteworthy from the standpoint of being the first examples of butadiene complexes with group 14 metals. In contrast to the π-bonding character of the Sn−C bonds, the Hf−C bonds (2.144(4)−2.229(5) Å) appear to be σ-bonds because they are shorter than the sum of the single-bond covalent radii of Hf and C (2.27 Å),[23] and the corresponding bonds in the reported (η^4-butadiene)hafnium complexes (approximately 2.3−2.4 Å).[24] The C−C bonds in the butadiene moieties of 2 and 3 are between normal C−C single and double bonds, suggesting that the π-electrons delocalize over the butadiene moieties of 2 and 3. Importantly, the Hf⋯C_β distance in 2 (2.565(4) Å) is much
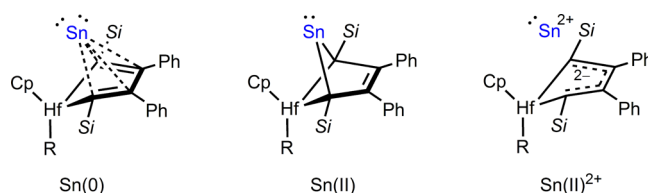
shorter than those in **3** (2.823(4), 2.830(5) Å), which is caused by the number of valence electrons on the hafnium atom. The hafnium atoms in **2** and **3** have 12 and 16 valence electrons, respectively, when the hafnacycles are considered as 1-hafnacyclopenta-2,4-dienes. The hafnium center in **2** is therefore rather electrophilic, leading the shorter $Hf\cdots C_\beta$ distances to efficiently receive the π-electrons of the butadiene moiety. In fact, the $C_\beta-C_\beta$ bond in **2** is longer than the corresponding bond in **3** (1.450(7) vs 1.423(6) Å). As a result, the bent angle of the five-membered hafnacycle in **2** is larger than that of **3** (60.39° vs 47.09°) (Figure 1B).

To gain further insight into the electronic structure of **2**, theoretical calculations were performed using the Gaussian 03 program.[25] The geometry of **2** was fully optimized with hybrid density functional theory at the B3PW91[26] level using the Lanl2dz basis set for Hf[27] and augmented by d polarization functions (d exponent 0.186) for Sn[28] along with the 6-31G(d) basis set for the others.[29] The optimized structure of **2** is in good agreement with the experimental structure (Figure S11 and Table S1). The Sn−C interaction was corroborated by Wiberg bond indices (WBI)[30] of 0.376 and 0.174 for Sn−C_α and Sn−C_β, respectively. Importantly, two types of lone pairs on the Sn were found as shown in Figure 2. In the HOMO, a lone pair in a p-orbital of the tin atom has interaction with both C_α and the π-orbital on $C_\beta-C_\beta$, while a d_z orbital of Hf forms σ-bonds with each C_α. The lone pair on the p-orbital strongly suggests the Sn(0) character of **2**. Notably, the MO derived

Figure 2. Selected canonical molecular orbitals (CMOs) for **2** (isovalue = 0.04; left, front views; right, side views).

from the butadiene moiety in the HOMO corresponds to the LUMO of the parent butadiene, suggesting that the lone pair in the p-orbital of Sn donates its electron to the butadiene moiety. Another lone pair with high s-character was found in HOMO − 3, HOMO − 10, and HOMO − 16. The stabilization energies of $\pi(C_\beta-C_\beta) \rightarrow$ p(Sn) and $\pi(C_\beta-C_\beta) \rightarrow$ d(Hf) were calculated to be 16.5 and 14.4 kcal mol^{-1}, respectively, by second-order perturbation theory analysis, revealing that the butadiene functions as a donor, while the tin and hafnium atoms are acceptors. It should be noted that compound **2** is stabilized by a donor−acceptor interaction between the 4π-electron donor (butadiene) and the vacant p-orbitals of Sn, which is in sharp contrast to the fact that the E(0) species reported to date are stabilized by σ-donating ligands
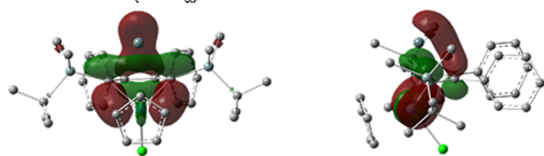
Chart 2 displays possible resonance structures for **2** and **3**.[31,32] In addition to the butadiene complex of Sn(0) [Chart 2
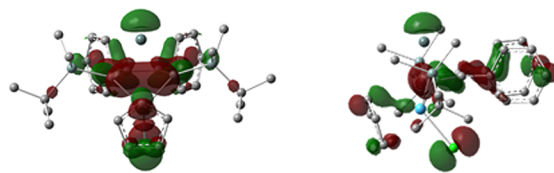
Chart 2. Plausible Electronic Structures of 2 and 3^a

^{a}Stannylone stabilized by a butadiene (left), stannylene (center), and stannylene dication (right).

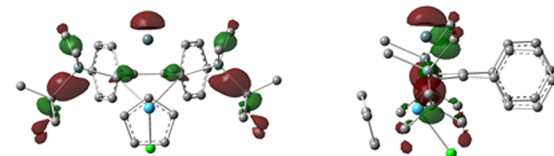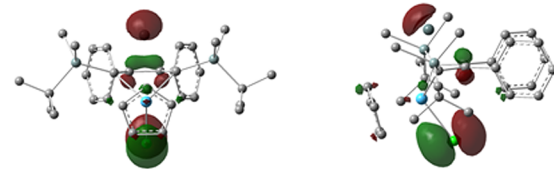(left)], stannylene [Chart 2 (center)] and the stannylene dication stabilized by the dianionic hafnacycle [Chart 2 (right)] are also possible. However, judging from the extraordinarily long Sn−C bonds in **2** and **3**, they cannot be regarded as stannylenes. Moreover, the existence of the two types of lone pairs on Sn strongly support that **2** and **3** are the Sn(0) species rather than the stannylene dications.[4c]

To further elucidate the Sn(0) character of **2**, the first and second proton affinities (PAs) were calculated (Scheme 2). The

Scheme 2. Protonation of 2 and the Calculated Proton Affinities

First PA = 216.7 kcal·mol^{-1} Second PA = 157.8 kcal·mol^{-1}
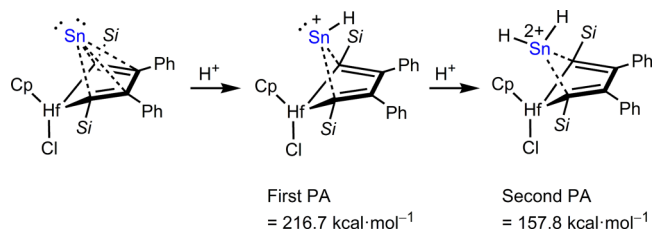
PA values are diagnostic to distinguish E(0) and E(II) species;[4c] the second PAs of E(0) species are larger than those of the E(II) species because the E(0) species have two lone pairs. The first and the second PA values of **2** were calculated to be 216.7 and 157.8 kcal mol^{-1}, respectively, using the same method as for the geometrical optimization. The second PA of **2** is as large as that of stannylones stabilized by NHC or PPh$_3$.[4c] The difference between the first and the second PA in **2** is smaller than that of Sn(NHC)$_2$ and Sn(PPh$_3$)$_2$ (58.9 vs 136.4 and 108.2 kcal mol^{-1}, respectively). Moreover, the position of the first proton is an additional piece of evidence for the Sn(0) character of **2**. Upon the first protonation of **2**, the proton is coordinated by the lone pair in

the p-orbital of Sn found in the HOMO (Figure 2). These results strongly support that the tin atom in **2** is in the zero oxidation state. The structural features of the resulting protonated complexes are described in Figure S12 and Table S2.

To investigate the mechanism for the formation of the products, variable-temperature (VT) NMR was examined next. A sealed NMR tube containing **1**, hafnocene dichloride, and THF-d_8 was kept under −30 °C to retain the green color that originates from intermediates for compounds **2** and **3**. A broad ^{119}Sn NMR signal was observed at 984 ppm at −30 °C (Figure S10). Because signals in the low-field area approximately 1000−1700 ppm are characteristic of stannylene-group 4 metal complexes,[16b,33] the green color originates from stannylene-hafnium complexes **4** and **5** (Scheme 3). As such, a stannylene

Scheme 3. Mechanism for the Formation of 2 and 3

$Si = Si^tBuMe_2$

4 (R = Cl)
5 (R = Cp)
δ([119]Sn) 984
stable at −30 °C

2 (R = Cl)
3 (R = Cp)
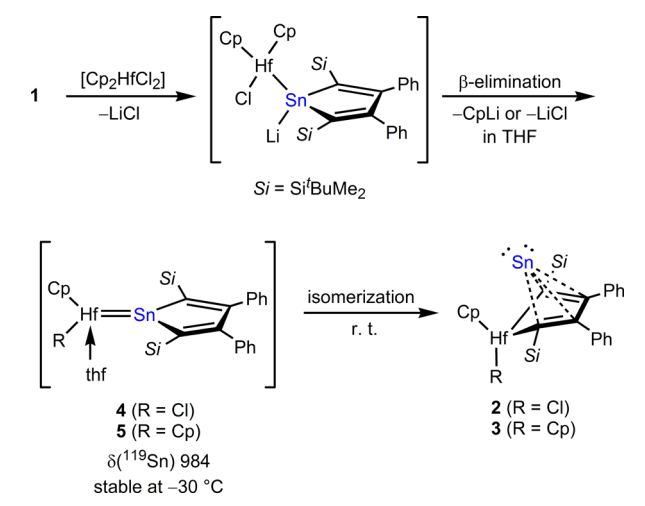
complex was not observed in toluene;[34] THF coordination is essential to stabilize the intermediates. The color of the solution changed from green to brown upon warming to room temperature, and the ^{119}Sn NMR signals of the resulting brown solution at both −30 °C and room temperature were found in the high-field region around −900 ppm, similar to those of **2** and **3**. The mechanism for the formation of **2** and **3** can therefore be proposed as follows (Scheme 3): a salt-elimination reaction followed by β-elimination results in the generation of the intermediates, stannylene-hafnium complexes **4** and **5**, in which each of the hafnium atoms is coordinated by a THF molecule. However, these complexes are unstable at around room temperature and readily isomerize to **2** and **3**. Because the major product was **2**, elimination of CpLi takes place prior to that of LiCl because of the steric hindrance between the bulky silyl groups and the hafnocene moiety.

To support the proposed mechanism, theoretical studies were performed using the same method as that for the geometrical optimization of **2** (Figure S13). The calculated Sn−Hf length of **4** was 2.790 Å, which is similar to the Sn−Hf bond found in Marschner's stannylene-hafnocene complex stabilized by PEt$_3$ (2.7585(11) Å).[33] Moreover, the ^{119}Sn NMR chemical shift of **4** was calculated to be 879.4 ppm, similar to the experimental value obtained from the VT-NMR (984 ppm) and that of Marschner's stannylene-hafnium complex (1079 ppm).[33] Remarkably, the total energy of **2** and a THF molecule is more stable than that of **4** by 31.2 kcal mol^{-1}. These results

strongly support our hypothesis that **2** and **3** were generated by the isomerization of **4** and **5**, respectively.

■ CONCLUSIONS

We succeeded in the synthesis and characterization of Sn(0) species **2** and **3** coordinated by butadiene ligands. The present findings exhibit a new strategy to stabilize zero-valent heavy group 14 elements using a butadiene ligand as a 4π-electron donor. The products are worth mentioning not only because they are the first examples of η^4-butadiene complexes of group 14 metals but also because of their transition-metal-like behavior in main group metals.[35] Because the heavy group 14 elements in butadiene complexes are sterically hindered much less than those stabilized by two bulky carbene ligands, butadiene complexes of E(0) would be a good choice to discover novel reactivity and catalytic reactions derived from the E(0) characteristic.

■ EXPERIMENTAL SECTION

General Procedures. All experiments were performed under argon atmosphere in a glovebox or using standard Schlenk techniques. THF, toluene, hexane, THF-d_8, and benzene-d_6 were purified by potassium mirror before used. Hafnocene dichloride was purchased from Tokyo Chemical Industry (TCI) and used as received. The ^{1}H NMR (500 MHz), ^{13}C NMR (101 MHz), ^{29}Si NMR (99 MHz), and ^{119}Sn NMR (187 MHz) were recorded on a Bruker DPX-400 Cryo or an AVANCE-500T. The intensity data for X-ray crystallographic analyses were collected at −198 °C on a Bruker SMART APEX equipped with a CCD area detector with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) and graphite monochromator. The structures were solved by direct methods, and refined by full-matrix least-squares method by SHELXL program.[36]

Crystallographic Data Deposition. Crystallographic data for compounds **2** and **3** have been deposited with the Cambridge Crystallographic Data Centre as CCDC 1487416 and 1487415, respectively (www.ccdc.cam.ac.uk/data_request/cif).

■ ASSOCIATED CONTENT

⑤ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b07304.

> Experimental details, NMR and crystal data, and Cartesian coordinates for **2**, **2**·H$^+$, **2**·(H$^+$)$_2$, and **4** (PDF)
> Crystallographic details for **2** and **3** (CIF)

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Notes
The authors declare no competing financial interest.

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Professor Takayuki Kawashima on the occasion of his 70th birthday.

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