DOI: 10.1002/anie.201308565

Diversity of the Structures in a Distannene Complex and its Reduction to Generate a Six-Membered Ti$_2$Sn$_4$ Ring Complex**

*Takuya Kuwabara, Jing Dong Guo, Shigeru Nagase, and Masaichi Saito**

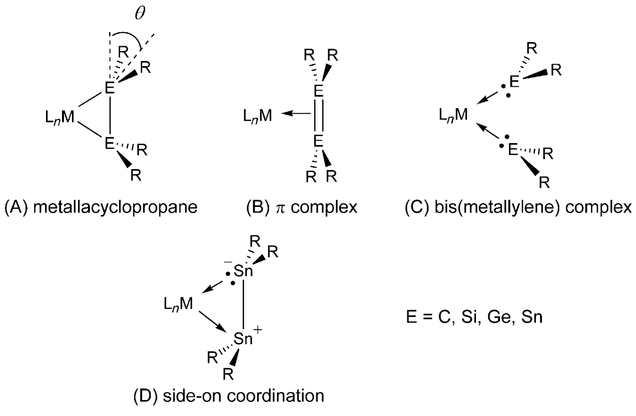
Dedicated to Professor Robert West on the occasion of his 85th birthday

***Abstract:** In contrast to olefin complexes, their congeners of heavier elements display various coordination modes, and their complexes may be present as bis(metallylene) complexes, with side-on coordination, as metallacyclopropanes, or as π complexes. In the course of our studies on the reactivity of dilithiostannoles towards transition-metal reagents, three-membered TiSn$_2$ and six-membered Ti$_2$Sn$_4$ ring complexes were obtained. According to its geometric parameters, NMR analysis, and theoretical calculations, the TiSn$_2$ complex cannot be categorized into any of these previously described bonding modes. Therefore, a novel resonance structure has been proposed for a complex that has a delocalized σ-orbital over the TiSn$_2$ ring to understand its electronic structure. The mechanism for the formation of the Ti$_2$Sn$_4$ ring complex and its EPR spectrum are also discussed.*

The substitution of carbon atoms in compounds such as olefins and alkynes by heavier elements has attracted significant attention because the resulting structures are different from those of the carbon derivatives, and these compounds thus display unique properties and reactivity.[1] In contrast to the planar and linear geometries of olefins and alkynes, respectively, their analogues of heavier elements generally have *trans*-bent structures.[2] Similar structural differences are also found for olefin complexes and their heavier-element analogues.[3] According to the Dewar–Chatt–Duncanson model,[4] the bonding modes in olefin complexes can be classified into two types (Scheme 1): 1) In a metallacyclopropane (A), strong π-back-donation results in large bent-back angles and an elongated C−C bond. 2) In a π complex (B), σ donation of the C=C bond to a metal center is the dominant interaction, which leads to high planarity of the olefin moiety. In contrast, complexes that feature double bonds of heavier elements have various coordination modes in addition to (A) and (B). DFT calculations on a disilene zirconium complex revealed that the contribution of the bis(metallylene) complex (C) is predominant;[3d] compounds that are prepared by the reaction of stannylenes and Zr^{II} are thus considered to be bis(stannylene) zirconium complexes.[5] Marschner and co-workers also reported a bis(stannylene) titanium complex in which the Ti−Sn bonds have a partial double-bond character.[6] The Sn$\cdots$Sn distances in those bis(stannylene) complexes are long (3.5567(17)–4.2364(13) Å), which indicates that no or only weak interactions occur between the two tin atoms. A distannene complex with side-on coordination (D) has recently been synthesized by Wesemann and co-workers.[7]

As part of our studies on the reactivity of dilithiostannoles[8] toward transition-metal reagents,[9] we herein report the reaction of tetraethyldilithiostannole with [Cp$_2$TiCl$_2$] (Cp = η^5-C$_5$H$_5$), which resulted in the formation of a distannene complex that cannot be categorized into any of the bonding modes (A) to (D) shown in Scheme 1. By changing the stoichiometry of the reaction, a six-membered Ti$_2$Sn$_4$ ring complex that bears heavier lithocene moieties was also formed. The mechanism for the formation of the six-membered ring complex is also discussed.

The reaction of tetraethyldilithiostannole **1**,[8c] which is coordinated by a diethyl ether molecule, with [Cp$_2$TiCl$_2$]



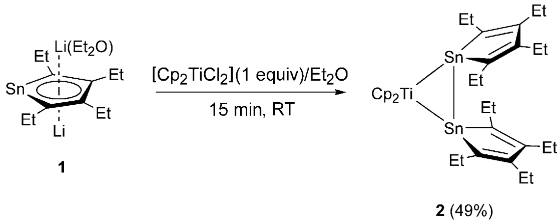
Scheme 1. Various structures for olefin complexes and congeners of heavier elements.

---

[*] T. Kuwabara, Prof. Dr. M. Saito
Department of Chemistry
Graduate School of Science and Engineering
Saitama University
Shimo-okubo, Sakura-ku, Saitama-city, Saitama 338-8570 (Japan)
E-mail: masaichi@chem.saitama-u.ac.jp
Dr. J. D. Guo, Prof. Dr. S. Nagase
Fukui Institute for Fundamental Chemistry
Kyoto University
Takano-Nishihiraki-cho, Sakyo-ku, Kyoto 606-8103 (Japan)

[**] This work was partially supported by Grant-in-Aid for Scientific Research (B; 22350015 for M.S.) and by the Nanotechnology Support Project and Specially Promoted Research from the Ministry of Education, Culture, Sports, Science, and Technology of Japan. M.S. acknowledges a research grant from the Mitsubishi Foundation. T.K. acknowledges the JSPS for a Research Fellowship for Young Scientists.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201308565.



Scheme 2. Reaction of dilithiostannole **1** with $[Cp_2TiCl_2]$ (1 equiv).

(1 equiv) yielded dark purple crystals after recrystallization (Scheme 2).[10] X-ray diffraction analysis revealed that the product is the three-membered $TiSn_2$ ring complex **2** (Figure 1). After recrystallization, the residue consisted of several unidentified Ti^{III} species, as determined by EPR spectroscopy (Supporting Information, Figure S1). The Ti–Sn bond lengths are 2.6867(16) and 2.7254(17) Å; these bond lengths are remarkably shorter than the distances of previously reported Ti–Sn single bonds (2.842–2.984 Å),[11] but nearly the same as those of the bis(stannylene) titanium complexes described by Marschner et al. (2.7122(13) and 2.7154(14) Å).[6] The distance between the two tin atoms is 3.0576(11) Å and therefore longer than typical Sn=Sn bond lengths (2.575(4) to 2.85126(19) Å)[12] and the corresponding single-bond lengths of bistannoles (2.7682(2) and 2.7822(7) Å).[13] However, it is noteworthy that the Sn–Sn distance in **2** is considerably shorter than those observed for bis(stannylene) group 4 metal complexes (4.2364(13), 4.038 and 3.5567(17) Å),[5,6] which indicates a strong interaction between the two tin atoms. The bent-back angles θ, which are defined as $180° - \measuredangle[x\text{-Sn-Sn}']$, where x is the midpoint between C_α of each R group, are 67° and 80°. These structural features suggest that complex **2** has a metallacyclopropane character (A; Scheme 1). The relationship between the substituents on the tin atoms, the angles (θ), and the Sn···Sn distances in the bis(stannylene) Group 4 metal complexes are of interest. As the complexes described by the groups of Marschner and Piers bear bulky substituents on the tin atoms, they have small θ angles (ca. 30°) and long Sn···Sn distances (4.038 and 4.2364(13) Å) because of steric repulsion.[5b,6] For a stannylene complex that bears C,N-chelating ligands with the nitrogen atoms coordinated to the vacant p orbitals of the tin center, Růžička et al. reported larger angles (65.8 and 68.6°) and a shorter Sn···Sn distance (3.5567(17) Å).[5c] Compound **2**, however, bears neither a bulky substituent nor a donating ligand. Therefore, compound **2** has the largest θ angle and the shortest Sn···Sn distance among all bis(stannylene) Group 4 metal complexes that have been reported to date.

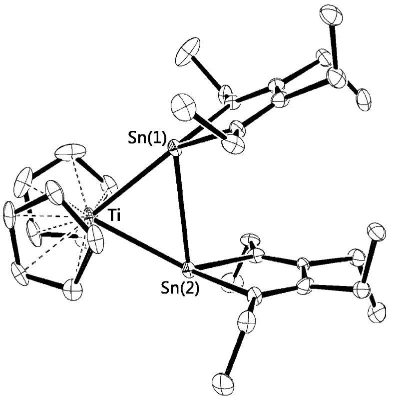
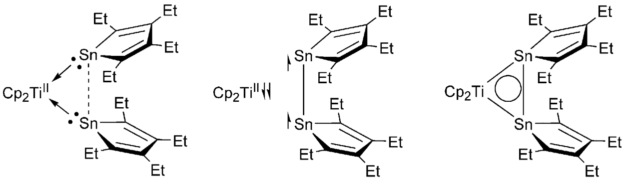


Figure 1. ORTEP representation of **2** (thermal ellipsoids set at 30% probability). All hydrogen atoms were omitted for clarity. Selected bond lengths [Å] and angles [°]: Ti–Sn(1) 2.6867(16), Ti–Sn(2) 2.7254(17), Sn(1)–Sn(2) 3.0576(11); Sn(1)-Ti-Sn(2) 68.79(4).

In the ^{119}Sn NMR spectrum of **2**, only one signal was observed at low field at 1332.5 ppm, an area where signals of stannylene Group 4 metal complexes are typically observed,[5,6] which indicates that the two tin atoms of **2** have considerable stannylene character. More interestingly, a coupling constant between the ^{119}Sn and ^{117}Sn nuclei of 3433 Hz was observed, which lies in the range where $^1J_{Sn,Sn}$ coupling constants are normally observed (2500—4500 Hz),[14] but it is much larger than that of the stannylene zirconium complex ($J = 630$ Hz) described by Piers et al.;[5b] it was assigned to be a $^2J_{Sn,Sn}$ coupling constant. This spectroscopic feature suggests that there is a strong bonding interaction between the two tin atoms of the stannylene moieties ((E); Scheme 3).



(E) Bis(stannylene) complex with Sn–Sn interaction

(F) Complex between triplet bistannole diradical and triplet titanocene(II)

(G) Aromatic character (Donation from σ(Sn–Sn) to d*(Ti) and π*(Ti–Sn))

Scheme 3. Possible resonance structures of **2**.

To gain further insight into the electronic structure of **2**, theoretical calculations were performed using the Gaussian 03 program.[15] The geometry of **2** was fully optimized with hybrid density functional theory at the B3PW91[16] level of theory using the [4333111/433111/43] basis set that was augmented by two d polarization functions (with d exponents of 0.253 and 0.078) for tin[17] and the 6-31G(d) basis set for titanium, carbon, and hydrogen.[18] Natural population analysis and perturbation-theory energy analysis were performed with the NBO 3.1 program in Gaussian 03. The optimized geometry is consistent with the structure that was obtained by X-ray diffraction analysis (Table S1). Based on the optimized structure, the Wiberg bond index (WBI)[19] of the Sn–Sn bond was calculated to be 0.52, which is remarkably larger than that of 0.20 for $Cp_2Zr(stannylene)_2$ with a Sn···Sn distance of 4.038 Å.[6] Canonical and natural localized molecular orbital (CMO and NLMO) calculations both revealed three types of molecular orbitals (MOs) that are localized on the three-membered ring (Figure 2). Based on the bonding theory of olefin complexes, the HOMO appears to result from back-donation from the d(Ti^{II}) to the p(Sn) orbital, while HOMO-3 and HOMO-6 originate from the electron donation from Sn

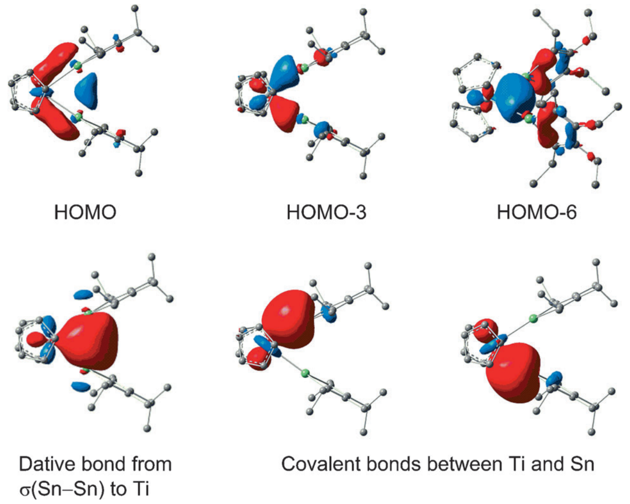


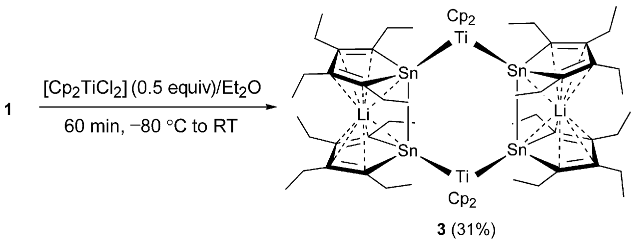
Figure 2. CMOs and NLMOs of **2** (isodensity values of 0.05 and 0.03, respectively). HOMO (π (Sn-Ti-Sn)), HOMO-3 (σ (Sn-Ti-Sn), and HOMO-6 (donation from σ (Sn–Sn) into d*(Ti) and σ*(Ti–Sn)) for CMOs. Dative bond from Sn_2 to Ti and two covalent bonds between Ti and Sn for NLMOs.

to Ti atoms. However, after performing calculations on the Cp_2Ti and Sn_2 moieties to depict the orbital correlation of **2**, we unexpectedly found that **2** results from interactions between the Cp_2Ti and Sn_2 moieties in their triplet ground states (Figure S2).[20] According to orbital correlation, HOMO and HOMO-3 have a covalent-bond character that is caused by SOMO–SOMO interactions of the two triplet ground-state moieties. However, the σ-symmetric HOMO-6 is derived from a donor–acceptor interaction between the LUMO of Cp_2Ti and an occupied orbital of the Sn_2 moieties and is delocalized over the three-membered ring. Natural LMOs reveal the nature of these three interactions more clearly. NBO and second-order perturbation-theory analyses revealed that the Sn–Sn bond donates its electrons into the $d^*_{x^2-y^2}$ and $d^*_{z^2}$ orbitals of the titanium, with large stabilization energies of 88 and 48 $kcal\,mol^{-1}$, respectively (Figure S4). Furthermore, the Sn–Sn bond acts as a donor towards each of the two π*(Ti–Sn) bonds, and the resulting stabilization energy was estimated to be 13 $kcal\,mol^{-1}$. Because of this donating nature, the calculated electron occupancy (1.474) for the σ(Sn–Sn) bond is less than 2. Furthermore, the NICS(0) and NICS(1) values (NICS = nucleus-independent chemical shift)[21] of the three-membered ring were calculated to be −36.7 and −18.6 ppm, respectively, which reflects a certain degree of aromatic delocalization of the electrons over the $TiSn_2$ ring;[22] this hypothesis is corroborated by a WBI value for the Sn–Sn bond of less than unity. In contrast, no back-donation was found in **2**, which indicates that **2** does not feature the metallacyclopropane bonding mode (Scheme 1; (A)). These calculations and the finding that the Sn–Sn bond is longer than the corresponding single bond indicate that **2** can also be regarded as a complex that is derived from a triplet bistannole biradical and a triplet titanocene (F), as an aromatic compound along the lines of structure (G) in Scheme 3, and as an Sn–Sn σ complex. These σ complexes are well-studied key intermediates of the oxidative additions of various σ bonds.[23]

The UV/Vis spectrum of **2** in hexane at room temperature shows two strong absorption bands at $\lambda_{max} = 515$ and 620 nm (Figure S5). These two absorption peaks were calculated to be at 484 ($f = 0.17$) and 602 ($f = 0.07$) nm using the time-dependent (TD) B3PW91 method; these bands are primarily assignable to the HOMO→LUMO+1 and HOMO→LUMO transitions, respectively (see also Figure S5).

The large $^1J_{Sn,Sn}$ coupling constant, X-ray crystal and calculated structures, and NBO analysis revealed that compound **2** has various characters and can be regarded as a bis(stannylene) complex, as a Sn–Sn σ complex or as a structure with electron delocalization, which is a novel resonance structure for complexes with double bonds of heavier elements (Scheme 3).

To understand the mechanism for the formation of **2**, the reaction of **1** with $[Cp_2TiCl_2]$ (0.5 equiv) was examined (Scheme 4). Compound **2** was not formed; instead, red crystals were obtained. X-ray diffraction analysis of these red crystals revealed that the product is the six-membered Ti_2Sn_4 ring complex **3**, which bears heavier lithocene moieties (Figure 3).[10] The skeletal Ti_2Sn_4 six-membered ring is compelled to have a boat conformation because of the rigid lithocene moieties. In contrast to the short Ti–Sn bonds in **2**, the Ti–Sn lengths of **3** are 2.9245(10) and 2.9080(11) Å and therefore in the normal range of the corresponding single bonds. The Sn–Sn bond length is 3.0098(6) Å, which is nearly



Scheme 4. Reaction of dilithiostannole **1** with $[Cp_2TiCl_2]$ (0.5 equiv).

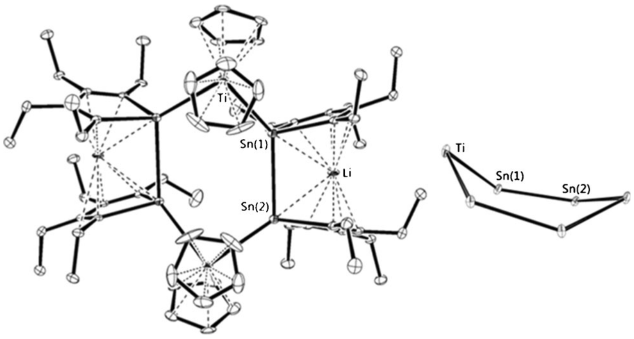


Figure 3. ORTEP drawing of **3** (left) and its skeletal six-membered ring (right; thermal ellipsoids set at 30% probability). All hydrogen atoms were omitted for clarity. Selected bond lengths [Å] and angles [°]: Ti–Sn(1) 2.9246(10), $Ti^{\#}$–Sn(2) 2.9080(11), Sn(1)–Sn(2) 3.0098(6); Sn(1)-Ti-$Sn(2)^{\#}$ 89.22(3).

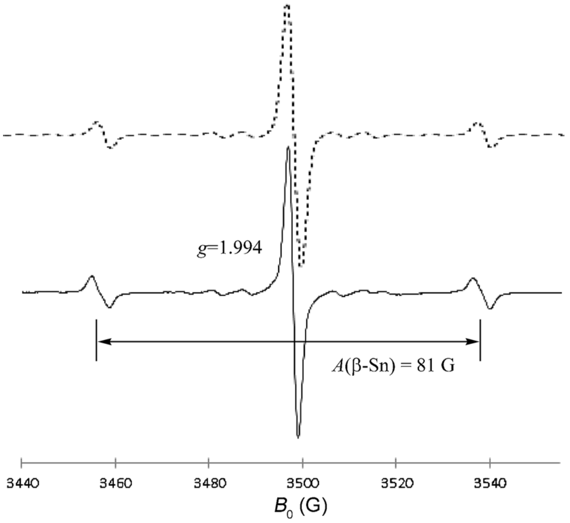
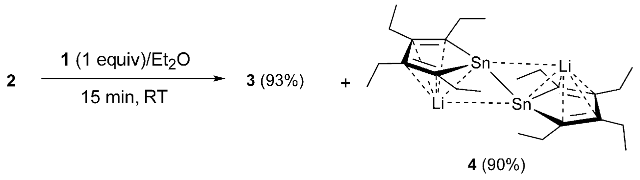


Figure 4. EPR spectrum of **3** in toluene at room temperature (——) and simulated version (-----); A_{Ti} hyperfine (^{47}Ti abundance = 7.4 %, I = 5/2; ^{49}Ti abundance = 5.4 %, I = 3/2) = 6.5 G; A_{Sn} (^{117}Sn abundance = 7.7 %, I = 1/2; ^{119}Sn abundance = 8.6 %, I = 1/2) = 81.2 G; line broadening = 3.5 G.

the same as that of the parent heavier lithocene (3.0255(16) Å).[24]

Because of the paramagnetic character of the Ti^{III} atoms, no signals were observed in the NMR spectrum of **3**. The EPR spectrum showed broadened signals that were accompanied by hyperfine coupling satellites derived from the Sn nuclei (Figure 4). A g_{iso} value of 1.994 was determined, which is nearly the same as that of the Ti^{III} species.[25] The hyperfine coupling constant for A(β-Sn) of 81 G is smaller than that of 187 G for another A(β-Sn),[26] although the satellite signals resulting from the ^{119}Sn and ^{117}Sn nuclei cannot be distinguished because of the broadening of the signal. The A(Ti) hyperfine coupling constant is estimated to be 6.5 G from the simulated spectrum (dashed line in Figure 4), which is comparable to that of a Ti^{III} complex (12.48 G).[25b]

As complex **3** may be regarded as a reduced version of **2**, the reduction of **2** with **1** was investigated (Scheme 5).[10] As expected, **1** functioned as a one-electron reductant to form 1,1′-dilithiobistannole **4** and compound **3** nearly quantitatively, as determined by NMR[8] and EPR spectroscopy. Therefore, in the reaction of [Cp_2TiCl_2] with two equivalents of **1** (Scheme 4), **2** is first formed by the 1:1 reaction of [Cp_2TiCl_2] and **1**, and the remaining one equivalent of **1** then reduces **2** to afford Ti_2Sn_4 **3**.[27]



Scheme 5. Reduction of **2** with dilithiostannole **1**.

In summary, we successfully isolated two novel complexes, the three-membered $TiSn_2$ ring complex **2** and the six-membered Ti_2Sn_4 ring complex **3**, from the reactions of tetraethyldilithiostannole **1** with [Cp_2TiCl_2]. Compound **3** was also obtained quantitatively by the reduction of **2** with **1**, which indicates that dilithiostannole **1** is a novel and useful homogeneous one-electron reductant. Based on the low-field ^{119}Sn NMR signal accompanied by the large $^{1}J_{Sn,Sn}$ coupling constant, the short Sn=Sn distance compared with those of other bis(stannylene) complexes, and theoretical calculations, it can be concluded that complex **2** can be regarded as a bis(stannylene) complex, a Sn=Sn σ complex, and as a novel structure with a σ orbital that is delocalized over the $TiSn_2$ ring.

Received: October 1, 2013

Keywords: metallacycles · multiple bonds · sandwich complexes · tin · titanium

---

[1] a) T. Tsumuraya, S. A. Batcheller, S. Masamune, *Angew. Chem.* **1991**, *103*, 916–944; b) P. P. Power, *Organometallics* **2007**, *26*, 4362–4372; c) R. C. Fischer, P. P. Power, *Chem. Rev.* **2010**, *110*, 3877–3923; d) V. Y. Lee, A. Sekiguchi in *Organometallic Compounds of Low-Coordinate Si, Ge, Sn and Pb*, Wiley, Hoboken, **2010**, pp. 199–334.

[2] a) L. Pu, B. Twamley, P. P. Power, *J. Am. Chem. Soc.* **2000**, *122*, 3524–3525; b) M. Stender, A. D. Phillips, R. J. Wright, P. P. Power, *Angew. Chem.* **2002**, *114*, 1863–1865; *Angew. Chem. Int. Ed.* **2002**, *41*, 1785–1787; c) L. Pu, A. D. Phillips, A. F. Richards, M. Stender, R. S. Simons, M. M. Olmstead, P. P. Power, *J. Am. Chem. Soc.* **2003**, *125*, 11626–11636; d) A. Sekiguchi, R. Kinjo, M. Ichinohe, *Science* **2004**, *305*, 1755–1757; e) Y. Sugiyama, T. Sasamori, Y. Hosoi, Y. Furukawa, N. Takagi, S. Nagase, N. Tokitoh, *J. Am. Chem. Soc.* **2005**, *127*, 1023–1031; f) T. Sasamori, K. Hironaka, Y. Sugiyama, N. Takagi, S. Nagase, Y. Hosoi, Y. Furukawa, N. Tokitoh, *J. Am. Chem. Soc.* **2008**, *130*, 13856–13857; g) D. Gau, T. Kato, N. Saffon-Merceron, A. De Cózar, F. P. Cossío, A. Baceiredo, *Angew. Chem.* **2010**, *122*, 6735–6738; *Angew. Chem. Int. Ed.* **2010**, *49*, 6585–6588.

[3] a) E. K. Pham, R. West, *J. Am. Chem. Soc.* **1989**, *111*, 7667–7668; b) D. H. Berry, J. H. Chey, H. S. Zipin, P. J. Carroll, *J. Am. Chem. Soc.* **1990**, *112*, 452–453; c) P. Hong, N. H. Damrauer, P. J. Carroll, D. H. Berry, *Organometallics* **1993**, *12*, 3698–3704; d) H. Hashimoto, Y. Sekiguchi, T. Iwamoto, C. Kabuto, M. Kira, *Organometallics* **2002**, *21*, 454–456; e) H. Hashimoto, Y. Sekiguchi, Y. Sekiguchi, T. Iwamoto, C. Kabuto, M. Kira, *Can. J. Chem.* **2003**, *81*, 1241–1245; f) M. Kira, Y. Sekiguchi, T. Iwamoto, C. Kabuto, *J. Am. Chem. Soc.* **2004**, *126*, 12778–12779; g) R. Fischer, M. Zirngast, M. Flock, J. Baumgartner, C. Marschner, *J. Am. Chem. Soc.* **2005**, *127*, 70–71; h) T. Iwamoto, Y. Sekiguchi, N. Yoshida, C. Kabuto, M. Kira, *Dalton Trans.* **2006**, 177–182; i) M. Zirngast, M. Flock, J. Baumgartner, C. Marschner, *J. Am. Chem. Soc.* **2009**, *131*, 15952–15962; j) T. Abe, T. Iwamoto, M. Kira, *J. Am. Chem. Soc.* **2010**, *132*, 5008–5009.

[4] a) M. J. S. Dewar, *Bull. Soc. Chim. Fr.* **1951**, *18*, 71–79; b) J. Chatt, L. A. Duncanson, *J. Chem. Soc.* **1953**, 2939–2947.

[5] a) R. M. Whittal, G. Ferguson, J. F. Gallagher, W. E. Piers, *J. Am. Chem. Soc.* **1991**, *113*, 9867–9868; b) W. E. Piers, R. M. Whittal, G. Ferguson, J. F. Gallagher, R. D. J. Froese, H. J. Stronks, P. H. Krygsman, *Organometallics* **1992**, *11*, 4015–4022; c) J. Bareš, P.

Richard, P. Meunier, N. Pirio, Z. Padělková, Z. Černošek, I. Císařová, A. Růžiča, *Organometallics* **2009**, *28*, 3105 – 3108.

[6] H. Arp, J. Baumgartner, C. Marschner, P. Zark, T. Müller, *J. Am. Chem. Soc.* **2012**, *134*, 10864 – 10875.

[7] J. Henning, L. Wesemann, *Angew. Chem.* **2012**, *124*, 13041 – 13045; *Angew. Chem. Int. Ed.* **2012**, *51*, 12869 – 12873.

[8] a) M. Saito, R. Haga, M. Yoshioka, *Chem. Commun.* **2002**, 1002 – 1003; b) M. Saito, R. Haga, M. Yoshioka, K. Ishimura, S. Nagase, *Angew. Chem.* **2005**, *117*, 6711 – 6714; *Angew. Chem. Int. Ed.* **2005**, *44*, 6553 – 6556; c) M. Saito, T. Kuwabara, C. Kambayashi, M. Yoshioka, K. Ishimura, S. Nagase, *Chem. Lett.* **2010**, *39*, 700 – 701.

[9] T. Kuwabara, M. Saito, J.-D. Guo, S. Nagase, *Inorg. Chem.* **2013**, *52*, 3585 – 3587.

[10] For details on experiments and X-ray diffraction, see the Supporting Information. CCDC 929230 (**2**) and 929229 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[11] Six examples from the Cambridge Crystal Structure Database.

[12] a) C. Schrenk, A. Schnepf, *Chem. Commun.* **2010**, *46*, 6756 – 6758; b) V. Y. Lee, T. Fukawa, M. Nakamoto, A. Sekiguchi, B. L. Tumanskii, M. Karni, Y. Apeloig, *J. Am. Chem. Soc.* **2006**, *128*, 11643 – 11651; c) H. Lei, J. C. Fettinger, P. P. Power, *Organometallics* **2010**, *29*, 5585 – 5590; d) N. Wiberg, H.-W. Lerner, S.-K. Vasisht, S. Wagner, K. Karaghiosoff, H. Nöth, W. Ponikwar, *Eur. J. Inorg. Chem.* **1999**, 1211 – 1218.

[13] a) M. Saito, R. Haga, M. Yoshioka, *Eur. J. Inorg. Chem.* **2005**, 3750 – 3755; b) T. Kuwabara, M. Saito, *Acta Crystallogr. Sect. E* **2011**, *67*, m949.

[14] A. G. Davies, M. Gielen, K. H. Pannell, E. R. T. Tiekink, *Tin Chemistry Fundamentals, Frontiers, and Applications*, Wiley, Chichester, **2008**, chap. 2.1.

[15] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, GAUSSIAN03, Revision E.01, Gaussian, Inc., Wallingford CT, **204**.

[16] a) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648 – 5652; b) J. P. Perdew, Y. Wang, *Phys. Rev. B* **1992**, *45*, 13244 – 13249.

[17] S. Huzinaga, J. Andzelm, M. Klobukowski, E. Radzio-andzerm, Y. Sakai, H. Tatewaki, *Gaussian Basis Sets for Molecular Calculations*, Elsevier, Amsterdam, **1984**.

[18] M. N. Francl, W. J. Pietro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. Defrees, J. A. Pople, *J. Chem. Phys.* **1982**, *77*, 3654 – 3665.

[19] K. B. Wiberg, *Tetrahedron* **1968**, *24*, 1083 – 1096.

[20] Calculations based on closed-shell singlet fragments could not be employed because the wave functions for the Ti and Sn_2 parts are unstable; see also the Supporting Information, Figure S3.

[21] a) P. v. R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao, N. J. R. van Eikema Hommes, *J. Am. Chem. Soc.* **1996**, *118*, 6317 – 6318; b) P. v. R. Schleyer, M. Manoharan, Z.-X. Wang, B. Kiran, H. Jiao, R. Puchta, N. J. R. van Eikema Hommes, *Org. Lett.* **2001**, *3*, 2465 – 2468.

[22] a) X. Li, A. E. Kuznetsov, H.-F. Zhang, A. I. Boldyrev, L.-S. Wang, *Science* **2001**, *291*, 859 – 861; b) X. Huang, H.-J. Zhai, B. Kiran, L.-S. Wang, *Angew. Chem.* **2005**, *117*, 7417 – 7420; *Angew. Chem. Int. Ed.* **2005**, *44*, 7251 – 7254; c) M. Maruyama, J.-D. Guo, S. Nagase, E. Nakamura, Y. Matsuo, *J. Am. Chem. Soc.* **2011**, *133*, 6890 – 6893.

[23] a) R. H. Crabtree, *Angew. Chem.* **1993**, *105*, 828 – 845; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 789 – 805; b) G. Berthon-Gelloz, B. de Bruin, B. Tinant, I. E. Markó, *Angew. Chem.* **2009**, *121*, 3207 – 3210; *Angew. Chem. Int. Ed.* **2009**, *48*, 3161 – 3164; c) P. Gualco, A. Amgoune, K. Miqueu, S. Ladeira, D. Bourissou, *J. Am. Chem. Soc.* **2011**, *133*, 4257 – 4259; d) N. Lassauque, P. Gualco, S. Mallet-Ladeira, K. Miqueu, A. Amgoune, D. Bourissou, *J. Am. Chem. Soc.* **2013**, *135*, 13827 – 13834.

[24] M. Saito, T. Kuwabara, K. Ishimura, S. Nagase, *Chem. Asian J.* **2011**, *6*, 2907 – 2910.

[25] a) R. Shu, L. Hao, J. F. Harrod, H. G. Woo, E. Samuel, *J. Am. Chem. Soc.* **1998**, *120*, 12988 – 12989; b) N. A. Jones, S. T. Liddle, C. Wilson, P. L. Arnold, *Organometallics* **2007**, *26*, 755 – 757.

[26] T. Fukawa, V. Y. Lee, M. Nakamoto, A. Sekiguchi, *J. Am. Chem. Soc.* **2004**, *126*, 11758 – 11759.

[27] For the mechanism for the formation of **3**, see the Supporting Information.