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Dynamic Behavior and Isomerization Equilibria of Distannenes Synthesized by Tin Hydride/Olefin Insertions: Characterization of the Elusive Mono-Hydrido Bridged Isomer

Shuai Wang,† Madison L. McCrea-Hendrick,† Cory M. Weinstein, †,§ Christine A. Caputo,†,‡ Elke Hoppe,† James C. Fettinger,† Marilyn M . Olmstead, † and Philip P. Power*

† Department of Chemistry, University of California, 1 Shields Avenue, Davis, CA 95616, United States.

Abstract

The tin(II) hydride $[Ar^{iPr6}Sn(\mu\text{-}H)]_2$ (Ar^{iPr6} = C_6H_3-2,6(C_6H_2-2,4,6-^{i}Pr$_3$)$_2$) (**1a**) reacts with two equivalents of ethylene or *t*-butylethylene at *ca.* 25 °C to yield $Sn_2(Ar^{iPr6})_2R_2$ (R = ethyl or *t*-butylethyl), which exist either as a symmetric distannene $Ar^{iPr6}(R)SnSn(R)Ar^{iPr6}$ (**2a** or **5a**) or an unsymmetric stannylstannylene $Ar^{iPr6}SnSnR_2Ar^{iPr6}$ (**3a**). In contrast, the less crowded Sn(II) hydride $[Ar^{iPr4}Sn(\mu\text{-}H)]_2$ (Ar^{iPr4} = C_6H_3-2,6(C_6H_3-2,6-^{i}Pr$_2$)$_2$) (**1b**) reacts with excess ethylene to give $Ar^{iPr4}(CH_2CH_3)_2Sn(CH_2CH_2)Sn(CH_2CH_3)(CHCH_2)Ar^{iPr4}$ (**4**) featuring five ethylene equivalents, one of which is dehydrogenated to an alkenyl, -CH=CH_2 group. The Ar^{iPr4} isomers of **2a** and **3a**, *ie*. $[Ar^{iPr4}Sn(C_2H_5)]_2$ (**2b**) and $Ar^{iPr4}SnSn(C_2H_5)_2Ar^{iPr4}$ (**3b**) are obtained by reaction of $[Ar^{iPr4}Sn(\mu\text{-}Cl)]_2$ with EtLi or EtMgBr. The isomeric pairs **2a**/**2b** and **3a**/**3b** are separated by crystallization at different temperatures. Variable temperature ^{1}H NMR spectroscopy indicates fast ethyl group exchange between $Ar(C_2H_5)SnSn(C_2H_5)Ar$ (Ar = Ar^{iPr6} (**2a**) or Ar^{iPr4} (**2b**)) and $ArSnSn(C_2H_5)_2Ar$ (Ar = Ar^{iPr6} (**3a**) or Ar^{iPr4} (**3b**)) with $\Delta G^{\ddagger}$ = 14.2±0.65 kcal mol^{-1} for **2a**/**3a** and 14.8±0.36 kcal mol^{-1} for **2b**/**3b**. The bulkier distannenes $[ArSn(CH_2CH_2{}^tBu)]_2$ (Ar = Ar^{iPr6} (**5a**) or Ar^{iPr4} (**5b**)), obtained from **1a** or **1b** and *t*-butylethylene, dissociate to $ArSnCH_2CH_2{}^tBu$ monomers in solution. At lower temperature they interconvert with their stannylstannylene isomers with parameters K_{eq} = 4.09±0.16 for **5a** and and 6.38±0.41 for **5b** and ΔG_{eq} = -1.81±0.19 kcal mol^{-1} for **5a**, and −1.0±0.03

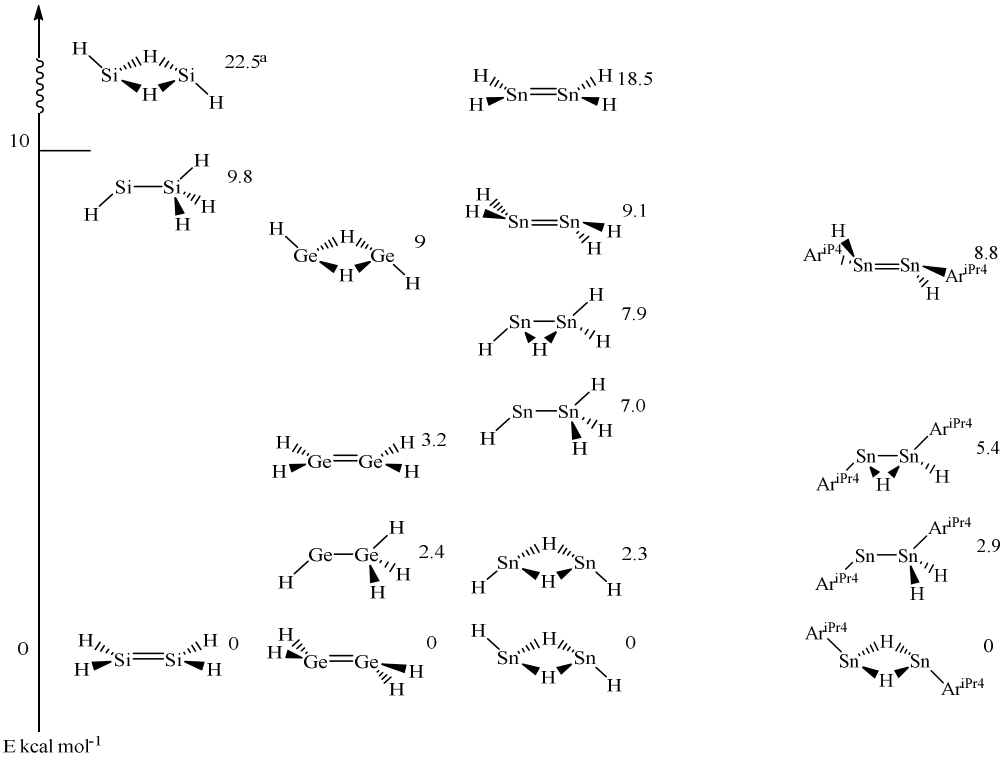
kcal mol^{-1} for **5b** at 298 K. The 1:1 reaction of **1a** or **1b** with **5a** or **5b** yield the unknown monohydrido species Sn_2RHAr_2 which have the structures $Ar^{iPr6}Sn\text{-}Sn(H)(CH_2CH_2{}^tBu)Ar^{iPr6}$ (**6a**), or the mono-hydrido bridged $Ar^{iPr4}Sn(\mu\text{-}H)Sn(CH_2CH_2{}^tBu)Ar^{iPr4}$ (**6b**). The latter is the first structural characterization of a mono-hydrido bridged isomer of a ditetrelene.

Introduction

Since the discovery of stable low valent group 14 hydrides in 2000,[1] several Sn(II) and Ge(II) hydride species supported by a variety of bulky aryl,[2-7] amido,[8-10] β-diketiminate,[11-15] *N*-heterocyclic carbene,[16-19] and phosphine groups[20] have been reported. Most were synthesized by reduction of a halogen substituted precursor, but it was shown also that the direct reactions of H_2 with a digermyne, $Ar^{iPr4}GeGeAr^{iPr4}$,[21] and distannyne, ArSnSnAr (Ar = Ar^{iPr4}-4-X, X = H, $SiMe_3$, F),[22] under ambient conditions gave Ge(II) and Sn(II) hydrides. Their reactions have attracted increasing attention.[23,24] For example, they react with alkali metals Li, Na and K to give reduced products with variety of structures.[25] They also undergo several facile reactions that include C-H activation and the hydroelementation of small molecules.[7,26-30] Roesky and coworkers reported that the monomeric Sn(II) hydride, $[HC(CMeNAr)_2]SnH$ (Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$), could hydrostannylate ketones, CO_2, and terminal alkynes to give Sn(II) alkoxides, stannylene formates, and alkenyl stannylenes.[26-28] Jones and coworkers used the bulky amido ligand, –N(Ar†)($SiPr^i_3$) (Ar† = C_6H_2-2,6-{$C(H)Ph_2$}$_2$-4-^{i}Pr), to stabilize a singly bonded digermyne which reacted with H_2 to form monomeric Ar†($SiPr^i_3$)NGeH that catalyzed the hydroboration of carbonyl groups to afford alcohols.[30] In addition, *in situ* generated Sn(II) hydrides were shown to catalyze the dehydrocoupling of amines and boranes.[31,32] The high reactivity of the group 14 metal hydrides ArEH (E = Ge, Sn) is due to their partially open shell structures which have an occupied *s* and an empty *p*-orbital which can interact with the frontier orbitals of unsaturated hydrocarbons and related molecules.[7,10]

In 2012, it was shown that the reaction of $Ar^{iPr4}GeGeAr^{iPr4}$ (E = Ge, Sn) with cyclopentene, which resulted in C-H activation to afford the unsymmetrical digermene $Ar^{iPr4}Ge(H)Ge(c\text{-}C_5H_9)Ar^{iPr4}$, proceeded via a Ge(II) hydride (ie. $(Ar^{iPr4}GeH)_2$ or $Ar^{iPr4}GeH$) intermediate.[7] Jones and coworkers also showed that the divalent amido hydrides, L†-EH (E = Sn or Ge) hydroelementate a variety of cyclic and linear unactivated olefins to give monomeric germylenes and stannylenes.[10]

Scheme 1. Calculated relative energies (kcal mol^{-1}) of different isomeric forms of the parent species E_2H_4 (E = Si - Sn)[33,34] with energies for the substituted $[Ar^{iPr4}SnH]_2$ (Ar^{iPr4} = C_6H_3-2,6-(C_6H_3-2,6-iPr$_2$)$_2$)given on the right hand side[35]



[a]The numbers represent the energies of the isomeric forms found as minima on the potential surface.

From the experimental standpoint, stable group 14 derivatives of the parent E_2H_4 species can be isolated using bulky co-ligands such as terphenyl groups in place of hydrogen. For tin they have been shown to exist in two isomeric forms based either on the doubly bridged $(HE(\mu\text{-}H)_2EH)$[1,2] or

the unsymmetrical $HEEH_3$ structures.[2] For germanium the most stable isomer is a digermene based on the multiple bonded trans-pyramidalized $H_2E{=}EH_2$ structure.[6] Sekiguchi and coworkers have reported the reaction of a dislyne RSi≡SiR (R = Si*i*Pr[$CH(SiMe_3)_2$]$_2$ with H_2 to afford a mono-hydrido substituted asymmetric disilenes R(R'$_2$E)Si=SiHR (R = Si*i*Pr[$CH(SiMe_3)_2$]$_2$ R' = Et_2N or Ph_2N).[36] Tokitoh and coworkers have synthesized the terminal dihydridodisilene, ArHSi=SiHAr (Ar = C_6H_2-2,6-$CH(SiMe_3)_2$, R = H or $CH(SiMe_3)_2$).[37] Rivard and coworkers have shown that, using a combination of Lewis acids and bases complexes of the symmetric H_2EEH_2 isomers can be isolated and characterized.[16,17] Nonetheless the reactions of the low valent/low oxidation state heavier group 14 hydrides are complicated by the fact that they can exist in several isomeric forms separated by relatively small energies. In 1990, Trinquier calculated the structures and energies of the parent divalent heavier group 14 hydrides, E_2H_4 (E = Si – Sn) (Scheme 1),[34] and showed that several isomers corresponding to minima on the potential surface are separated by less than 10 kcal mol^{-1} for tin. The lowest energy doubly bridged *trans*-isomer, *trans*-HSn(μ-H)$_2$SnH is 7.0 kcal mol^{-1} more stable than the stannylstannylene, H_3SnSnH, 7.9 kcal mol^{-1} more stable than the singly bridged H_2Sn(μ-H)SnH, and 9.1 kcal mol^{-1} more stable than the *trans*-pyramidal distannene H_2SnSnH_2. Planar isomeric forms H_2EEH_2 (E = Sn – Pb) are never minima on the potential surface and in the case of tin lie at a significantly higher energy of 18.5 kcal mol^{-1}.[34] Work by this group on the organo-substituted hydrides, in collaboration with Nagase and Guo, showed that the stability of the asymmetric isomers increases with the increasing size of the substituents.[2] Schleyer and coworkers performed calculations on [Ar^{iPr4}SnH]$_2$ (Scheme 1).[36] The energy difference between the mono-bridging hydrido isomer Ar^{iPr4}Sn(μ-H)Sn(H)Ar^{iPr4} and the doubly bridged hydrido distannene [Ar^{iPr4}Sn(μ-H)]$_2$ of 5.4 kcal mol^{-1} is lower than that of the parent Sn_2H_4; however, stable derivatives of a singly hydrido bridged distannene isomer have been unknown up to now.

In this paper, we report the reactions of the Sn(II) hydrides, [Ar^{iPr6}Sn(μ-H)]$_2$ (**1a**) and [Ar^{iPr4}Sn(μ-H)]$_2$ (**1b**) with unactivated alkenes which afford tetraorgano-ditin products. We show that the

symmetric isomer, $[Ar^{iPr6}Sn(C_2H_5)]_2$ (**2a**), which dissociates to monomers in solution, is in equilibrium with the unsymmetric stannylstannylene, $Ar^{iPr6}SnSn(C_2H_5)_2Ar^{iPr6}$ (**3a**) with a fast exchange rate for the ethyl group sites. The isomers can be isolated by crystallization at different temperatures. In contrast, **1b** reacts with five equivalents of ethylene to give the unique product, $Ar^{iPr4}Sn(CH_2CH_3)_2(CH_2CH_2)Sn(CH_2CH_3)(CHCH_2)Ar^{iPr4}$ (**4**), featuring a CH_2CH_2 moiety bridging two tin atoms one of which carries an ethenyl rather than an ethyl group. However, the synthesis of $Ar^{iPr4}SnSn(C_2H_5)_2Ar^{iPr4}$ (**3b**) can be effected via salt metathesis and this species is also in equilibrium with $[Ar^{iPr4}Sn(C_2H_5)]_2$ (**2b**) in solution. In addition, we report the first mono-hydrido stannylstannylene $Ar^{iPr6}SnSn(H)(CH_2CH_2{}^tBu)SnAr^{iPr6}$ (**6a**) and the mono-hydrido bridged distannene, $Ar^{iPr4}Sn(\mu\text{-}H)Sn(CH_2CH_2{}^tBu)SnAr^{iPr4}$ (**6b**) via reaction of **1a** or **1b** with *t*-butylethylene. The latter represents the first characterization of this isomeric form.

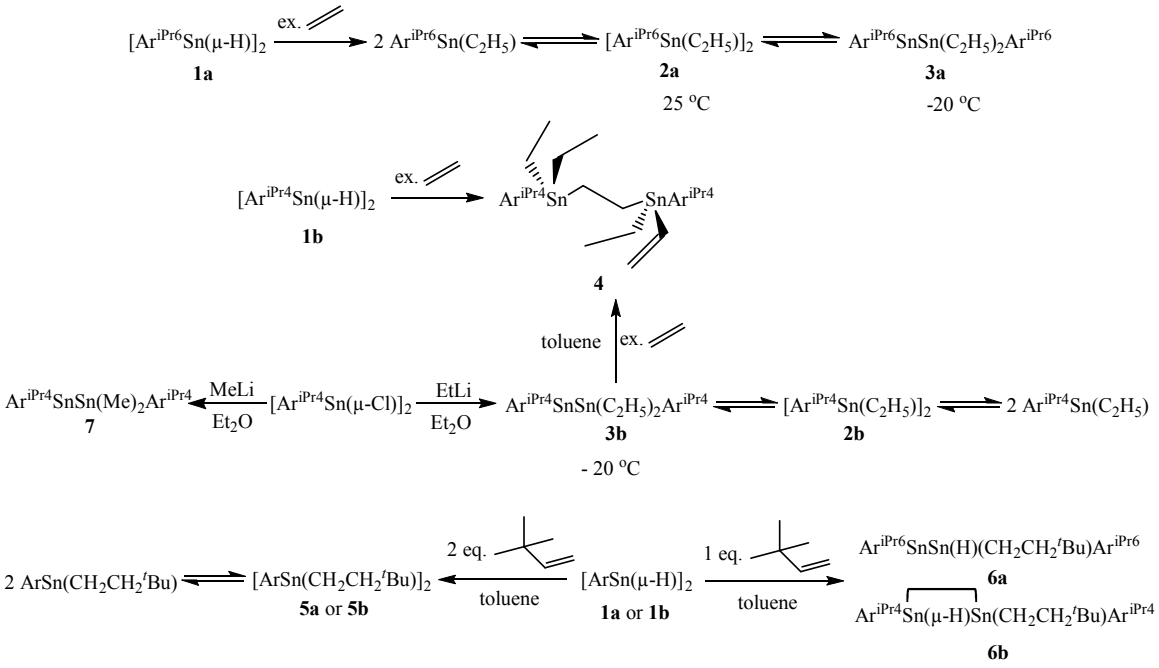
Results

Synthesis. The compounds discussed in this paper are summarized in Scheme 2. A toluene solution of $[Ar^{iPr6}Sn(\mu\text{-}H)]_2$ (**1a**) was treated at room temperature with an excess of ethylene gas to afford two products that could be selectively crystallized at different temperatures. A symmetric distannene, $[Ar^{iPr6}Sn(CH_2CH_3)]_2$ (**2a**), was isolated as a red crystalline solid at *ca.* 25°C, while its isomer, the Sn(I)/Sn(III) stannylstannylene $Ar^{iPr6}SnSn(CH_2CH_3)_2Ar^{iPr6}$ (**3a**), was obtained as a green crystalline material from the same solution at *ca.* −20°C. Attempts to synthesize similar products derived from the less bulky Sn(II) hydride, $[Ar^{iPr4}Sn(\mu\text{-}H)]_2$ (**1b**), via the same route were unsuccessful. Instead, a white solid was crystallized at *ca.* −20°C from the dark red mother liquor of its reaction with excess ethylene. This was identified as the unique bimetallic Sn(IV) species, $Ar^{iPr4}Sn(CH_2CH_3)_2(\mu\text{-}CH_2CH_2)Sn(CH_2CH_3)(CHCH_2)Ar^{iPr4}$ (**4**), in which one of the tin atoms carries an ethenyl, -$CHCH_2$, instead of an ethyl group.

The detailed mechanisms whereby **1a** or **1b** react with ethylene are currently unknown. One scenario assumes that solutions of **1a** or **1b** involve equilibrium concentrations of the highly reactive monomers $Ar^{iPr6}SnH$, $Ar^{iPr4}SnH$, or other species which rapidly undergo insertion reactions with the olefins (see Supporting Information). However the different reactivities shown by **1a** or **1b** toward ethylene suggest a more complicated explanation in which the different structures of **1a** and **1b** in solution may be relevant.

Since **1a** and **1b** display different reactivity towards excess ethylene, parallel reactions of **1a** and **1b** with 3,3-dimethylbut-1-ene (ie. *t*-butylethylene, CH_2CH^tBu) were also investigated to test its generality. However, treatment of **1a** or **1b** with two equivalents of 3,3-dimethylbut-1-ene at ambient temperature led to their quantitative conversion to the parallel insertion products, $[ArSn(CH_2CH_2{}^tBu)]_2$ (Ar^{iPr6} (**5a**), Ar^{iPr4} (**5b**)). No derivative analogous to **4** was observed. Reaction of *t*-butylethylene, CH_2CH^tBu, with one equivalent of **1a** or **1b** gave the unique hydrido stannylstannylene, $Ar^{iPr6}SnSn(H)(CH_2CH_2{}^tBu)SnAr^{iPr6}$ (**6a**) and the bridged-hydrido species $Ar^{iPr4}Sn(\mu\text{-}H)Sn(CH_2CH_2{}^tBu)SnAr^{iPr4}$ (**6b**). These products can be obtained also from the 1:1 redistribution reactions of **5a** or **5b** with **1a** or **1b** in toluene.

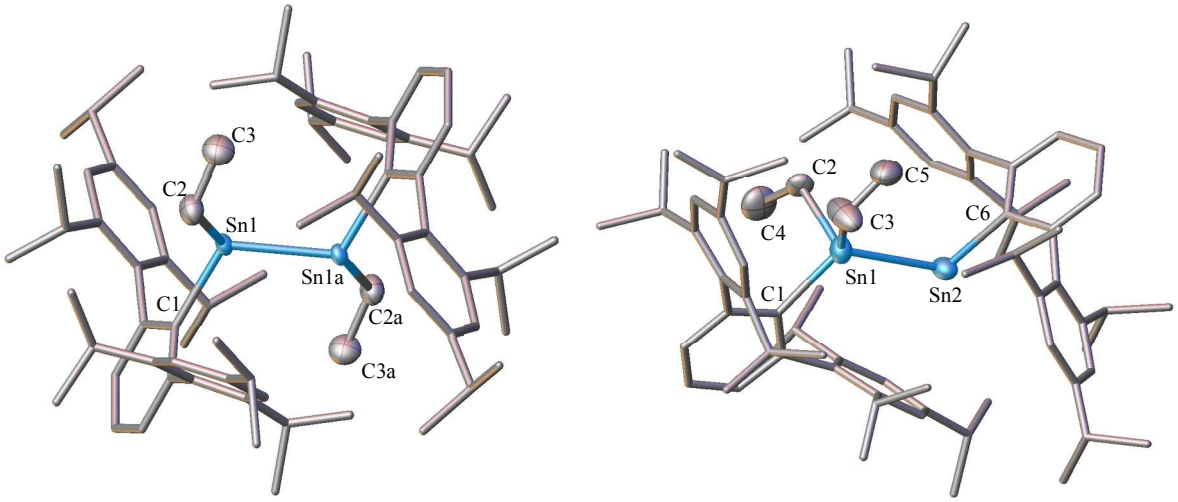
Scheme 2. Summary of the Synthesis and Behavior of Aryl/Alkyl Tin Species.



In order to shed further light on the formation of **4**, we investigated the reaction of $[Ar^{iPr4}Sn(\mu\text{-}Cl)]_2$[37] with a stoichiometric amount of EtMgBr or ethyllithium at room temperature which yielded a red solution. The expected symmetric distannene, $[Ar^{iPr4}Sn(CH_2CH_3)]_2$ (**2b**) an analog of $[Ar^{iPr6}Sn(CH_2CH_3)]_2$ (**2a**) could not be isolated at room temperature although spectroscopic data indicated that it exists in solution. However, the unsymmetrical distannene, $Ar^{iPr4}SnSn(CH_2CH_3)_2Ar^{iPr4}$ (**3b**) analogous to $Ar^{iPr6}SnSn(CH_2CH_3)_2Ar^{iPr6}$ (**3a**), was crystallized as a green solid at *ca.* −20°C. VT 1H NMR studies of a toluene solution of this species indicated an equilibrium mixture of **2b** and **3b**. An increased amount of **2b** was observed as the temperature is increased (see below). Upon introducing ethylene gas to a solution of this species at *ca.* 25 °C in the presence of a radical trap, 4-methyl-2,6-di-*t*-butylpyridine, an immediate color change from green to dark red which is very similar to the one produced by the reaction of **1b** with ethylene was observed. Upon workup the same product, *ie.* $Ar^{iPr4}Sn(CH_2CH_3)_2(CH_2CH_2)Sn(CH_2CH_3)(CHCH_2)Ar^{iPr4}$ (**4**), as discussed above, was isolated at *ca.* −20°C from the mother liquor. This suggests that **2b**/**3b**

converts to **4** via a non-radical pathway. An asymmetric substituted analogue of **3a**, $Ar^{iPr4}SnSn(Me)_2Ar^{iPr4}$ (**7**) is obtained by the reaction of $[Ar^{iPr4}Sn(\mu\text{-}Cl)]_2$[38] with two equivalents of methyllithium in diethyl ether.

Structures. The crystal structure of the symmetric distannene, $[Ar^{iPr6}Sn(CH_2CH_3)]_2$ (**2a**) (Figure 1, left), shows that it has a center of symmetry at the mid-point of the Sn-Sn bond. The tin atoms are pyramidally coordinated, Σ^{o}_{Sn}= 335.2°, and are bound to the carbon from a terphenyl group (Sn(1)-C(1) = 2.184(18) Å), an ethyl group (Sn(1)-C(2) = 2.175(2) Å) as well as the partner tin atom (Sn(1a)). The Sn(1)-Sn(1a) distance and the *trans*-bending out of plane angle of 2.732(5) Å and 57.4(9)° lie within the range of the previously reported values for distannenes,[39] such as those of the distannenes, $[Sn\{CH(SiMe_3)_2\}_2]_2$ (2.764(2) Å and 41.6(7)°)[40] and $[Sn(Ar^{iPr4})(CH_2C_6H_4\text{-}4\text{-}^{t}Bu)]_2$ (2.770(8) Å and 50.0(8)°)[41].



2a **3a**

Figure 1. Drawings of the crystallographically characterized structures of the red distannene, $[Ar^{iPr6}Sn(CH_2CH_3)]_2$ (**2a**) and its green stannylstannylene isomer $Ar^{iPr6}SnSn(CH_2CH_3)_2Ar^{iPr6}$ (**3a**). Thermal ellipsoids (50 %) are shown for the core atoms. Hydrogen atoms are not shown. Selected bond lengths [Å] and bond angles [°] for **2a**: Sn(1)-C(1) 2.184(18), Sn(1)-C(2) 2.175(2), Sn(1)-Sn(1a) 2.732(5), C(2)-C(3) 1.527(3), C(1)-Sn(1)-Sn(2) 117.8(5), C(1)-Sn(1)-C(2) 105.6(8), C(2)-Sn(1)-

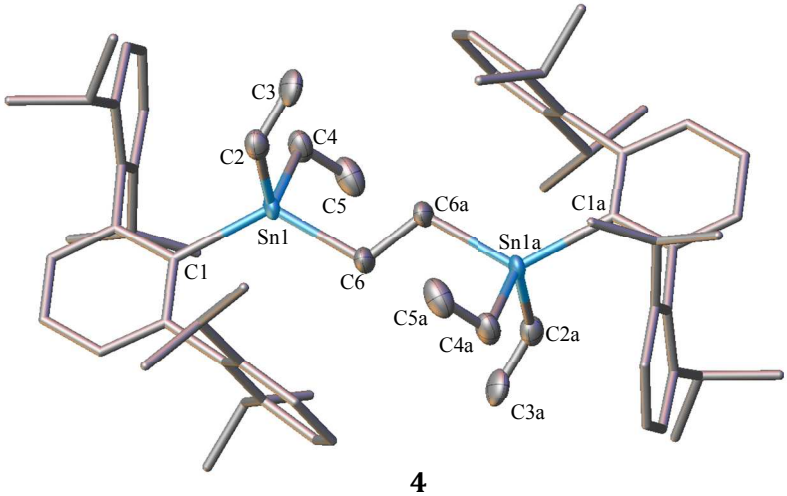
Sn(1a) 111.8(6); **3a**: Sn(1)-C(1) 2.209 (6), Sn(1)-C(2) 2.145 (7), Sn(1)-C(3) 2.187 (8), Sn(1)-Sn(2) 2.885(2), Sn(2)-C(6) 2.193(6), C(1)-Sn(1)-Sn(2) 117.4(15), C(1)-Sn(1)-C(2) 110.4(2), C(1)-Sn(1)-C(4) 103.9(3), C(6)-Sn(2)-Sn(1) 108.0(16), Sn(2)-Sn(1)-C(2) 118.3(2), Sn(2)-Sn(1)-C(3) 105.7(2)

The asymmetric stannylstannylenes, $Ar^{iPr6}SnSn(CH_2CH_3)_2Ar^{iPr6}$ (**3a**) and $Ar^{iPr4}SnSn(CH_2CH_3)_2Ar^{iPr4}$ (**3b**) were isolated as green crystals by cooling the solutions to *ca.* −20°C. The analogous methyl substituted species $Ar^{iPr4}SnSn(Me)_2Ar^{iPr4}$ (**7**) (see Supporting Information) was isolated by storage of the solution at *ca.* 7°C. The crystal structure of **3a** is displayed in Figure 1 right, (for illustration of the structures of the other asymmetric stannylstannylenes **3b** and **7**, see the Supporting Information). Selected bond lengths and angles for **3a**, **3b**, **7** and the previously known $Ar^{iPr6}SnSn(Me)_2Ar^{iPr6}$[32] are listed in Table 1. These stannylstannylenes all feature a four-coordinate Sn(III) atom, bound to a bulky terphenyl and two alkyl groups, as well as a partner Sn(I) atom which also carries a terphenyl group. The relatively long Sn-Sn distances in these species are in the range 2.842(13) – 2.948(3) Å, which exceeds the sum of the covalent single bonded radii of tin, 2.80 Å.[42] This is probably due to increased *p*-character of the orbital used by the divalent tin for Sn-Sn bonding. As the bulkiness of the substituents increases from methyl to ethyl, and the steric hindrance increases from Ar^{iPr4} to Ar^{iPr6}, the C(2)-Sn(1)-C(3) angle between the alkyl groups decrease from 113.6(3)° in **7** to 97.2(6)° in **3a**. It noteworthy that the Sn(2)-Sn(1)-C(3) bond angles are narrower than the Sn(2)-Sn(1)-C(2) angles in all these stannylstannylene species. In addition the relatively large C(6)-Sn(2)-Sn(1)-C(3) angle indicates that a (C(3)) methyl or ethyl substituent is aligned with the empty *p*-orbital on the Sn(2) atom which lies perpendicular to the coordination plane at Sn(2) suggesting incipient methyl or ethyl bridging. This is consistent with the calculated transition state for the conversion of the related distannene $(SnPh_2)_2$ to its asymmetric isomer $PhSnSnPh_3$.[43]

Table 1. Selected bond lengths [Å] and angles [°] for the asymmetrical stannylstannylenes

	$Ar^{iPr6}SnSn(CH_2CH_3)_2Ar^{iPr6}$(**3a**)[a]	$Ar^{iPr4}SnSn(CH_2CH_3)_2Ar^{iPr4}$(**3b**)[a]	$Ar^{iPr6}SnSn(Me)_2Ar^{iPr6}$ [b]	$Ar^{iPr4}SnSn(Me)_2Ar^{iPr4}$(**7**)[a]
Sn(1)-C(ipso)	2.209 (6)	2.232 (3)	2.201 (2)	2.193 (10)
Sn(2)-C(ipso)	2.193 (6)	2.257 (3)	2.227 (2)	2.227 (8)
Sn(1)-Sn(2)	2.885 (2)	2.948 (3)	2.891 (2)	2.842 (13)
Sn(1)-C(2)	2.145 (7)	2.183 (3)	2.164 (2)	2.156 (10)
Sn(1)-C(3)	2.187 (8)	2.197 (3)	2.182 (3)	2.182 (8)
C(ipso)-Sn(1)-Sn(2)	117.4 (15)	112.7 (9)	119.3 (6)	120.5 (3)
Sn(1)-Sn(2)-C(ipso)	108.0 (16)	107.8 (7)	101.2 (5)	102.4 (3)
C(ipso)-Sn(1)-C(2)	110.4 (2)	102.8 (12)	93.6 (9)	98.4 (3)
C(ipso)-Sn(1)-C(3)	103.9 (3)	111.5 (11)	112.7 (9)	111.2 (3)
C(2)-Sn(1)-C(3)	97.8 (4)	102.8 (12)	109.4 (10)	113.6 (3)
Sn(2)-Sn(1)-C(2)	118.3 (2)	113.4 (11)	112.7 (9)	116.4 (8)
Sn(2)-Sn(1)-C(3)	105.7 (2)	112.7 (11)	102.6 (6)	93.6 (9)
C(2)-Sn(2)-Sn(1)-C(6)	32.1 (4)	77.6 (4)	23.8 (9)	25.2 (11)
C(3)-Sn(2)-Sn(1)-C(6)	77.6 (4)	87.9 (10)	95.1 (9)	93.4 (11)

[a] This work [b] Ref 32

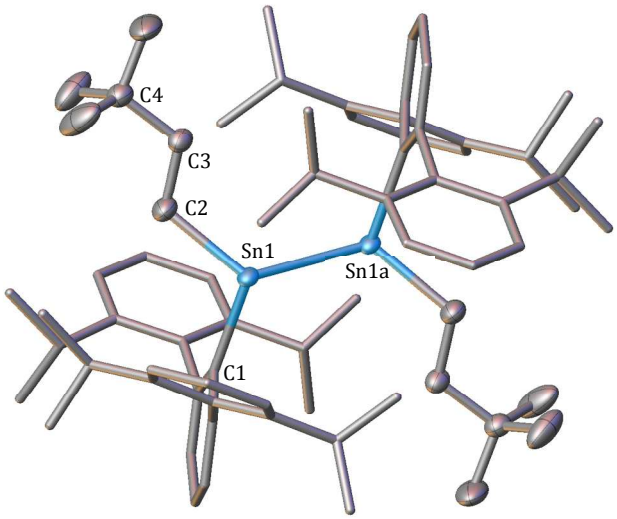


4

Figure 2. Drawing of $Ar^{iPr4}(CH_2CH_3)_2Sn(CH_2CH_2)Sn(CH_2CH_3)(CHCH_2)Ar^{iPr4}$ (**4**). Thermal ellipsoids (50 %) are shown for the core atoms. H atoms are not shown. Selected bond lengths [Å] and bond angles [°]: Sn(1)-C(1) 2.175(3), Sn(1)-C(2) 2.180(2), Sn(1)-C(4) 2.146(5), Sn(1)-C(6) 2.159(4), C(2)-C(3) 1.352(10) (ethenyl) 1.474(16) (ethyl), C(4)-C(5) 1.494(8), C(6)-C(6a) 1.523(7), C(1)-

Sn(1)-C(6) 120.8(14), C(1)-Sn(1)-C(2) 104.2(7), C(1)-Sn(1)-C(4) 115.4(18), C(2)-Sn(1)-C(4) 108.5(7), C(2)-Sn(1)-C(6) 103.1(8), C(4)-Sn(1)-C(6) 103.7(18), Sn(1)-C(6)-C(6a) 111.4(4).

The structural data for $Ar^{iPr4}(CH_2CH_3)_2Sn(CH_2CH_2)Sn(CH_2CH_3)(CHCH_2)Ar^{iPr4}$ (**4**) reveal the inclusion of five ethylene equivalents in its structure in Figure 2. The tin atoms have distorted tetrahedral coordination with interligand angles in the range 103.1(8)° – 120.8(14)°. The crystal structure is disordered over two orientations with 74% and 26% occupancy, and is further split into two parts to accommodate a disordered C(2)-C(3) unit, 50% of which has single bond character with a C-C distance of 1.474(16) Å, and the other 50% has double bond character with a C-C distance of 1.352(10) Å. In effect, the ethenyl and an ethyl group are disordered 50:50 over the two tin atoms.

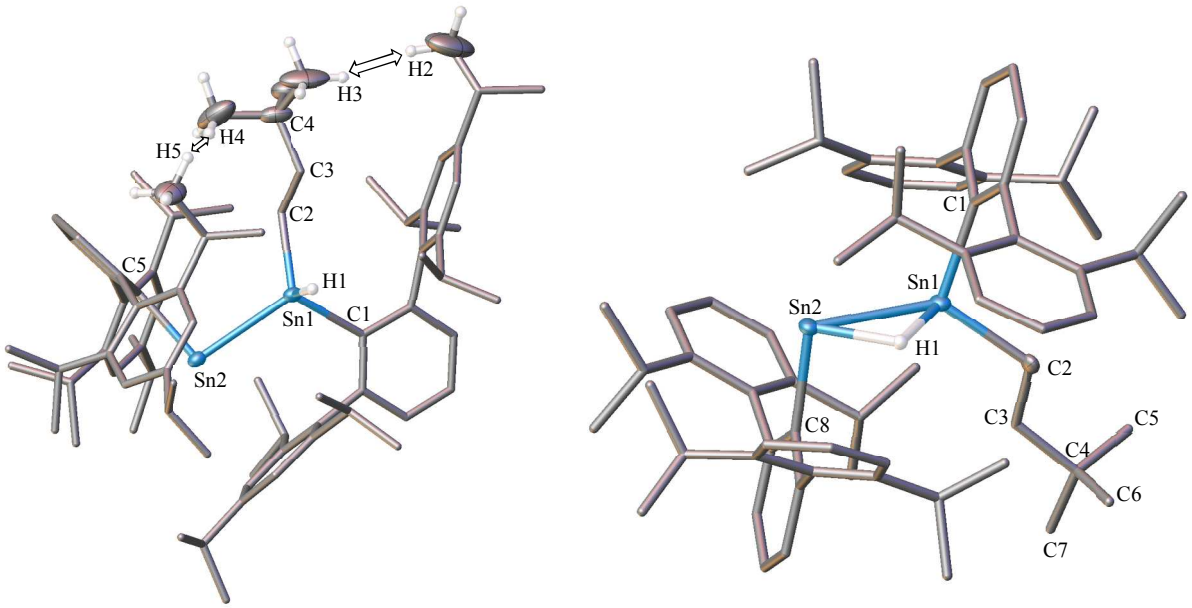


5b

Figure 3. A plot of the symmetric distannene, $[Ar^{iPr4}Sn(CH_2CH_2{}^tBu)]_2$ (**5b**). Thermal ellipsoids (50 %) are shown for the core atoms. H atoms are not shown. Selected bond distances [Å] and bond angles [°]: Sn(1)-C(1) 2.196(4), Sn(1)-C(2) 2.163(5), C(2)-C(3) 1.517(7), Sn(1)-Sn(1a) 2.714(6), C(1)-Sn(1)-Sn(1a) 111.32(9), C(2)-Sn(1)-Sn(1a) 119.06(11), C(1)-Sn(1)-C(2) 108.91(16).

The crystal data for the symmetric distannene, $[Ar^{iPr4}Sn(CH_2CH_2{}^tBu)]_2$ (**5b**) show that the core possesses a trans-pyramidal conformation with Σ°Sn = 339.3° and an out-of-plane angle C(1)-Sn(1)-Sn(1a)-C(2a) of 55.5 (4)° which are similar to the values of 335.2° and 57.4 (9)° in **2a**. As in **2a**,

there is a center of symmetry at the mid-point of the Sn=Sn bond and consequently, there is no torsion angle between the two SnC_2 planes. The Sn-Sn distance is 2.714(2) Å, which lies well within the range of known Sn=Sn double bond distances (2.601(1) – 3.087(2) Å).[44] Each *t*-butylethyl group is bound to the Sn atom with a Sn(1)-C(2) bond length of 2.164(5) Å. The hydrostannylation was confirmed by the C(2)-C(3) distance of 1.517(7) Å which is consistent with a C-C single bond.[42] Structural data for **5a** are listed in the Supporting Information.



6a **6b**

Figure 4. Drawings of the structures of $Ar^{iPr6}SnSn(H)(CH_2CH_2{}^tBu)SnAr^{iPr6}$ (**6a**) and $Ar^{iPr4}\overline{Sn(\mu\text{-}H)Sn}(CH_2CH_2{}^tBu)SnAr^{iPr4}$ (**6b**). Thermal ellipsoids (50 %) are shown for the core atoms. H atoms except for the terminal or bridging hydride (H1) are not shown. Selected bond distances [Å] and bond angles [°]: **6a**, Sn(1)-C(1) 2.244(11), 2.168(9), Sn(2)-C(5) 2.228(13), Sn(1)-H(1) 1.575(7), Sn(1)-Sn(2) 2.899(15), H(2)---H(3) 2.253(10), H(4)---H(5) 2.272(14), C(1)-Sn(1)-C(2) 113.4(4), C(1)-Sn(1)-Sn(2) 114.3(14), C(2)-Sn(1)-Sn(2) 116.2(2), C(5)-Sn(2)-Sn(1) 96.4(11), H(1)-Sn(1)-C(1) 100.0(3), H(1)-Sn(1)-C(2) 103.0(3), H(1)-Sn(1)-Sn(2) 107.7(4); **6b**, Sn(1)-C(1) 2.198(3), Sn(1)-C(2) 2.185(8), Sn(2)-C(8) 2.210(3), Sn(1)-H(1) 1.86(6), Sn(2)-H(1) 1.95(6), Sn(1)-Sn(2) 2.763(15), C(1)-

Sn(1)-C(2) 106.7(3), C(1)-Sn(1)-Sn(2) 110.9(9), C(2)-Sn(1)-Sn(2) 135.7(3), C(8)-Sn(2)-Sn(1) 100.7(9), C(1)-Sn(1)-H(1) 105.0(2), C(2)-Sn(1)-H(1) 103.1(16), Sn(1)-H(1)-Sn(2) 93.0(3).

The crystal data for Ar^{iPr6}SnSn(H)(CH_2CH_2*t*Bu)SnAr^{iPr6} (**6a**) (Figure 4, left) reveal it to have an asymmetric mono-hydrido stannylstannylene structure. The Sn(1) atom has a distorted tetrahedral coordination and is bound to its partner tin atom Sn(2), a *t*-butylethyl group, a terphenyl ligand, and a hydride with a Sn-H distance of 1.575(7) Å. The bond angles at Sn(1) lie between 100.0(3)° – 116.2(2)°. The Sn(2) atom possesses a bent coordination with a relatively narrow C(ipso)-Sn(2)-Sn(1) angle of 96.4 (11)°. The Sn-Sn distance of 2.899(15) Å is similar to those of **3a** (2.899(2) Å), **3b** (2.948(3) Å) and **7** (2.842(13) Å). It is noteworthy that the distances between hydrogens of the *t*-butyl group and those of the *para* isopropyls of the flanking aryl rings H(2)---H(3) and H(4)---H(5) of 2.253(10) Å and 2.272 (14) Å are shorter than the sum of the van der Waals' radii for hydrogen (2.40 Å),[45] suggesting that the molecular geometry may be affected by the intramolecular dispersive interactions between the terphenyl ligands and the *t*-butylethyl group.[46-50] The crystal structure of the mono-hydrido bridged distannene, Ar^{iPr4}Sn(μ-H)Sn(CH_2CH_2*t*Bu)SnAr^{iPr4} (**6b**) (Figure 4, right) reveals that Sn(1) has a distorted tetrahedral geometry and is bound to the *ipso*-carbon (C(1)) of the terphenyl, C(2) of the *t*-butylethyl group, the bridging hydrogen (H(1)), and the other tin atom Sn(2) which carries a terphenyl group. The bridging Sn-H distances are 1.86(6) Å and 1.95(6) Å, which are significantly longer than the terminal Sn-H distance of 1.575(7) Å in **6a**, but are within the range (1.806 – 2.067 Å) of Sn-H distances in doubly bridged tin(II) hydrides.[1,2] The Sn-Sn distance of 2.763(15) is consistent with single bonding, but it is also well within the range of known distannene tin-tin double bond distances.[42] It is slightly longer than the Sn-Sn bonds in **2a** (Figure 1, left), **5a** (see Supporting information), and **5b** (Figure 3), probably as a result of the weakening of the tin-tin bond due to binding to hydrogen (*cf*. sum of interligand angles between the organic and tin substituents at Sn(1) = 353.3°). The structure of **6b** is a substituted analogue of the singly bridged isomer HSn(μ-H)SnH_2 calculated by Trinquier in 1991,[34] and later calculated for

$Ar^{iPr4}Sn(\mu\text{-}H)Sn(H)Ar^{iPr4}$ by Schleyer and coworkers.[35] It represents the first structural characterization of a mono-hydrogen bridged ditetrelene.

NMR spectroscopy. All ^{1}H, $^{13}C\{^{1}H\}$, and $^{119}Sn\{^{1}H\}$ NMR spectroscopic data are listed in greater detail in the Supporting Information. The $^{119}Sn\{^{1}H\}$ NMR spectrum of **2a** was recorded at room temperature and displayed a broad resonance at 1908 ppm which lies within the previously reported range for monomeric stannylene species (442 – 2235 ppm),[39,51-54] and is similar to that in the monomer $Ar^{iPr6}Sn^{t}Bu$ at 1904 ppm,[32] indicating that **2a** dissociates to the monomer $Ar^{iPr6}Sn(C_2H_5)$ in solution at room temperature. The ^{1}H NMR spectrum of **2a** was recorded at 330 K in a d_8-toluene solution. A broad resonance at 0.43 ppm corresponding to four α-protons of the ethyl groups attached to tin was observed. Two sets of methine resonances at 3.14 and 2.83 ppm with the integration ratio of 2:1 are consistent with the eight *ortho* and four *para* isopropyl groups on the flanking rings of the terphenyl group.

Cooling a solution of **2a** to 250 K yielded a sharp signal at 289 ppm and a broad signal at 2915 ppm in the $^{119}Sn\{^{1}H\}$ NMR spectrum, which represent the tetravalent and the divalent Sn atoms of the unsymmertic isomer **3a**. Very similar chemical shifts at 284 and 2910 ppm were observed for **3b**. These resemble to those in $Ar^{iPr6}SnSnPh_2Ar^{iPr6}$ and $Ar^{iPr4}SnSn(C{\equiv}C\text{-}{}^{t}Bu)_2Ar^{iPr4}$.[52,53] The ^{1}H NMR spectrum of **3a** shows that the α-proton resonances are shifted from 0.43 to 0.50 ppm at 250 K. The two septets at 3.31 and 3.11 ppm in an intensity ratio of 1:1 are assignable to the *ortho*-isopropyl groups of the flanking ring of the terphenyl groups at the Sn(III) and Sn(I) atoms, which is consistent with the structural data for **3a**. (see Supporting Information for NMR data of **7**)

The ^{1}H NMR spectrum of $Ar^{iPr4}(CH_2CH_3)_2Sn(CH_2CH_2)Sn(CH_2CH_3)(CHCH_2)Ar^{iPr4}$ (**4**) displays three vinyl resonances between δ = 5.43 and 6.08 ppm due to the different magnetic environments of the hydrogens (Sn-C<u>H</u>=C<u>H$_2$</u>). The integration ratio of the vinyl and the methine resonances from the isopropyl groups of 3:8 further confirm the existence of one but not two ethenyl groups in the

compound. Two sharp signals at very similar chemical shifts (−96.8 and −59.8 ppm) in the $^{119}Sn\{^{1}H\}$ NMR spectrum are consistent with the presence of two tetravalent tin atoms with slightly different magnetic environments due to the substitution of a vinyl for an ethyl group.[54]

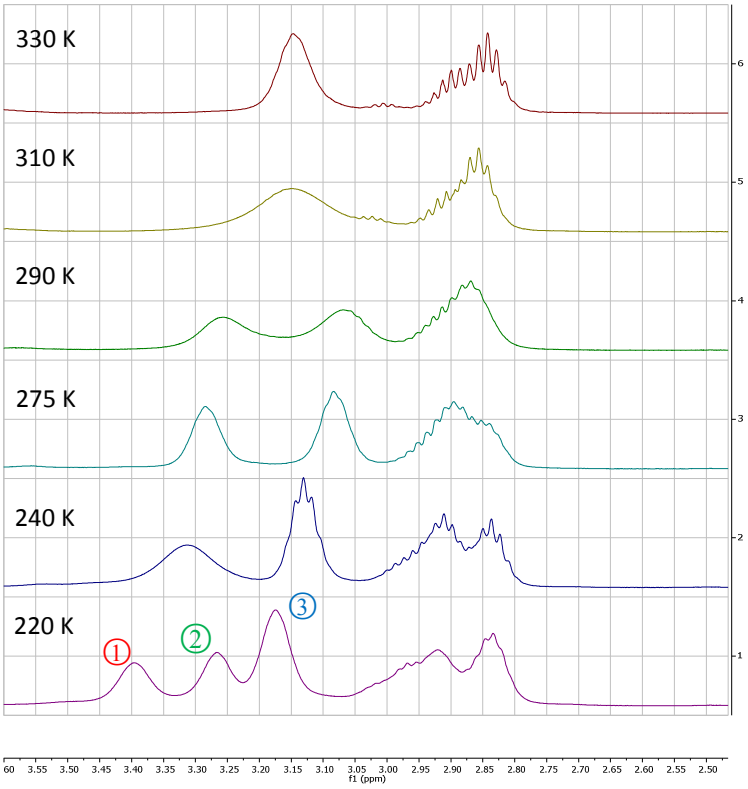
A sharp ^{119}Sn NMR resonance at 398 ppm represents the dimeric form of **5a**. Another broad signal at 1845 ppm, which represents the monomeric stannylene $Ar^{iPr6}SnCH_2CH_2{}^tBu$, indicates **5a** is in equilibrium with the monomer $Ar^{iPr6}SnCH_2CH_2{}^tBu$ in solution.[39,51-53] Very similar ^{119}Sn NMR resonances were observed at 320 and 1875 ppm for **5b**. This is further supported by the intensity ratio of 4:9 between the methine resonances of the *ortho*-isopropyl groups on the flanking rings of the terphenyls and the methyl resonances of the *t*-butyl groups in the ^{1}H NMR spectra of **5a** and **5b** (see Supporting Information).

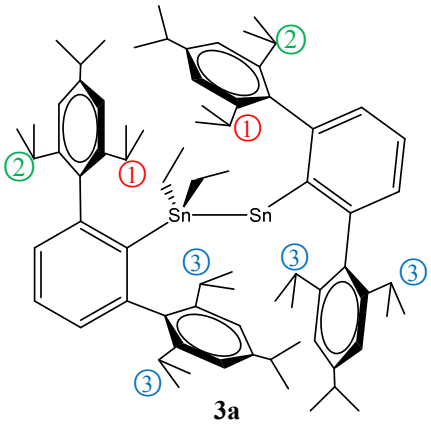
The $^{119}Sn\{^{1}H\}$ NMR spectrum of $Ar^{iPr6}SnSn(H)(CH_2CH_2{}^tBu)Ar^{iPr6}$ (**6a**) in d_8-toluene at *ca*. 25 °C indicates that in solution it has a similar structure to that determined by X-ray crystallography (Figure 4 left). A sharp singlet at 168 ppm and a broad signal at 1904 ppm were observed, which can be assigned to four-coordinated alkyl hydrido substituted Sn(III) and a two-coordinated Sn(I). The $J_{Sn\text{-}H}$ coupling associated the four-coordinate tin signal at 168 ppm is 980 Hz, which is about half of $J_{Sn\text{-}H}$ coupling that is generally seen for the terminal Sn-H bonds in tetravalent tin compounds[54] but larger than that in the unsymmtric isomeric form (*ie*. $Ar^{iPr6}SnSn(H)_2Ar^{iPr6}$) of doubly bridged **1a**.[1] However, the Sn-H couplings have been shown to be variable and dependent on the temperature. For example the $J_{Sn\text{-}H}$ coupling in the related unsymmetric species $Ar^{iPr8}SnSn(H)_2Ar^{iPr8}$ (Ar^{iPr8} = C_6H-2,6-(C_6H_2-2,4,6-$^i Pr_3$)-3,5-$^i Pr_2$) is 1288 Hz at - 70 °C.[2] In contrast, the $J_{Sn\text{-}H}$ couplings in the symmetrically bonded hydride species **1b** and related molecules are much lower and are in the range 89 – 95 Hz.[2] The ^{119}Sn NMR spectrum of $Ar^{iPr4}Sn(\mu\text{-}H)Sn(CH_2CH_2{}^tBu)Ar^{iPr4}$ (**6b**) displays two signals at 177 and 2173 ppm that are similar to the values seen for **6a** in benzene at 25°C. The $J_{Sn\text{-}H}$ coupling for the signal at 177 ppm was observed to be 914 Hz which is near to the 980 Hz observed

for **6a**. These data indicate that in solution **6b** assumes a similar structure to that of **6a**. The spectrum also reveals two other tin resonances at 658 and 1896 ppm which correspond to the compounds $[Ar^{iPr4}Sn(\mu\text{-}H)]_2$ (**1b**) and $[Ar^{iPr4}Sn(CH_2CH_2{}^tBu)]_2$ (**5b**), indicating that **6b** is in equilibrium with **1b** and **5b** in solution. This is further confirmed by the two methine signals at 2.89 and 3.13 ppm in the ^{1}H NMR spectrum, in agreement with those observed for pure samples of **1b** and **5b**. The presence of the terminal hydride in **6a** in the crystalline state was also confirmed by a Sn-H stretching band at 1845 cm^{-1} in the IR spectrum. Unfortunately, the bridging hydrogen, whose signal is probably obscured in the phenyl region, was not located from the ^{1}H NMR spectrum of **6b**. The IR spectrum of **6b** shows no terminal Sn-H stretching band between 1800 – 1900 cm^{-1} which further supports the bridging character of the hydride in the solid state.[2]

VT ^{1}H NMR Studies. The dynamic solution behavior of the compounds was examined by variable temperature ^{1}H NMR spectroscopy. Unfortunately, attempts to determine the equilibrium parameters for both distannene/stannylstannylene pairs **2a**/**3a** and **2b**/**3b** were unsuccessful. This is due to fast ligand exchange observed for the less bulky substituents which results in overlapping of the resonances so that they become indistinguishable. However, the activation energies for the ethyl groups site exchange ($\Delta G^{\ddagger}$) could be determined. Cooling a d_8-toluene solution of **2a/3a** to 220K revealed a spectrum consistent with the unsymmetrical dimeric structure, in which a septet signal near 3.17 ppm represents the methine protons of the four *ortho*-isopropyls of the terphenyl group that are away from the ethyl groups. For the four *ortho*-isopropyl groups of the terphenyl group that are close to the ethyl groups, there are two methine protons septets at 3.26 and 3.39 ppm corresponding to their different orientations with respect to the ethyl groups (see signal assignments in Figure 4). Upon warming, the signals at 3.26 and 3.39 ppm begin to broaden and merge as a consequence of the faster rotation of the flanking rings causing their magnetic environments to become equivalent. The coalescence point for the ethyl group site exchange is reached at 310 K and the activation energies ($\Delta G^{\ddagger}$) and exchange rate (k) at this point were

calculated as 14.2±0.65 kcal mol^{-1} and 158±8 s^{-1}. At 330K, complete conversion from **3a** to the symmetric distannene **2a** was observed and only a single *ortho*-methine resonance at 3.09 ppm is present at this temperature. Similar results were obtained for Ar^{iPr4}SnSn(C$_2$H$_5$)$_2$Ar^{iPr4} (**3b**) and Ar^{iPr4}SnSn(Me)$_2$Ar^{iPr4} (**7**). The coalescence point was observed at 310 K for **2b**/**3b** and 303 K for **7**. The activation energy (ΔG‡) and exchange rate (k) were determined to be 14.8±0.36 kcal mol^{-1} and 164±14.5 s^{-1} for **2b**/**3b** and 14.1±2.4 kcal mol^{-1} and 194±11 s^{-1} for **7**.





3a

Figure 4. Left, Variable temperature ^{1}H NMR spectrum of [Ar^{iPr4}Sn(C$_2$H$_5$)]$_2$ (**2a**)/Ar^{iPr4}SnSn(C$_2$H$_5$)$_2$Ar^{iPr4} (**3a**) equilibrium in d_8-toluene, illustrating the ligand site exchanging between **2a** and **3a**; Right, diagram of **3a** and methine groups assignments correspond to the spectrum.

Variable temperature ^{1}H NMR spectroscopy of the bulkier distannnenes, [Ar^{iPr6}Sn(CH$_2$CH$_2$^{t}Bu)]$_2$ (**5a**) and [Ar^{iPr4}Sn(CH$_2$CH$_2$^{t}Bu)]$_2$ (**5b**), showed that they are dissociated to monomeric stannylenes in solution. Below room temperature, reversible equilibria were observed involving the dissociated monomeric stannylenes and the asymmetric stannylstannylenes isomers ArSnSn(CH$_2$CH$_2$^{t}Bu)$_2$Ar (Ar = Ar^{iPr6} or Ar^{iPr4}). This is manifested by the intensified methyl resonances from the stannystannylene *t*-butylethyl group at 0.84 ppm for **5a** and 0.85 ppm for **5b** and diminished methyl resonances from the stannylene at 0.88 for **5a** and 0.82 ppm for **5b** upon cooling. The equilibrium constant K_{eq} and ΔG_{eq} at 298 K that were determined via van't Hoff analysis are 4.09±0.16 and -1.81±0.19 kcal mol^{-1} for **5a** and 6.38±0.41 and −1.00±0.03 kcal mol^{-1} for **5b**, respectively.

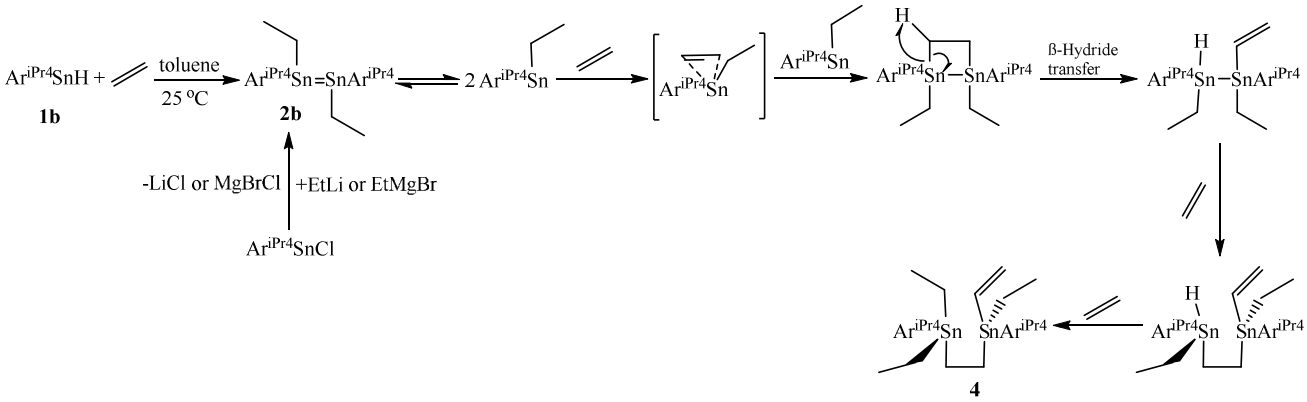
For the heteroligated Sn(II) species, Ar^{iPr4}Sn(μ-H)Sn(CH$_2$CH$_2$^{t}Bu)SnAr^{iPr4} (**6b**), evidence of a reversible dissociation reaction to afford [Ar^{iPr4}Sn(μ-H)]$_2$ (**1b**) and [Ar^{iPr4}Sn(CH$_2$CH$_2$^{t}Bu)]$_2$ (**5b**) was provided by the intensification of the two methine signals at 2.72 and 2.96 ppm due to the increasing concentration of **1b** and **5b** with increasing temperature. The dissociation parameters K_{diss} and ΔG_{diss} were determined to be 2.63±0.15 and −0.59±0.01 kcal mol^{-1} at 298 K. No evidence of dissociation of **6a** was observed in the variable temperature ^{1}H NMR or ^{119}Sn{^{1}H} NMR spectra, which is in agreement with the behavior of the previously reported unsymmetrically substituted digermene, Ar^{iPr4}Ge(H)Ge(*c*-C$_5$H$_9$)Ar^{iPr4}.[7] This further suggests that the geometry of **6a** may be stabilized at least in part by the intramolecular dispersive interactions between the terphenyl ligands and the *t*-butylethyl group.

UV-Vis Spectroscopy. The dissociation of **2a** and **2b** in hexanes is also supported by the observation of strong absorptions at 492 nm (ε =850 L M^{-1} cm^{-1}) and 486 nm (ε =920 L M^{-1} cm^{-1}) in the UV/Vis spectra at *ca*. 25°C. Similar absorptions are observed for **5a** at 484 nm (ε =860 L M^{-1} cm^{-1}) and **5b** at (ε =960 L M^{-1} cm^{-1}). These absorptions are due to an electronic transition involving

the lone pair *n* and empty *p*-orbital of the tin atom in the monomeric stannylene.[55] The corresponding green asymmetric stannylstannylenes **3a** and **3b** display weaker absorptions at 692 nm (ε =120 L M^{-1} cm^{-1}) and 702 nm (ε =100 L M^{-1} cm^{-1}) at room temperature, which are presumably due to the *n*-*p* electron transitions on the Sn(I) atom from the stannylstannylene. This shift to lower energy (*ie*. longer wavelength) is due to the less electronegative stannyl substituent at the tin, which leads to an increase in energy of the lone pair electrons and a smaller energy gap with respect to the empty *p*-orbital. The UV/Vis spectrum of **6a** displays a weak absorption at λ_{max} = 726 nm (ε =130 L M^{-1} cm^{-1}), which is consistent with its unsymmetic geometry and its non-dissociated character in solution. In contrast, the UV/Vis spectrum of **6b** shows a strong absorption signal at 486 nm, due to the presence of **5b**, and one weak absorption at λ_{max} = 715 nm (ε = 100 L M^{-1} cm^{-1}), which further supports the equilibrium between **6b** and **1b** and **5b**.

Proposed Mechanism for the formation of 4. The alkyl/alkenyl product, $Ar^{iPr4}(CH_2CH_3)_2Sn(CH_2CH_2)Sn(CH_2CH_3)(CHCH_2)Ar^{iPr4}$ (**4**), can be synthesized by either the reaction of $[Ar^{iPr4}Sn(\mu\text{-}H)]_2$ (**1b**) with an excess of ethylene or by salt metathesis of $[Ar^{iPr4}Sn(\mu\text{-}Cl)]_2$ with ethylMgBr or ethyllithium followed by the addition of ethylene gas. A free radical pathway has been proposed for the oxidative additions to a tin(II) alkyl $Sn[CH(SiMe_3)_2]_2$ or amide $Sn[N(SiMe_3)_2]_2$.[56] Introducing 4-methyl-2,6-di-*t*-butylpyridine as a radical trap into the reaction of **3b** with ethylene afforded **4** with no side product which tends to rule out the radical pathway.

Scheme 3. The Proposed mechanism for the formation of **4**



A non-radical formation mechanism for this unique species is proposed in Scheme 3. We suggest that **1b** is dissociated to monomers to some extent in solution. These can react with ethylene to give initially the monomeric stannylene, $Ar^{iPr4}Sn(C_2H_5)$ (see Scheme S1 in the Supporting Information) which is in equilibrium with its dimer $Ar^{iPr4}(C_2H_5)SnSn(C_2H_5)Ar^{iPr4}$. In the presence of excess ethylene, a second equivalent of ethylene could then bind to the Sn atom to form a transition state complex, $Ar^{iPr4}Sn(C_2H_5)(C_2H_4)$, that may react with another equivalent of $Ar^{iPr4}Sn(C_2H_5)$ to afford a CH_2CH_2 bridged Sn(III) distannane (Scheme 3). A β-hydride transfer rearrangement may then occur which leads to the formation of an unsymmetrical Sn(III) hydride, $Ar^{iPr4}(H)(C_2H_5)SnSn(C_2H_3)(C_2H_5)Ar^{iPr4}$, which has a hydride and an ethenyl group on adjacent tins. The product **4** can be obtained from this Sn(III) hydride species by the addition of a fourth equivalent of ethylene followed by hydrostannylation with a fifth ethylene equivalent. The different reactivity observed for **1a** and **1b** may be connected to their different behavior in solution[2] which apparently arises from the different *para*-substitution on the flanking rings of the terphenyl groups. Thus different olefin addition mechanisms involving di-metallic tin species cannot be discounted. Further work to elucidate these mechanisms is in hand.

Conclusions

The reactivity of $[Ar^{iPr6}Sn(\mu\text{-}H)]_2$ (**1a**) and $[Ar^{iPr4}Sn(\mu\text{-}H)]_2$ (**1b**) with ethylene and *t*-butylethylene was studied. Reaction of **1a** with ethylene in toluene afforded crystals of the distannene at room temperature, $[Ar^{iPr6}Sn(C_2H_5)]_2$ (**2a**) which transform to the stannylstannylene at *ca*. -20 °C $Ar^{iPr6}SnSn(C_2H_5)_2Ar^{iPr6}$ (**3a**). The less crowded Ar^{iPr4} substituted analog of **3a**, $Ar^{iPr4}SnSn(C_2H_5)Ar^{iPr4}$ (**3b**), could only be obtained via salt elimination through the reaction of $[Ar^{iPr4}Sn(\mu\text{-}Cl)]_2$ with ethyllithium or EtMgBr. Variable temperature ^{1}H NMR studies showed that **3a** or **3b** are in fast ethyl group exchange with **2a** or **2b** which are also in equilibrium with the dissociated monomeric stannylene, $ArSn(C_2H_5)$ (Ar = Ar^{iPr6} or Ar^{iPr4}). The exchange rate k and activation energies $\Delta G^{\ddagger}$ were determined to be 158±7.9 s^{-1} and 14.2±0.65 kcal mol^{-1} at 310 for **2a**/**3a** and 164±14.5 s^{-1} and 14.8±0.36 kcal mol^{-1} for **2b**/**3b**. The reaction of **1b** with ethylene resulted in the absorption of five ethylene equivalents to give the Sn(IV) species, $Ar^{iPr4}(CH_2CH_3)_2Sn(CH_2CH_2)Sn(CH_2CH_3)(CHCH_2)Ar^{iPr4}$ (**4**). A possible mechanism for the formation of this species was proposed partly based on experimental data which proposed that the formation of **4** is via an oxidation addition followed by a hydrostannylation of two ethylene equivalents to a Sn(III) intermediate, $Ar^{iPr4}(H)(C_2H_5)SnSn(C_2H_3)(C_2H_5)Ar^{iPr4}$, which can be generated from **2a** with one equivalent of ethylene. Reaction of t-butylethylene with **1a** or **1b** yielded the symmetric distannenes $[ArSnCH_2CH_2{}^tBu]_2$ (Ar = Ar^{iPr6} **5a**, or Ar^{iPr4} **5b**) which in solution are in equilibrium with the corresponding stannylstannylene isomers. Combining the bridging hydride **1a** or **1b** with **5a** and **5b** led to the unsymmetric stannylstannylene hydride **6a** and the first mono-bridged hydrido distannene, $Ar^{iPr4}\overline{Sn(\mu\text{-}H)Sn}(CH_2CH_2{}^tBu)Ar^{iPr4}$ (**6b**), substituted analogue of one of the distannene isomers. VT ^{1}H NMR studies of the various compounds described in this paper show that in general their various isomeric forms are separated by relatively small amounts of energy which is in agreement with earlier calculations.[2,33-35]

Associated content

Supporting Information

The General Procedure, synthesis of **2a** – **7**, ^{1}H, ^{13}C, and ^{119}Sn NMR spectra, UV/Vis spectra, and Infrared spectra for **2a** – **7**, and VT 1H NMR spectra for **2a**/**3a**, **2b**/**3b**, **5a**, **5b**, **6b**, and **7** are listed in the Supporting Information.

The Supporting Information is available free of charge on the ACS Publications website at DOI:

Crystallographic information for **2a** – **7**(CIF)

Author Information

Corresponding Authors

*P.P.P.: fax, +1-530-732-8995; tel, +1-530-752-8900; e-mail, pppower@ucdavis.edu.

Present Address

‡ Department of Chemistry, University of New Hampshire, Durham, NH 03824, USA

§ Department of Chemistry and Biochemistry, University of California San Diego, La Jolla, CA 92093, USA.

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