1,2-Distannylation and -disilylation of cyclic allenes

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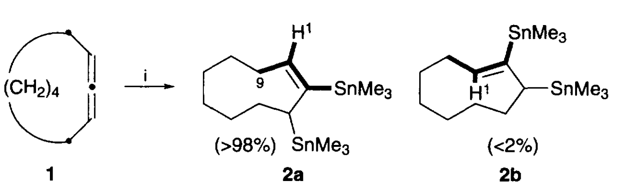
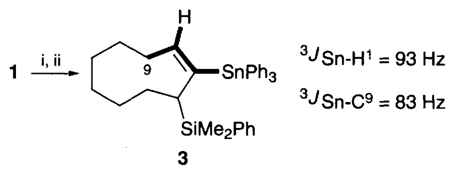
Cyclo-1,2-dienes (C_9–C_{13}) are converted into the synthetically promising 2,3-bis(trimethylsilyl)- and 2,3-bis(trimethylstannyl)cycloalk-1-enes by disilylation with lithium chlorotrimethylsilane in tetrahydrofuran, and Pd⁰-catalysed addition of hexaalkyldistannes, respectively.

There is considerable interest in the stoichiometric metallofunctionalisation of allenes[1,2] (because the derived vinyl or allylic metallic species are potentially valuable synthetic intermediates) as well as in transition-metal promoted additions to allenes.[3,4] Medium-ring allenes are of special interest because considerable mechanistic insight may be provided. In this connection, we wish to describe the Pd⁰-promoted 1,2-distannylation and the 1,2-disilylation of medium-ring allenes which furnish useful doubly functionalised medium-ring cycloalkenes, and the structures of η^3-allylpalladium complexes, analogous to likely intermediates in the Pd⁰-promoted additions.

Reaction of cyclonona-1,2-diene **1**,[5] the smallest cyclic allene easily handled in the temperature range 20–80 °C, with Sn_2Me_6 and $[Pd(PPh_3)_4]$ in the absence of solvent at 80 °C, (Scheme 1),[2] provides in excellent yield, essentially one distannane, formulated† as **2a** on the basis of extensive NMR spectroscopy.[6]† [We use the terms *cis* and *trans* to indicate the disposition of the carbon atoms attached to the double bond. Thus **2a** is *cis*, but rigorously would be the (*E*) isomer]. NMR measurements (500 MHz) showed H^1 in **2** (δ 5.28, dd, *J* 10.7, 6.1 Hz) to be coupled to tin ($^3J_{^{119}Sn-H^1}$ 86 Hz) with a value at the high end of the range for a *cis* arrangement of Sn and H on the double bond,[6] but quite low for a *trans* arrangement, as present in **2b**.[6] In the ^{13}C NMR spectrum of **2**, C^9 exhibited $^3J_{Sn-C^9}$ 75 Hz, a value consistent with a 180° dihedral angle as in **2a**,[7] but quite large for a 0° dihedral angle, as present in **2b**.[7] The addition of Sn_2Et_6 and $Sn_2Bu^n_6$ under similar conditions provides the *cis* isomers, analogous to **2a**. These conclusions are supported by measurements on stannane **3** (Scheme 2) shown to incorporate a *cis* double bond by X-ray crystallography.[8] The three-bond couplings shown for **3** in Scheme 2 are in excellent agreement with those for **2a**, when a slight correction for the change $SnMe_3$ to $SnPh_3$ is made.§



Scheme 1 *Reagents and conditions:* i, Sn_2Me_6, Pd⁰, 80 °C, 12 h

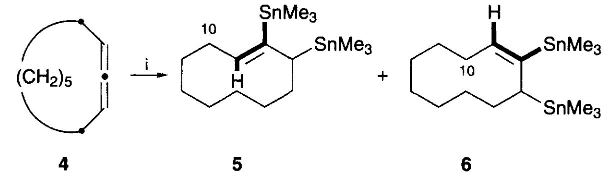


Scheme 2 *Reagents and conditions:* i, $Li[Cu(CN)(SiMe_2Ph)]$; ii, $SnClPh_3$; 50% yield after recrystallization

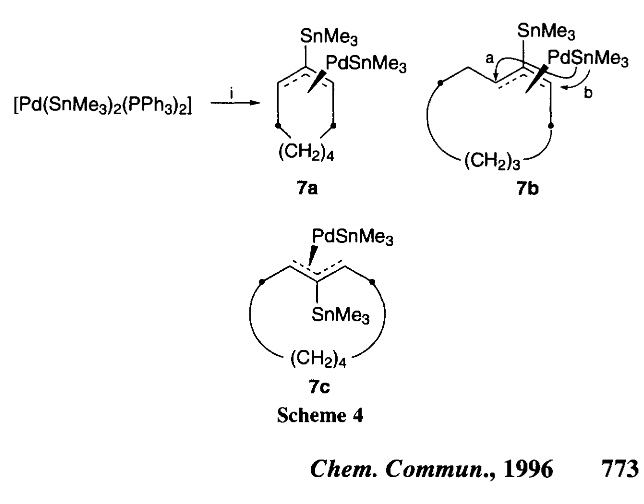
1,2-Distannylation of cyclodeca-1,2-diene **4**, as described for **1** is particularly instructive as both the *trans* (**5**) and *cis* (**6**) distannanes are present after purification (*ca.* 2 : 1 ratio, Scheme 3), but the kinetic product is very predominantly **5**. In the major isomer, $^3J_{Sn-H^1}$ = 165 Hz, whereas in the minor isomer, $^3J_{Sn-H^1}$ = 82 Hz, leading unambiguously to the structures shown in Scheme 3, and confirming the conclusion for **2a**. Of further interest was the presence of a single diastereoisomer of **5**.

The Pd⁰-promoted addition probably proceeds by oxidative addition of Sn_2Me_6, followed by formation of an η^3-allylpalladium complex **7**[2] within which the second $SnMe_3$ group is delivered from the palladium-bearing face (Scheme 4) providing one diastereoisomer of **5**. Three η^3-allyl palladium isomers are possible, but **7a** and **7b** (path *a*) can provide **2a** whereas **7b** (path *b*) and **7c** would provide **2b**, which is not observed.[6] Other evidence supports the intermediacy of **7a**, and in particular the η^3-allyl palladium complex formed directly from cyclononene **8** and $PdCl_2$ under modified Hüttel conditions[9] ($PdCl_2$–NaCl–NaOAc–H_2O–CH_3CO_2H) is the *anti–anti* complex **9a** (Scheme 5) whose structure has been established by NMR spectroscopy and X-ray crystallography.[10] There is no evidence for formation of the *syn–anti* or *syn–syn* complexes **9b** and **9c** respectively.

Reactions of cycloundeca-1,2-diene and cyclotrideca-1,2-diene were similar in that one diastereoisomer of each of the *trans* ring-configured distannanes (*ca.* 90%) was the major product. These results are similarly consistent with the nature of the η^3-allylpalladium complexes formed in the direct palladation of the cycloalkenes,[9,10] for which there is an increasing



Scheme 3 *Reagents and conditions:* i, Sn_2Me_6, $[Pd(PPh_3)_4]$; 73% yield



Scheme 4

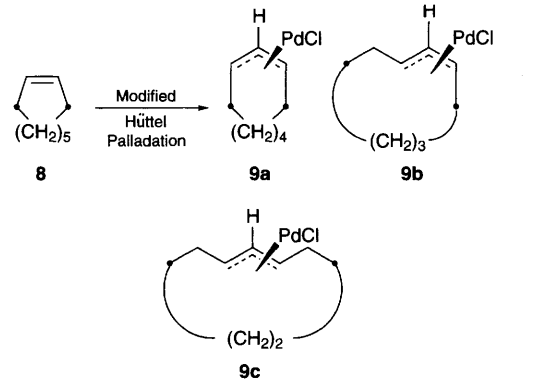
proportion of *syn–anti* and *syn–syn* complexes with increasing ring size.

Disilylation of **1** with $SiClMe_3$–Li–THF[11] (Scheme 6) provided a single isomer of 2,3-bis(trimethylsilyl)cyclonon-1-ene, assigned the *cis* arrangement **10**,¶ with H^1 at δ 5.64 (dd, *J* 13, 5 Hz) and δ (^{29}Si) at −4.18 (vinyl Si) and +2.79 (allyl Si). This disilane resisted deprotonation and was stable to fluoride ion and heating (*ca.* 180 °C).[12] Cyclodeca-1,2-diene **4** provides (Scheme 7) roughly equal amounts of two isomers of the disilane (M = 282; δ_{H1} 5.71, dd, *J* 11.7, 4.9 Hz; δ 5.57, dd, *J* 12, 3.7 Hz) and at least one must incorporate a *trans* double bond.

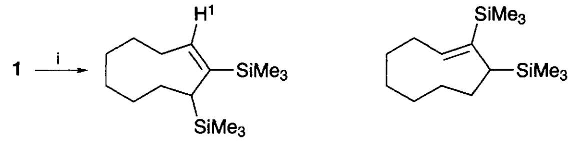
MM3 (92) calculations were performed on the cyclonon-1-enyl and cyclodec-1-enyl systems using locally derived force-field parameters for silicon.[13] In both ring systems, the optimised structure of the *cis* isomer is of significantly lower steric energy (SE, cal = 4.184 J) than that for either of the *trans* diastereoisomers, suggesting **12** is one of the products from **4**.

Similar reductive silylation of the C_{10}–C_{13} cyclic allenes was conducted because of the increased possibility of *trans* isomers as demonstrated above for the Pd^0-promoted distannylations. The higher allenes[5] (C_{11}, C_{12}, C_{13}) each afford two disilanes and we presume the major isomer in each case (90% for C_{11} and C_{12} and 70% for C_{13}) has a *trans*-configured double bond. Attempts to acquire crystalline derivatives in the disilane series have been unsuccessful.

The ready conversion of the easily accessible medium ring 1,2-dienes to distannanes and disilanes provides opportunities for selective reactions based on the higher reactivity towards electrophiles of the allylic silane (stannane) moiety, and possible Pd^0-coupling reactions of the stannanes. These are now being examined.[14]

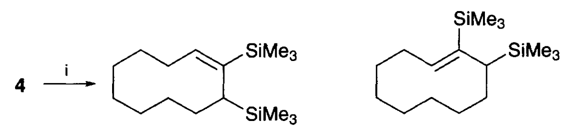


Scheme 5



10 (SE=22.45kcal mol^{-1}) **11** (SE=28.89, 35.73kcal mol^{-1})

Scheme 6 *Reagents and conditions:* i, $SiClMe_3$, Li, THF, room temp.



12 (SE=22.8kcal mol^{-1}) **13** (SE=24.97, 31.9kcal mol^{-1})

Scheme 7 *Reagents and conditions:* i, $SiClMe_3$, Li, THF, room temp.

Footnotes

† All new compounds provided satisfactory spectral data (multinuclear NMR and MS) and microanalytical or high-resolution MS data.

‡ In one reaction of allene **1** (Scheme 1) a very minor product, characterised only by its ^{119}Sn NMR spectrum (δ −10.01, 37.5; $^3J_{Sn-Sn}$ 183 Hz) was formed and could be the *trans* isomer **2b**. The corresponding data for the major *cis* isomer **2a** are δ_{Sn} −0.3; −31.2; $^3J_{Sn-Sn}$ 179 Hz.

§ $^{119,117}Sn$ couplings to ^1H, ^{13}C are slightly greater from a $SnPh_3$ group compared with $SnMe_3$.

¶ A difference-NOE experiment shows close proximity between H^1 and the vinylic $SiMe_3$ group as expected for **10**, but not for **11**.

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10 A full discussion of this structure and the nature of the η^3-allyl complexes formed by palladation of medium-ring cycloalkenes and cycloalk-1,2-dienes will be found in J.-M. Rosset, C. H. L. Kennard, K. A. Byriel, B. H. Riches and W. Kitching, *J. Chem. Soc., Perkin Trans. 1*, to be submitted.

11 R. Calas and J. Dunogues, *J. Organomet. Chem. Libr.*, 1976, **2**, 277; R. Calas, *J. Organomet. Chem.*, 1980, **200**, 11.

12 The product of this reaction was described originally (M. Laguerre, J. Dunogues and R. Calas, *Tetrahedron Lett.*, 1978, 57) as the *trans* isomer **11**, on the basis of the NMR signal for H^1, reported as a doublet of doublets (δ 5.73, *J* 5.5, 11 Hz), in good agreement with our data. The view, present at that time, that a doublet of doublets pattern for H^1 was indicative of a *trans* double bond (as in **11**) (see for example, C. B. Reese and A. Shaw, *J. Chem. Soc., Perkin Trans. 1*, 1975, 2422; H. J. J. Loozen, J. W. de Haan and M. M. Buck, *J. Org. Chem.*, 1977, **42**, 418) is not justified. For example, compound **3**, shown by X-ray crystallography to incorporate a *cis* double bond, shows H^1 as a doublet of doublets (δ 5.76, *J* 11.7, 5.5 Hz), with other coupling constants as in Scheme 2. The CP MAS solid-state ^{13}C NMR spectrum of **3** was well resolved and exhibited chemical shifts similar to those obtained for solution in $CDCl_3$.

13 D. J. Brecknell, unpublished work.

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