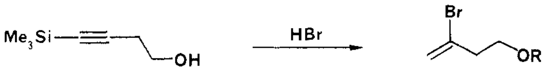
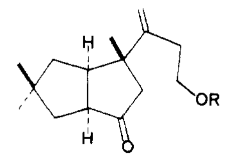
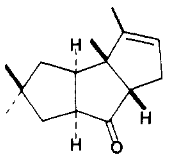
under the conditions required for its removal, caused migration of the exocyclic double bond into the endocyclic position.



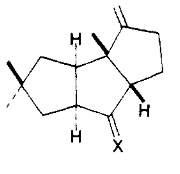
8 R = H
9 R = SiBu^{t}Me$_2$



10 R = SiBu^{t}Me$_2$
11 R = H
12 R = SO$_2$C$_6$H$_4$Me-p



13



14 X = O
15 X = OH, H
16 X = OCS$_2$Me, H

The alcohol 11 was converted into the *p*-toluenesulfonate ester 12 in the standard way and treated with lithiohexamethyldisilazane (2.0 equiv) in ether at −78 °C to give the tricyclic ketone 14 (75%).

While there are many methods for directly reducing a ketone to methylene, particularly the Wolff–Kishner reduction and more recent sophistications of this method, the literature indicates that these methods might be expected to proceed in very low yield.[16] The tricyclic ketone 13 was reduced to *endo*-hirsutene in only 8% yield.[16] Consequently, 14 was treated with NaBH$_4$/MeOH to give the alcohol 15 as a mixture of epimers which was converted into its xanthate derivative 16 by treatment with CS$_2$/MeI/NaH/THF.[17] Exposure of 16 to tri-*n*-butyltin hydride in benzene heated at reflux in the presence of AIBN (catalytic) cleanly gave (±)-hirsutene (1) in 65% yield from 14.[18,19]

In summary, all the key steps in this short convergent route to (±)-hirsutene utilize organosilicon chemistry. The number of steps from 3 through to 1 is nine and proceeds in an overall yield of 7%.

Acknowledgment. The National Science Foundation is gratefully thanked for their support of this work (Grant No. CHE 8110674). The National Science Foundation provided funds for the purchase of a Bruker 360 NMR spectrometer. Professor Daniel Little is thanked for IR, NMR, and mass spectra of authentic hirsutene for comparison purposes.

Registry No. 1, 59433-37-3; **2**, 33404-85-2; **3**, 78064-83-2; **4**, 62762-20-3; **5**, 82494-86-8; **6**, 60064-71-3; **8**, 76334-36-6; **9**, 82511-02-2; **10**, 82511-03-3; **11**, 82511-04-4; **12**, 82511-05-5; **13**, 79897-51-1; **14**, 82511-06-6; **15** isomer 1, 82511-07-7; **15** isomer 2, 82536-00-3; **16** isomer 1, 82511-08-8; **16** isomer 2, 82536-01-4; 4-(trimethylsilyl)but-3-yn-1-ol, 2117-12-6; lithiohexamethyldisilazane, 4039-32-1.

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[19] Selected NMR data: 11 (CDCl$_3$), δ 0.87 (3 H, s), 0.97 (3 H, s), 1.08 (3 H, s), 3.00–1.20 (10 H, m), 3.70 (2 h, t, J = 8 Hz), 4.77 (1 H, s), 4.80 (1 H, s); 14, δ 0.92 (3 H, s), 0.98 (3 H, s), 1.10 (3 H, s), 2.90–1.20 (1 H, m), 4.90 (1 H, s), 4.92 (1 H, s); 1 (CDCl$_3$; 360 MHz), δ 0.93 (3 H, s), 0.96 (3 H, s), 1.06 (3 H, s), 1.22 (1 H, m), 1.43 (6 H, m), 1.65 (1 H, m), 1.73 (1 H, m), 2.18 (1 H, m), 2.47 (3 H, m), 4.78 (1 H, s), 4.82 (1 H, s), ^{13}C NMR 23.18, 26.82, 27.24, 29.73, 30.90, 38.62, 40.86, 41.86, 44.25, 48.97, 49.96, 53.43, 55.92, 103.50, 162.76 ppm. All new compounds were completely characterized by NMR, IR, and MS analysis and/or microanalysis.

(Pentaalkylditin)lithiums: Significant Species in Some (Trialkyltin)lithium Preparations

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Summary: (Pentaalkylditin)lithiums are demonstrated to be present in preparations of (trialkyltin)lithium reagents (from the trialkyltin halide and lithium in tetrahydrofuran) by direct observation (^{119}Sn NMR) and alkylation to R_5Sn_2R' (R = methyl, *n*-propyl, isopropyl; R′ = cyclohexyl, methyl). Cyclohexylation of $(i\text{-}C_3H_7)_5Sn_2Li$ proceeds by a free radical route. The R_5Sn_2Li species are considered to arise by oxidative addition of R_3SnLi to R_2Sn, formed by $R_3SnLi \rightleftharpoons R_2Sn{:}RLi$, dissociation of which is promoted by R_6Sn_2 scavenging of RLi.

The reactions of simple (alkyltin)- or (aryltin)lithium reagents usually can be understood in terms of R_3SnLi (or some aggregated or solvated assembly) functioning as an electron-transfer reagent, nucleophile, or base.[1-4] However, there are observations,[5-8] mainly with tributyl- and trimethyltin alkali reagents, consistent with the stannylene ($R_2Sn{:}$) being a significant component of the equilibrium below (eq 1).

$$R_3SnLi \rightleftharpoons R_2Sn{:} + RLi \qquad (1)$$

An attraction to this proposal is that some R_3SnLi have been synthesised by reaction of $SnCl_2$ with 3 equiv of RLi, a procedure[9-11] which could involve the reverse of (1) as the final step. Furthermore, a plausible scheme[8] for the transformation of $(CH_3)_3SnLi$ to $((CH_3)_3Sn)_3SnLi$, which occurs under certain conditions,[11] has eq 1 as the first step followed by oxidative addition of $(CH_3)_3SnLi$ to $(CH_3)_2Sn$ yielding $(CH_3)_5Sn_2Li$. In this communication we wish to describe the characterization of some R_5Sn_2Li species, the formation of which constitutes very persuasive evidence for the operation of eq 1 and the scheme[8] for $(R_3Sn)_3SnLi$ formation.

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[8] See also: Quintard, J. P.; Pereyre, M. *Rev. Silicon, Germanium, Tin Lead Compd* **1980**, *4*, 153.

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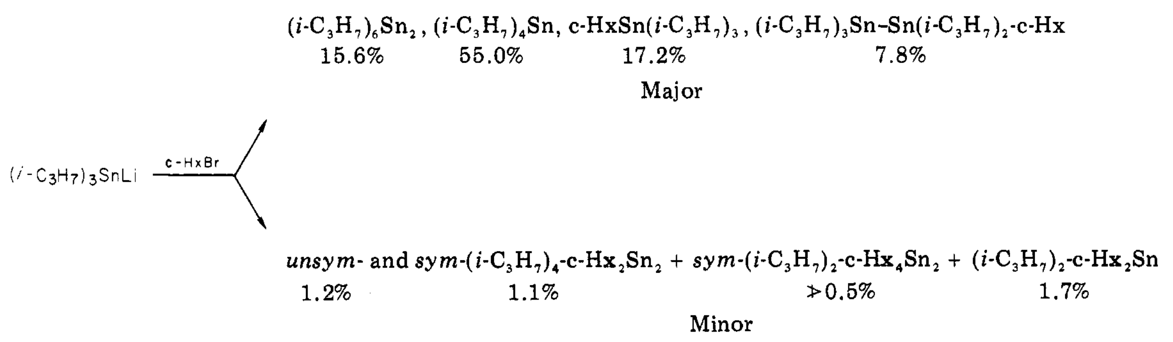
Scheme I



Reaction of analytically pure $(i\text{-}C_3H_7)_3SnBr$ with an excess of lithium (tetrahydrofuran solvent) proceeds readily, and reaction of this filtered apple green solution with cyclohexyl bromide was rapid. The total product mixture, before and after rapid workup but without any heating etc., was examined by ^{119}Sn NMR spectroscopy and at least eight significant signals to the high-field side of $(CH_3)_4Sn$ (TMT = O) appeared. The signals at −32.3 and −44.3 ppm of comparable intensity suggested the existence of an unsymmetrical ditin species, with the signals at −31.6, −42.6, and −55.4 ppm being assigned to $(i\text{-}C_3H_7)_6Sn_2$, $(i\text{-}C_3H_7)_4Sn$, and $(i\text{-}C_3H_7)_3Sn\text{-}c\text{-}Hx$ (c-Hx = cyclohexyl), respectively, by comparison with the spectra of authentic samples,[12] as well as the agreement with available literature values.[13] Titration of the total product with iodine/chloroform, which rapidly cleaves only Sn–Sn bonds, and subsequent complete isopropylation (with $i\text{-}C_3H_7MgBr$), provided only $(i\text{-}C_3H_7)_4Sn$, $(i\text{-}C_3H_7)_3Sn\text{-}c\text{-}Hx$, and $(i\text{-}C_3H_7)_2Sn\text{-}c\text{-}Hx_2$, thus establishing the presence in the product mixture of $(i\text{-}C_3H_7)_3Sn$, $(i\text{-}C_3H_7)_2Sn\text{-}c\text{-}Hx$, or $(i\text{-}C_3H_7)Sn\text{-}c\text{-}Hx_2$ residues in ditin or more catenated species.

The constitution of the unsymmetrical ditin was shown to be $(i\text{-}C_3H_7)_5\text{-}c\text{-}HxSn_2$ in the following way. $(i\text{-}C_3H_7)_3Sn\text{-}c\text{-}Hx$[12] was treated with bromine (methanol; 1 equiv), and the resulting mixture of $(i\text{-}C_3H_7)_3SnBr$ and $(i\text{-}C_3H_7)_2\text{-}c\text{-}HxSnBr$ (^{13}C and ^{119}Sn spectroscopy; after equalizing the concentrations by addition of $(i\text{-}C_3H_7)_3SnBr$) was treated with lithium (1 equiv in THF) necessarily producing the ditins shown in eq 2, by "symmetrical" and "cross"-coupling of the tin bromides.

$$(i\text{-}C_3H_7)_3Sn\text{-}c\text{-}Hx \xrightarrow[\text{MeOH}]{Br_2} (i\text{-}C_3H_7)_3SnBr + (i\text{-}C_3H_7)_2\text{-}c\text{-}HxSnBr \xrightarrow[\text{THF}]{Li} (i\text{-}C_3H_7)_6Sn_2 + (i\text{-}C_3H_7)_4\text{-}c\text{-}Hx_2Sn_2 + c\text{-}HxSn_2(i\text{-}C_3H_7)_5 \quad (2)$$

The ^{119}Sn NMR spectrum of this total product exhibited signals at −31.2 ppm ($J_{^{119}Sn-^{117}Sn}$ = 1162 Hz) for $(i\text{-}C_3H_7)_6Sn_2$ and −44.4 (J = 1182 Hz) for sym-$(i\text{-}C_3H_7)_4\text{-}c\text{-}Hx_2Sn_2$ and equiintense signals at −31.90 (J = 1172 Hz) and −43.90 ppm (J = 1172 Hz) assignable only to $(i\text{-}C_3H_7)_3\mathit{Sn}\text{-}Sn(i\text{-}C_3H_7)_2\text{-}c\text{-}Hx$ and $(i\text{-}C_3H_7)_3Sn\text{-}\mathit{Sn}(i\text{-}C_3H_7)_2\text{-}c\text{-}Hx$, respectively. (The AB pattern for the nonequivalent ^{119}Sn nuclei in the above compound was identified with $J_{^{119}Sn-^{119}Sn}$ = 1226 Hz). Authentic sym-$(i\text{-}C_3H_7)_4\text{-}c\text{-}Hx_2Sn_2$ (δ −45.0) and sym-$(i\text{-}C_3H_7)_2\text{-}c\text{-}Hx_4Sn_2$ (δ −57.8) were obtained by bromination of $(i\text{-}C_3H_7)_2\text{-}c\text{-}Hx_2Sn$ followed by (lithium) coupling. This procedure also provides unsymmetrical $(i\text{-}C_3H_7)_2\text{-}c\text{-}Hx^{*}Sn\text{-}^{+}Sn(i\text{-}C_3H_7)\text{-}c\text{-}Hx_2$ with ^{119}Sn NMR shifts of −45.6 (*) and −58.2 ppm (+). The complete reaction outcome is shown, with weighted percentage yields of the various stannanes (Scheme I), based on the ^{119}Sn NMR spectrum (long accumulation time).

Regarding the major products, we envisage $(i\text{-}C_3H_7)_5\text{-}c\text{-}HxSn_2$ and $(i\text{-}C_3H_7)_3\text{-}c\text{-}HxSn$ as arising from cyclohexylation of $(i\text{-}C_3H_7)_5Sn_2Li$ and $(i\text{-}C_3H_7)_3SnLi$, respectively, with cyclohexyl bromide. The ditinlithio species is considered to form as in eq 3 and 4 with $(i\text{-}C_3H_7)_6Sn_2$ scavenging[14] of $i\text{-}C_3H_7Li$ promoting dissociation of the complex.

$$(i\text{-}C_3H_7)_3SnLi \rightleftharpoons \overline{(i\text{-}C_3H_7)_2Sn\!:i\text{-}C_3H_7Li} \xrightarrow{(i\text{-}C_3H_7)_6Sn_2} (i\text{-}C_3H_7)_2Sn\!: + (i\text{-}C_3H_7)_4Sn + (i\text{-}C_3H_7)_3SnLi \quad (3)$$

$$(i\text{-}C_3H_7)_2Sn\!: + (i\text{-}C_3H_7)_3SnLi \rightarrow (i\text{-}C_3H_7)_5Sn_2Li \quad (4)$$

The exact nature of the stannylene species resulting from dissociation is unclear, but there is evidence (yellow-brown precipitate) for some aggregation, presumably into $[(i\text{-}C_3H_7)_2Sn]_x$,[15] such aggregation probably competing with insertion into the Sn–Li bond.

We noted always the formation of substantial amounts of $(i\text{-}C_3H_7)_4Sn$, which is attributed primarily to scavenging of complexed $i\text{-}C_3H_7Li$ by $(i\text{-}C_3H_7)_6Sn_2$ present in the formation stage of R_3SnLi. (This was indicated by quenching the "R_3SnLi" solution with water, and R_4Sn and R_6Sn_2 were detected by ^{119}Sn NMR spectroscopy.)

$$2R_3SnCl + 2Li \rightarrow R_6Sn_2 + 2LiCl$$

$$R_6Sn_2 + 2Li \rightarrow 2R_3SnLi \rightleftharpoons \overline{2R_2Sn\!: + RLi}$$

$$\overline{R_2Sn\!: + RLi} + R_6Sn_2 \rightarrow R_4Sn + R_3SnLi + R_2Sn\!: \text{ etc.}$$

There is ample precedent for this latter reaction.[16] Cyclohexene is also found in readily detected amounts (^{1}H

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[12] Authentic samples have been characterized by ^1H, ^{13}C, and ^{119}Sn NMR spectra and elemental analyses. Mixtures of organostannanes have been characterized by ^{13}C and ^{119}Sn NMR spectra, which agreed with those of samples synthesized by unambiguous routes (see text) from structurally authenticated precursors. The ditin fraction from the reaction of $(i\text{-}C_3H_7)_3SnLi$ with cyclohexyl bromide (after removal of the more volatile monostannanes) was calculated on the basis of the ^{119}Sn NMR spectrum to be 60.7% $(i\text{-}C_3H_7)_6Sn_2$, 30.35% $(i\text{-}C_3H_7)_5Sn_2\text{-}c\text{-}Hx$, and 8.9% $(i\text{-}C_3H_7)_4Sn_2\text{-}c\text{-}Hx_2$. Anal. Calcd: C, 45.35; H, 8.53. Found: C, 45.57; H, 8.30. Mass spectral fragmentations were completely consistent with this ditin mixture. Full details will be reported later.

[13] A ^{119}Sn shift of −29.1 ppm has been reported for $(i\text{-}C_3H_7)_6Sn_2$. See: Mitchell, T. N.; Walter, G. *J. Chem. Soc., Perkin Trans. 2* **1977**, 1842.

[14] See: Kobayashi, K.; Kawanisi, M.; Kitomi, T.; Kozima, S. *J. Organomet. Chem.* **1982**, *00*, 0000.

[15] This yellow-brown material is not consumed by the secondary cyclohexyl bromide but is by primary bromides and methyl iodide. $[(i\text{-}C_3H_7)_2Sn]_x$ made from $SnCl_2$ and 2 equiv of $i\text{-}C_3H_7MgBr$ (at low temperatures) reacts with methyl iodide to yield $(i\text{-}C_3H_7)_2CH_3SnI$ and $(i\text{-}C_3H_7)_3SnI$ (^{119}Sn NMR spectra of authentic samples) as major products. In contrast to preparations of $(CH_3)_3SnLi$ from $(CH_3)_3SnCl$ and excess lithium in THF, which are accompanied by deposition of metallic tin (and darkening of lithium), no tin deposition or darkening of lithium accompanies similar preparations of "$(i\text{-}C_3H_7)_3SnLi$".

[16] This reaction has been utilized and recommended for the rapid preparation of R_3SnLi from R_6Sn_2. Still, W. C. *J. Org. Chem.* **1976**, *41*, 3063; *J. Am. Chem. Soc.* **1977**, *99*, 4836.

NMR spectroscopy), and much of the R_6Sn_2 finally surviving may arise from decomposition of R_3SnH. The formation of the minor products appears to require the formation of intermediates such as $R_2Sn\text{-c-}HxLi$ (which could lead to $R_2Sn\text{-c-}Hx_2$ and $R_4Sn_2\text{-c-}Hx_2$) and $R\text{-c-}Hx_2SnLi$ which could produce *sym*-$R_2\text{-c-}Hx_2Sn_2$ and *unsym*-$R\text{-c-}Hx_2SnSnR_2\text{-c-}Hx$ etc. Reasonable routes to such species can be written. No tritins were detected in the ^{119}Sn NMR spectrum, but there is mass spectral evidence for tri and higher order tin species.

The stereochemistry of the postulated cyclohexylation of $(i\text{-}C_3H_7)_5Sn_2Li$ was examined. Reaction of either *cis*- or *trans*-4-methylcyclohexyl bromide provided (4-methylcyclohexyl)pentaisopropylditin (^{119}Sn and ^{13}C NMR spectroscopy) which was predominantly trans (~80%), on the basis of comparison of the ^{119}Sn and ^{13}C NMR shifts with those of authentic samples obtained from the bromination/Li coupling procedures (outlined above) with authentic (*cis*- 4-methylcyclohexyl)- and (*trans*-4-methylcyclohexyl)triisopropylstannanes.[12] Thus, apparently complete stereoequilibration accompanies this substitution. Furthermore, reaction with 6-bromo-1-heptene provided (cyclized) ((*cis*-2-methylcyclopentyl)methyl)- and ((*trans*-2-methylcyclopentyl)methyl)pentaisopropylditins with a cis/trans ratio (ca. 2.7:1). These results are consistent with an electron transfer/free radical mechanism for substitution, as has been established for cyclohexylation of $(CH_3)_3SnLi$[1-4] and $(i\text{-}C_3H_7)_3SnLi$.[17] Methylation (with CH_3I) provides $(i\text{-}C_3H_7)_5Sn_2CH_3$ (~1%) having ^{119}Sn NMR shifts (−29.0 and −49.3 ppm) and $J_{^{119}Sn-^{117}Sn}$ (1616 Hz; $J_{^{119}Sn-^{119}Sn}$ (AB pattern) = 1699 Hz) in agreement with those of an authentic sample obtained by coupling (Li in THF) of $(i\text{-}C_3H_7)_3SnBr$ and $(i\text{-}C_3H_7)_2CH_3SnBr$.[12] The major product of methylation is $(i\text{-}C_3H_7)_3SnCH_3$ (~83%).

The ^{119}Sn spectrum of "$(i\text{-}C_3H_7)_3SnLi$" (THF solvent) consists of signals at δ −13.0 (ca. 87% of total intensity) assigned to $(i\text{-}C_3H_7)_3SnLi$ and δ −42.7 assigned to $(i\text{-}C_3H_7)_4Sn$ (8%) and two equiintense signals at δ −48.2 and −39.3, with the latter being broader. We associate these signals with $(i\text{-}C_3H_7)_5Sn_2Li$ (5%).

Preparations of $(n\text{-}C_3H_7)_3SnLi$ (57.5%; $\delta_{^{119}Sn}$ −130) contain $(n\text{-}C_3H_7)_4Sn$ (22%; −18.0 ppm) as well as $(n\text{-}C_3H_7)_5Sn_2Li$ (12.6%; $\delta_{^{119}Sn}$ −123 and −194; on the basis of direct ^{119}Sn observations and derivatization to $(n\text{-}C_3H_7)_5Sn_2CH_3$ (~3%) and $(n\text{-}C_3H_7)_5Sn_2C_6H_{11}$ (~1.5%). (Pentamethylditin)lithium is a very minor component of $(CH_3)_3SnLi$ ($\delta_{^{119}Sn}$ −179) shortly after (~20 min) preparation from $(CH_3)_3SnCl$ and excess lithium in THF, but characterization as $(CH_3)_5Sn_2C_6H_{11}$ (0.7%; $\delta_{^{119}Sn}$ −95.7 and −107.9; comparison with authentic sample) was achieved.[18] No evidence for the existence of $(C_6H_5)_5Sn_2Li$ in (triphenyltin)lithium ($\delta_{^{119}Sn}$ −109) preparations has been obtained.

Steric congestion could be a factor in promoting dissociation of $(i\text{-}C_3H_7)_3SnLi$ and/or conferring stability on R_2Sn:. The known[19] $[((CH_3)_3Si)_2CH]_2Sn$: is analogous to the postulated $[(CH_3)_2CH]_2Sn$:. Our recent demonstration[20] of the presence of $(CH_3)_5Ge_2Li$ in preparations of $(CH_3)_3GeLi$ (in HMPA) is in line with the present findings. We are examining further aspects of sterically congested organotin alkalis and aspects of their substitution mechanisms etc.

Acknowledgment. This research was supported in part by the Australian Research Grants Committee to whom we are grateful. A very valuable exchange of information with Professor Sinpei Kozima (Kyoto University) is acknowledged.

Registry No. $(i\text{-}C_3H_7)_6Sn_2$, 17106-21-7; $(i\text{-}C_3H_7)_4Sn$, 2949-42-0; $(i\text{-}C_3H_7)_3Sn\text{-c-}Hx$, 82544-60-3; $(i\text{-}C_3H_7)_5\text{-c-}HxSn_2$, 82544-61-4; $(i\text{-}C_3H_7)_5Sn_2Li$, 82544-66-9; $(n\text{-}C_3H_7)_3SnLi$, 82544-67-0; $(i\text{-}C_3H_7)_3SnBr$, 19464-54-1; $(i\text{-}C_3H_7)_2\text{-c-}HxSnBr$, 20128-73-8; *unsym*-$(i\text{-}C_3H_7)_4\text{-c-}Hx_2Sn_2$, 82544-68-1; *sym*-$(i\text{-}C_3H_7)_2\text{-c-}Hx_4Sn_2$, 82544-69-2; $(i\text{-}C_3H_7)_2\text{-c-}Hx_2Sn$, 5764-57-8; $(i\text{-}C_3H_7)_2\text{-c-}HxSn\text{-}Sn(i\text{-}C_3H_7)\text{-c-}Hx_2$, 82544-70-5; *sym*-$(i\text{-}C_3H_7)_4\text{-c-}Hx_2Sn_2$, 82544-71-6; $(CH_3)_3SnLi$, 17946-71-3; $(CH_3)_3SnCl$, 1066-45-1; $(CH_3)_5Sn_2C_6H_{11}$, 3531-48-4; (*cis*-4-methylcyclohexyl)triisopropylstannane, 82544-62-5; (*trans*-4-methylcyclohexyl)triisopropylstannane, 82544-63-6; ((*cis*-2-methylcyclopentyl)methyl)pentaisopropylditin, 82544-64-7; ((*trans*-2-methylcyclopentyl)methyl)pentaisopropylditin, 82544-65-8; cyclohexyl bromide, 108-85-0; *cis*-4-methylcyclohexyl bromide, 28046-90-4; *trans*-4-methylcyclohexyl bromide, 28046-91-5; 6-bromo-1-heptene, 38334-98-4; (pentamethylditin)lithium, 82544-72-7.

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[17] Olszowy, H. A., unpublished results.

[18] Reaction of $(CH_3)_3SnLi$ with c-HxBr provided $c\text{-}HxSn(CH_3)_3$ (96%), $c\text{-}Hx_2Sn(CH_3)_2$ (~1%), $(CH_3)_5\text{-c-}HxSn_2$ (~1%), and $(CH_3)_6Sn_2$ (~2%), on the basis of the ^{119}Sn NMR spectrum (accumulation time ~15 h).

[19] Cotton, J. D.; Davidson, P. J.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **1976**, 2275.

[20] Wickham, G.; Young, D.; Kitching, W. *J. Org. Chem.*, accepted for publication.

Stereospecific Formation of Five-Membered Metallacycles. Zirconaindans from Thermally Generated (η^2-Dehydrobenzene)dicyclopentadienylzirconium(II) and *cis*- and *trans*-Stilbene

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Summary: *cis*- and *trans*-2,3-diphenylzirconaindans **7** and **8** are formed stereospecificly from thermally generated (η^2-dehydrobenzene)dicyclopentadienylzirconium(II) and *cis*- and *trans*-stilbene, respectively. This supports a concerted pathway suuggested for the cyclization reaction of bis(olefin) transition-metal complexes to form five-membered metallacycles.

The relation between bis(olefin) transition-metal complexes 1 and five-membered metallacycles 2 is of great importance for design and development of catalytic transformations of unsaturated organic substrates. A concerted pathway is commonly assumed for this basic organometallic reaction type, although direct experimental evidence supporting this assumption is quite rate.[1]

Stereospecificity of product formation is one of several equally important criteria for concertedness[2] which usually can be verified easily by experiment. Surprisingly, such a simple stereochemical analysis is lacking for most organometallic systems of type **1** $\rightleftarrows$ **2**.[3] We have tested the stereochemical outcome of one example of this reaction type, the cyclization of (aryne)(olefin)zirconocene complexes which yields substituted 1-zircononaindans.

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