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.

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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; $(i\text{-}C_3H_7)_2\text{-c-HxSn-Sn}(i\text{-}C_3H_7)\text{-c-Hx}_2$, 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 $\text{c-HxSn}(CH_3)_3$ (96%), $\text{c-Hx}_2Sn(CH_3)_2$ (~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).

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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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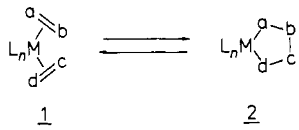
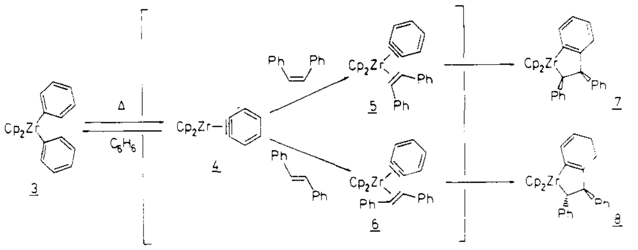
Scheme I



Scheme II



Diphenylzirconocene (**3**) in benzene solution is a suitable starting material for the generation of the elusive (η^2-dehydrobenzene)dicyclopentadienylzirconium(II) (**4**) under sufficiently mild conditions.[4] We have recently been able to show that a variety of olefins can compete successfully with the aromatic solvent as scavengers and can trap intermediate **4** from this thermal equilibrium to form metallaindans.[5] Thermolysis of 1.8 g (4.8 mmol) of **3** in 20 mL of benzene for 18 h at 80 °C in the presence of a tenfold excess of *cis*-stilbene yielded a single organometallic product (**7**) which was isolated in 31% yield after recrystallization from *n*-hexane. In an argon atmosphere the orange-red crystalline material is stable to about 160 °C; above that temperature it rapidly decomposes before melting. The compound analyzes correctly for a 1:1 adduct of (η^2-dehydrobenzene)dicyclopentadienylzirconium(II) (**4**) with the added olefin [Calcd for $C_{30}H_{26}Zr$: C, 75.42; H, 5.49. Found: C, 75.33; H, 5.52. MS: *m/e* 476 (M^+)[6]]. Treatment of a deep red benzene solution of **7** with HCl resulted in an almost quantitative yield of zirconocene dichloride and 1,1,2-triphenylethane.

The ^{13}C NMR spectrum (62.89 MHz, C_6D_6) of **7** shows carbon atoms of three chemically different aromatic frameworks[7] in addition to two nonidentical η^5-cyclopentadienylligands at δ_C 110.9 and 109.7. The presence of a metallacyclic σ structure becomes evident from resonances due to two benzylic carbons at δ_C 70.5 and 58.8 exhibiting coupling constants $^1J_{CH}$ = 126.9 and 122.3 Hz, respectively, characteristic for a saturated alkyl moiety in a five-membered metallacycle.[8] In the ^1H NMR spectrum (250 MHz, C_6D_6) **7** displays two Cp resonances at δ 5.63 and 5.00. Benzylic hydrogens appear as a well-separated AB system at δ 5.72 (ArCHPh) and 3.30 (ZrCHPh). An observed AB coupling constant $^3J_{HH}$ = 7.1 Hz does not by itself allow a clear distinction between a cis and trans arrangement of phenyl substituents at the five-membered ring system.[9] Tentatively, we assign a cis structure to this zirconocene complex **7** obtained from the reaction of intermediate **4** with added scavenger *cis*-stilbene.

We could not detect any trace of **7** upon thermolysis of **3** under similar conditions using a fivefold excess of *trans*-stilbene. A different organometallic compound **8** was formed instead which appears to be the configurational isomer of **7**. This we deduce from the formation of the identical organic product, 1,1,2-triphenylethane, upon hydrolysis and a distinctly different although in general quite similar appearance of the ^1H NMR spectrum, exhibiting features at δ 8.20–6.80 (m, 14 H, aromatic), 5.83 and 5.10 (s, 5 H each, Cp), 5.00 and 3.95 (AB system, 2 H, CHPh, $^3J_{HH}$ = 10.5 Hz). Independent crossover experiments revealed that the formation of about 1% of the cis isomer accompanying *trans*-2,3-diphenyl-1-zirconaindan **8** would have been detected by the method of analysis applied (FT ^1H NMR, 250 MHz). However, in a direct comparison of crude reaction mixtures obtained from thermolyses of **3** and the respective stilbene isomers in C_6D_6 solvent in sealed NMR tubes, we have not been able to observe any formation of the "wrong" isomer of the particular metallacyclic reaction product.

Our observation of a >99% selective, stereospecific formation of phenyl-substituted five-membered metallacycles **7** and **8** provides a strong indication for a concerted course of the ring closure reaction of intermediate bis(olefin)zirconocene complexes **5** and **6**. This example, therefore, contrasts favorably with the reaction of (η^2-benzophenon)zirconocene with dimethyl fumarate and maleate, the latter forming a five-membered metallacycle with loss of stereochemistry as expected for a stepwise reaction mechanism.[3]

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Registry No. 3, 51177-89-0; 4, 71191-32-7; 7, 82555-26-8; 8, 82597-45-3; *cis*-stilbene, 645-49-8; *trans*-stilbene, 103-30-0.

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(6) A *m/e* value corresponding to naturally most abundant isotopes, i.e., ^{90}Zr (51.5%).

(7) NMR: δ 179.3 (s), 164.3 (s), 146.8 (s), 141.5 (s), 140.9 (d), 132.8 (d), 131.1 (d), 127.0 (d), 126.4 (d), 124.7 (d), 124.0 (d), 119.2 (d), two additional carbon resonances cannot be located accurately due to solvent signals.

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Reactions of Coordinated Molecules. 33. Conversion of a Metalla sp^2-CH Analogue to a Metalla sp^3-CH Analogue: A Comment about Structural and Electronic Formalism

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Summary: The conversion of α-enolate anions of metalla-β-diketonate complexes to η^3-allylic complexes is analyzed by using an isolobal approach. These reactions are described as the conversion of a metalla sp^2-CH moiety into a metalla sp^3-CH moiety.

We reported recently an intramolecular, interligand C–C bond formation reaction which occurred between adjacent acylic ligands, as shown in eq 1.[1] When the (ferra-β-di-