Metallated Bicyclo[3.2.2]nona-2,6,8-trienes, Their Rearrangement to Barbaralanes, and a Short Synthesis of the Bicyclo[3.2.2]nona-2,6,8-trien-4-yl Anion[☆]

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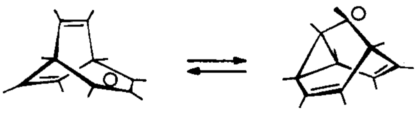
Five different anions are formed when bicyclo[3.2.2]nona-2,6,8-triene (**1a**) is deprotonated: the 6- and 7-yl anions when using *t*BuLi/TMEDA, the 4,6- and 4,7-diyl dianions when using *n*BuLi/*t*BuOK, and the 4-yl anion ($\mathbf{1}^-$) after quenching the dianions with THF. Reaction of the anions with Me$_3$SnCl gives the 6-, 7-, and 4-monostannylated bicyclo[3.2.2]nona-2,6,8-trienes **1b**, **1c**, and **1d** as well as the *exo*-4,7-, *endo*-4,6-, and *endo*-4,7-distannylated bicyclo[3.2.2]nona-2,6,8-trienes **1e**, **1f**, and **1g**, respectively. Reaction of $\mathbf{1}^-$ with Me$_3$SiCl and Me$_3$PbCl leads to the corresponding 4-silyl derivative **1h** and its plumbyl analogue **1i**. Inversely, cleavage of **1d** with MeLi allows to generate $\mathbf{1}^-$ under particularly mild conditions. The metallation of tricyclo[3.2.2.0^{2,4}]nona-6,8-diene (**3a**), which was tested for an alternative route to $\mathbf{1}^-$, gives two stannyl derivatives **3b** and **3c** which are substituted in the vinylic positions. – On heating **1d** and **1i** rearrange to yield 9-trimethylstannylbarbaralane (**2d**) and its plumbyl analogue **2i** quantitatively. The reactivity decreases on passing from **1i** to **1d** whereas **1h** does not react. Mercury and zinc derivatives of $\mathbf{1}^-$ are so labile that only dibarbaralylmercury (**2j**) and -zinc (**2k**) are observed by NMR spectroscopy. The title rearrangement proceeds by a 1,5-homodienyl metallatropic shift which involves an *endo*-type transition structure. – The new compounds **1b**–**i**, **2d**, **2i**, **3b** and **3c** are characterized with emphasis on the NMR data including ^{1}H, ^{13}C, ^{119}Sn, ^{207}Pb signal shifts and various heteronuclear couplings.

The bicyclo[3.2.2]nona-2,6,8-trienyl/barbaralyl couple **1**/**2** is an instructive and convincing example for the possibility to switch from one hydrocarbon skeleton to another by changing the charge of the species[1]. For instance, the attempt to generate the barbaralyl anion $\mathbf{2}^-$ gives the bicyclo[3.2.2]nona-2,6,8-trienyl anion $\mathbf{1}^-$[1]. Inversely, the cation $\mathbf{2}^+$ is produced instead of $\mathbf{1}^+$ when starting from a suitable precursor of $\mathbf{1}^+$[2]. The relative stability of these ions seemed to fit nicely into the concept of homoaromaticity[3], but for anions like $\mathbf{1}^-$ it turned out that, instead, inductive effects, hyperconjugation, and chelate effects caused by the counterion are important[4]. Another challenging aspect is the possibility that the concept of controlling structures **1** and **2** is not restricted to the charge. This follows from the cleavage of the C–Br bond of 9-bromobarbaralane which generates the radical $\mathbf{1}^\bullet$ rather than $\mathbf{2}^\bullet$[5]. It is then also conceivable that stable neutral bicyclo[3.2.2]nona-2,6,8-trienes and barbaralanes may be interconverted in one direction or the other. The rearrangement has synthetic appeal but does not seem to have been established yet for simple species C$_9$H$_9$X (X = H and various substituents).



$\mathbf{1}^-$ ⊖ anion $\mathbf{2}^-$
$\mathbf{1}^+$ ⊕ cation $\mathbf{2}^+$
$\mathbf{1}^\bullet$ ⊙ radical $\mathbf{2}^\bullet$

For a general study of this type of reactions derivatives with stannyl groups and the like should be well suited. One advantage is the higher mobility of the stannyl group owing to the rather weak tin-carbon bond. In addition, the ^{119}Sn nucleus simplifies the analysis of the reaction products. We gained access to corresponding bicyclo[3.2.2]nona-2,6,8-trienes during our work on the anion $\mathbf{1}^-$ as a ligand in metallocene-like molecules[6]. In this paper we report on various metallation experiments one of which considerably shortens the synthesis of $\mathbf{1}^-$, on bicyclo[3.2.2]nona-2,6,8-trien-4-yl main-group metal derivatives, and on their conversion into barbaralyl derivatives.

Deprotonation of Bicyclo[3.2.2]nona-2,6,8-triene (1a) and Quench with Me$_3$ECl (E = Si, Sn, Pb)

Up to now the potential of the anion $\mathbf{1}^-$ as a versatile precursor of substituted bicyclo[3.2.2]nona-2,6,8-trienes was limited because it is difficult to prepare. The most popular synthesis is a multistep procedure[7] with low yield which, nevertheless, has been applied until recently[8]. In order to improve the access to $\mathbf{1}^-$ we decided to study the deprotonation of **1a**.

The synthesis of the starting compound **1a** follows the procedure of Tsuji et al.[9] (Scheme 1). While the Diels-Alder adduct **3z** (and its *endo*-6-, *endo*-7-isomer[10]) and the ring-opened product **1z** can be obtained in more than 90 and 80% yield, respectively, anodic bisdecarboxylation under various conditions yields only 11% of **1a**. When starting from **3z** the same procedure gives a 15% yield of **3a**[11] which

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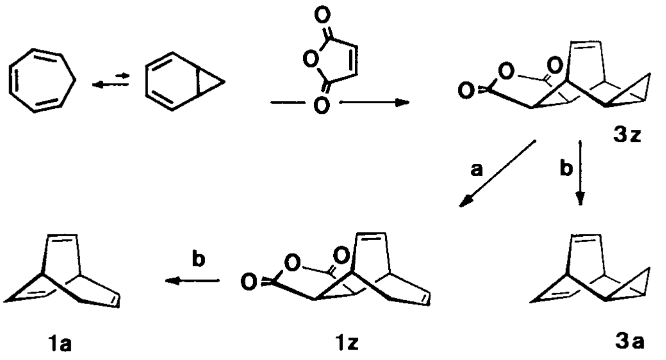
is another candidate for deprotonation experiments (see below).

Scheme 1



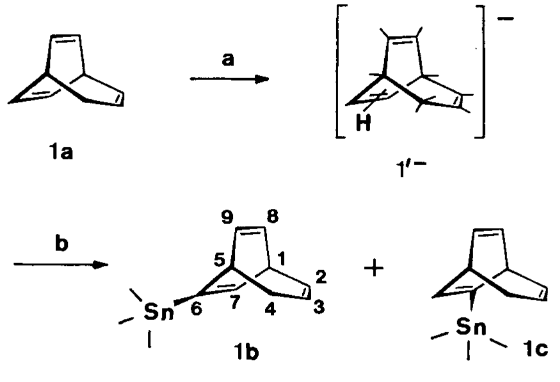
a: 230 °C. — b: Anodic oxidation.

Vinylic Stannylation

When **1a** is treated with an equimolar amount of *t*BuLi/TMEDA in hexane at low temperatures deprotonation takes place as can be shown by further reaction with Me_3SnCl. The only stannylated derivatives of **1a** are **1b** and **1c** (Scheme 2) which are obtained in a molar ratio of 8:7 and an overall yield of 41%.

The substitution in the vinylic positions 6 and 7 and the distinction of the isomers **1b** and **1c** follow unequivocally from the ^{1}H-, ^{13}C-, and ^{119}Sn-NMR spectra. Their analysis is based on the respective signal shifts and areas, on the coupling constants ${}^{n}J$(H,H), ${}^{1}J$(C,H), ${}^{n}J$(Sn,H), and ${}^{n}J$(Sn,C), and on criteria which we have worked out in detail earlier[12]. Here we note that $\delta(^{119}Sn) = -35.90$ and -38.15 is characteristic of Me_3Sn groups bound to vinylic carbon atoms[14] and that very unfavorable dihedral angles keep the values of ${}^{3}J$(Sn,C-4) for **1b** (4.9 Hz) and of ${}^{3}J$(Sn,C-2) for **1c** (7.1 Hz) smaller than those of ${}^{4}J$(Sn,C-2) for **1b** (11.2 Hz) and of ${}^{4}J$(Sn,C-4) for **1c** (11.2 Hz); the latter benefit from the favorable (although slightly distorted) W arrangement of the nuclei constituing the main coupling path. The NMR data are listed in detail in the experimental section.

Scheme 2



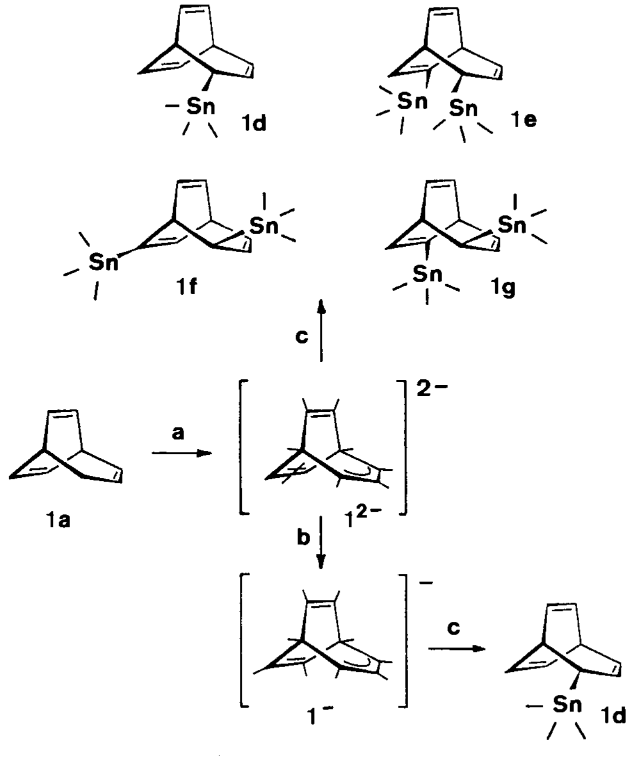
a: *t*BuLi/TMEDA. — b: Me_3SnCl.

These results imply that the anions formed with *t*BuLi/TMEDA should be the two isomers of $\mathbf{1'}^-$ and that a remarkable regioselectivity is effective here. We attribute this to the influence of the lithium ion on the transition state and a change of the C—H acidities of bicyclic hydrocarbons as compared to simple ones[12b]: a decrease for 4-H of **1a** and an increase for 6/7-H.

Allylic and Double Stannylation

Deprotonation of **1a** with a threefold excess of *n*BuLi/*t*BuOK[13] in hexane and successive reaction with Me_3SnCl (Scheme 3) leads to a different result. Now all stannylated products are substituted in the allylic position 4. The main product (54%) is **1d**; besides this, the doubly stannylated molecules **1e**, **1f**, and **1g** are obtained in a 21:16:10 mixture and an overall yield of 22%. Both fractions are pure as checked by elemental analysis.

Scheme 3



a: *n*BuLi/*t*BuOK. — b: THF. — c: Me_3SnCl.

All new compounds have been identified by their NMR spectra. Thus, **1d** has a ^{119}Sn-NMR signal shift of $\delta = -1.54$, a value that is expected for Me_3Sn bound to allylic carbon atoms[14], and the characteristic signal of C-4 is accompanied by largely split tin satellites typical for one-bond couplings. The ^{13}C-NMR signals of the distannylated species **1e**, **1f**, and **1g** have two sets of tin satellites except for C-3 with J(Sn,C) < 1 Hz. This pattern is very close to simple combinations of the coupling sets of the monostannylated species **1b**, **1c**, and **1d**. The fourth possible combination cannot be detected probably because serious steric congestion is predicted for the *exo*-4,6-distannyl derivative. A special and useful feature of the ^{119}Sn-NMR spectra are the tin–tin couplings across four and five bonds with ^{4}J(Sn-4,Sn-6) = 50.5 Hz in **1f** and ^{5}J(Sn-4,Sn-7) = 30.9 and 53.7 Hz in **1e** and **1g**, respectively. Obviously the ^{5}J values reflect the different orientations of the stannyl groups relative to each other and are thus an efficient probe for the stereochemistry. This is illustrated in Figure 1 where we define a pseudo-dihedral angle between the Sn–C bonds. Comparison of **1e** and **1g** shows that this angle is more favorable for **1g** so that its tin–tin coupling constant is larger. A more thorough treatment is necessary for relating the stereochemistry to these couplings quantitatively.

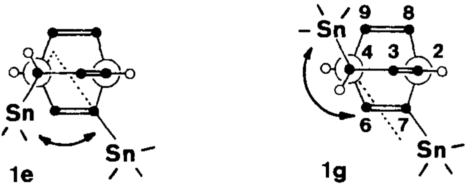


Figure 1. Newman-type projections of **1e** and **1g** looking down the bonds C-2–C-1 and C-4–C-5

From the occurrence of the doubly stannylated derivatives **1e–g** we conclude that the dianionic species 1^{2-} (Scheme 3) is formed with *n*BuLi/*t*BuOK. This can be verified indirectly by partially quenching 1^{2-}: Reaction with THF gives the monoanion 1^{-} which is identified by its ^{13}C-NMR signals and which is easily converted into the monostannyl derivative **1d** as shown in the lower part of Scheme 3. The reaction sequence is also interesting from the preparative point of view because it increases the yield of **1d** to 81%.

Bicyclo[3.2.2]nona-2,6,8-trien-4-yl Anion (1^{-})

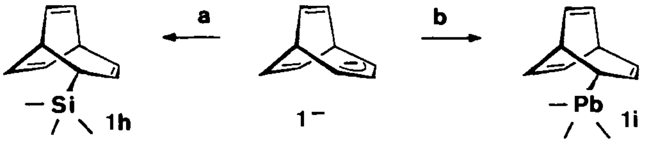
When Schemes 1 and 3 are combined a new synthesis of the anion 1^{-} results. It starts from cycloheptatriene like that of Grutzner and Winstein[7] but comprises only four steps: The addition of maleic acid anhydride to give **3z**, opening of the three-membered ring to give **1z**, electrolysis to give **1a**, and selective deprotonation resulting in the desired anion 1^{-}. The overall yield (8.2%) is somewhat lower than that estimated from the details given in ref.[7] (9–12%). A particularly easy-to-handle precursor of 1^{-}, and thus useful for storage, is **1d** which under very mild conditions (addition of MeLi at −78°C) yields 1^{-} quantitatively as evidenced by ^{13}C-NMR spectroscopy.

Silyl and Plumbyl Derivatives of 1a

Bicyclo[3.2.2]nona-2,6,8-trien-4-yllithium freshly prepared from **1d** reacts with Me$_3$SiCl and Me$_3$PbCl to give the corresponding silyl- and plumbyl-substituted molecules **1h** and **1i** in 89 and 76% yield, respectively (Scheme 4). When 1^{-} is formed by deprotonation of **1a** and Me$_3$SiCl is added in order to obtain **1h** no clean reaction is observed.

1h and **1i** are colorless liquids which react with water and oxygen; **1i** must be also protected against light. The ^{1}H- and ^{13}C-NMR spectra are very similar to those of **1d**, as expected, and the ^{29}Si and ^{207}Pb resonance lines (δ = 1.61 and 30.22, respectively) appear in the typical ranges[15].

Scheme 4

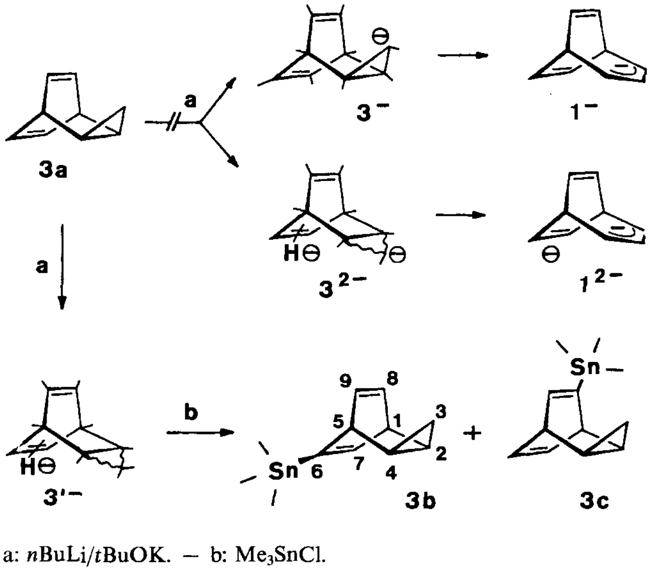


a: Me$_3$SiCl. – b: Me$_3$PbCl.

Deprotonation of Tricyclo[3.2.2.0^{2,4}]nona-6,8-diene (3a) and Quench with Me$_3$SnCl

It is well known that cyclopropyl derivatives undergo electrocyclic ring opening. Most pertinent to the present study is the conversion of 2,3,4-triphenyltricyclo-[3.2.1.0^{2,4}]octane to the 2,3,4-triphenylbicyclo[3.2.1]octane-4-yl anion by using *t*BuOK[16]. Similarly, the deprotonation of **3a** should be another attractive route to the anion 1^{-} all the more as the bisdecarboxylation of **3z** is more efficient than that of **1z** (Scheme 1). Also, from the above experiments we know that *n*BuLi/*t*BuOK does not only attack protons of strained double bonds but also reactive methylene protons. The formation of the anions 3^{-} (leading to 1^{-}) or 3^{2-} (two isomers leading to 1^{2-}) could therefore be anticipated (Scheme 5). However, the reaction of **3a** with *n*BuLi/*t*BuOK and, subsequently, with Me$_3$SnCl gives the monostannyl derivatives **3b** and **3c** as a 2:1 mixture in76% yield after distillation. Hence, the undesirable anion $3'^{-}$ (present as two isomers) is the main deprotonation product. A second less volatile fraction contains a mixture of products, the ^{1}H-, ^{13}C-, and ^{119}Sn-NMR spectra of which do not show the characteristic signals of bicyclo[3.2.2]nona-2,6,8-trien-4-yl or barbaralyl (resulting from rearrangement, see below) derivatives.

Scheme 5



a: *n*BuLi/*t*BuOK. – b: Me$_3$SnCl.

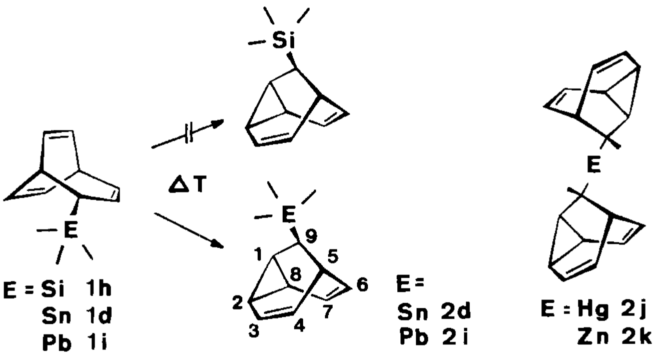
The ^{119}Sn-NMR spectra of **3b** and **3c** show signals in the expected range ($\delta = -37.45$ and -38.51). Both are accompanied by ^{13}C satellites [isotope shifts $^{1}\Delta^{119}$Sn(^{13}C) = 27 and 23 ppb; positive Δ means shifts to low frequency[17]] which are due to the coupling with CH_3. The ^{1}H- and ^{13}C-NMR spectra leave no doubt about the identity of **3b** and **3c**. Their signal pattern corresponds to that of the parent hydrocarbon[18] after perturbation by a stannyl group, and the signal assignment is further assured by the Sn,H and Sn,C couplings.

Bicyclo[3.2.2]nona-2,6,8-triene/Barbaralane Rearrangement

Formation of Barbaralanes

The stannyl derivative **1d** is thermally unstable. When heated to 150–160°C for less than one day its ^{119}Sn-NMR signal at $\delta = -1.54$ disappears, and a new one is observed at $\delta = 2.24$. Further characterization (see below) shows that the new quantitatively (NMR) formed compound is 9-trimethylstannylbarbaralane (**2d**) (Scheme 6). The plumbyl derivative **1i** is more labile and rearranges slowly at ambient temperature to give the corresponding barbaralane **2i**. This reaction may be monitored conveniently by observing the ^{207}Pb-NMR signals at $\delta = 30.22$ for **1i** and at $\delta = 38.18$ for **2i**. These signals show ^{13}C satellites with isotope shifts of $^{1}\Delta^{207}$Pb(^{13}C) = 85 and 102 ppb, respectively; as in most cases the lighter isotope is associated with the signal at higher frequency. After heating **1i** to 85–90°C for twelve hours only the signal of **2i** is retained.

Scheme 6



The two extreme examples we have investigated so far are derivatives substituted by Me_3Si (**1h**) and by mercury or zinc. No rearrangement is observed after keeping **1h** at 110–120°C for eight hours. Heating **1h** to 160°C for eighteen hours leads to complete decomposition. The NMR spectra of the reaction products show that the mixture of unknown species does not contain barbaralyl derivatives. By contrast, when the metal is mercury or zinc, the rearrangement is so rapid that instead of the bicyclo[3.2.2]nona-2,6,8-trien-4-yl derivatives only NMR resonances of the barbaralyl moiety can be detected after reaction of the anion $\mathbf{1}^-$ with $HgCl_2$ or $ZnCl_2$ and workup. The reaction products are colorless liquids which decompose at room temperature leaving behind a black metal powder. We have therefore limited our study to the characterization by NMR spectroscopy which does not prove the formulae of the compounds. However, the fact that two equivalents of intensive yellow $\mathbf{1}^-$ and one equivalent of colorless metal(II) halide react to yield colorless products leads us to suggest that dibarbaralylmercury (**2j**) and -zinc (**2k**) (Scheme 6) rather than species of the type RHgCl or RZnCl have been formed.

Spectroscopic Characteristics

The barbaralyl derivatives **2d**, **2i**, **2j**, and **2k** are fluxional molecules. This becomes evident from the ^{1}H- and ^{13}C-NMR spectra which, at room temperature and above, display only six rather than nine signals for the barbaralyl moiety. The origin is a rapid degenerate Cope rearrangement involving the carbon atoms 1 through 8 (Scheme 6). As a result a mirror plane seems to pass through C-3, C-7, and C-9. On cooling the sample the resonance lines of C-6/8, C-2/4, and C-1/5 broaden successively; a typical example is shown in Figure 2. This behavior has been first observed for other barbaralanes by Doering et al.[19] who used ^{1}H-NMR spectroscopy; a careful quantitative study has been performed by Günther et al.[20].

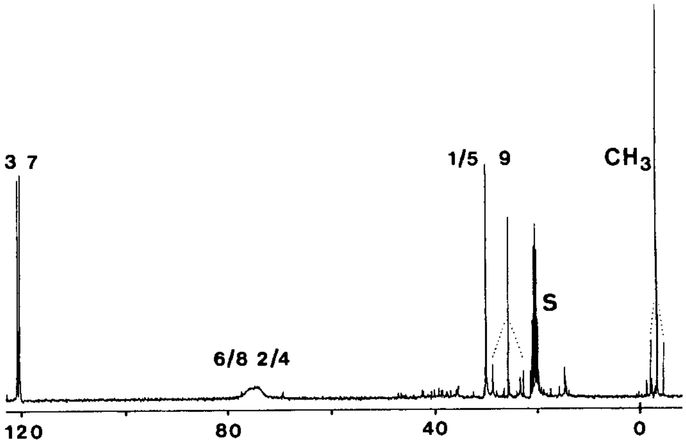


Figure 2. ^{13}C-NMR spectrum of trimethylplumbylbarbaralane (**2i**) in [D_8]toluene at -20°C; S = solvent; δ scale; large ^{207}Pb satellite splittings are indicated by dashed lines, for others see experimental part; essentially the same signals of impurities were present in the spectrum of the starting compound **1i**

Metal-hydrogen and metal-carbon couplings are observed for **2d**, **2i**, and **2j**, among them complete sets of $^{n}J(^{119/117}\mathrm{Sn},^{13}\mathrm{C})$ and $^{n}J(^{207}\mathrm{Pb},^{13}\mathrm{C})$ values. Couplings involving different nuclei E like ^{207}Pb and ^{119}Sn are best compared by using the reduced coupling constants $K(\mathrm{E},^{13}\mathrm{C})$; their square roots should increase with the atomic number of E[21]. In fact, the $^{3/4}K(^{207}\mathrm{Pb},^{13}\mathrm{C})$ values of **2i** and **1i** are ca. 1.9 times larger than the $^{3/4}K(^{119}\mathrm{Sn},^{13}\mathrm{C})$ values of **2d** and **1d**. This is somewhat more than the ratio of the atomic numbers (1.64).

The mass spectra reflect the higher stability of the barbaralyl moiety of **2d** and **2i** as compared to the bicyclo[3.2.2]nona-2,6,8-trien-4-yl moiety of **1d** and **1i**. For **2d** and **2i** successive loss of Me and loss of EMe_3 is observed before C_2H_2 is split off from the barbaralyl skeleton. By contrast, the bicyclic skeleton of **1d** and **1i** looses C_3H_4 while still being bound to the tin or lead atom.

Mechanistic Aspects

The experimental findings of the title rearrangement are in accord with a shift of the metal substituent (filled circle in Figure 3) of **1** from position 4 to 6 which corresponds to a 1,5-homodienyl metallatropic shift[22]. Thus, the reactivity increases on passing from Si (**1h**) to Sn (**1d**) and Pb (**1i**). This parallels the trend that is known for cyclopentadienes substituted by Me_3E and HgX groups[23]. The latter compounds experience a series of simple 1,5-dienyl shifts leading to identical molecules whereas the 1,5-homodienyl shift transforms **1** into **2** which does not rearrange further at the given temperature. It is unlikely that **2** forms in a radical reaction because $\mathbf{2}^{\bullet}$ is unstable[5]. At most, a concurrent homolysis of the C-4–E bond of **1** could produce $\mathbf{1}^{\bullet}$ and $Me_3E^{\bullet}$ which are expected to recombine to **1**. Another point of interest is that no barbaralyl derivatives are observed after heating the monostannyl isomers **1b** and **1c** (Scheme 2) or the distannyl isomers **1e**, **1f**, and **1g** (Scheme 3). One reason is that the rearrangement of **1e–g** should lead to geminal or vicinal Me_3E groups which suffer from steric hindrance. The other reasons become obvious when we draw a six-membered transition structure including the carbon atoms indicated in Figure 3A by open circles. A similar transition structure cannot be drawn for **1b** and **1c**, and the transformation of **1e–g** into less hindered products requires antarafacial reactions which are not allowed.

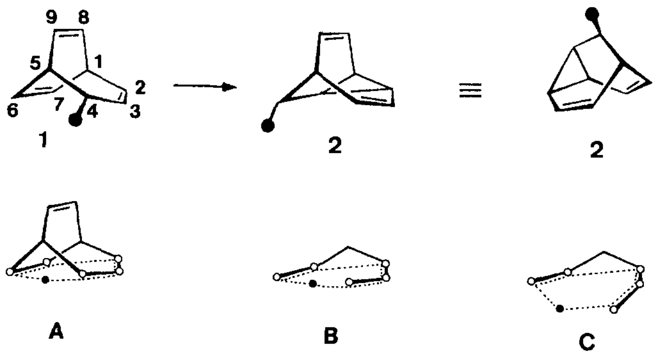


Figure 3. 1,5-Homodienyl shift transforming the bicyclo[3.2.2]nona-2,6,8-trien-4-yl skeleton **1** into the barbaralyl skeleton **2** (top); transition structure suggested for **1** → **2** (**A**), *endo* transition structure (**B**), *exo* transition structure[25] (**C**) (bottom)

The nature of the transition state and the barrier of activation are of general interest because both are related to the relative stability of the bicyclo[3.2.2]nona-2,6,8-trienyl and the barbaralyl skeleton as discussed in the introduction. The transition structures of 1,5-homodienyl prototropic shifts have been studied experimentally by Daub and Berson[24] and theoretically by Loncharich and Houk[25]. They demonstrate that for the *cis*-1-methyl-2-vinylcyclopropane system both the *endo* and *exo* transition structure (**B** and C in Figure 3, where the filled circles are hydrogen atoms) are allowed and that the *endo* version is more favorable. As for the bicyclic system **1** there is no choice between two transition structures. Comparison of Figures 3A, **B**, and C shows that the *endo* version is forced by the stereochemistry, a fact which might facilitate the reaction. However, more important for a clean and easy reaction to barbaralyl derivatives **2** should be the lowering of the activation barrier by introducing a metal–carbon bond. Its strength is well known to decrease when heavier metal atoms are engaged, and this is reflected in the increase of reactivity on going from silicon in **1h** via tin in **1d** to lead in **1i**. When a C–H bond is engaged the system is less well-behaved. Thus, as shown by Tsuji et al.[9], the thermal reaction of the parent hydrocarbon **1a** gives vinylcycloheptatrienes whereas its benzo analogue gives 3,4-benzobarbaralane.

The activation barrier may be also influenced by the polarity of the transition state. An example is (trimethylsilyl)-cyclopentadiene for which Schulman et al.[26] have shown that in case the silyl group experiences a 1,5-dienyl shift the polarization of the Si–C bond in the transition state is small. By contrast, a moving hydrogen atom is distinctly electropositive ($\delta+$). We apply this tentatively to the rearrangement **1** → **2** and conclude that the hydrocarbon skeleton should be $\delta-$ in the transition state when a hydrogen shift occurs. Since such a shift cannot be observed experimentally[9] the corresponding barrier must be high. This is expected when transition structures close to both **1** and **2** are engaged and when these structures are rather polar, because either $\mathbf{1}^+$ or $\mathbf{2}^-$ is high in energy[1,2]. It follows that metal substitution as in **1d** and **1i** should contribute to a lower activation barrier by leading to a less polar transition state.

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Experimental

If not stated otherwise all reactions were carried out under inert gas by using standard Schlenk techniques and solvents free of oxygen and moisture. The elemental analyses were performed in the microanalytical laboratory (Anorganisch-chemisches Institut). The mass spectra were obtained with a Varian MAT 311A instrument (electron-impact mode, 70 eV). All NMR spectra were recorded with a Jeol JNM-GX 270 spectrometer by using sample tubes with a 5-mm diameter for ^1H and ^{13}C and with a 10-mm diameter for all other nuclei. The ^1H- and ^{13}C-NMR signal shifts were measured relative to the solvent signals and calculated relative to TMS by using $\delta(^1H)$ = 7.24 and 7.15 for $CHCl_3$ and benzene, $\delta(^{13}C)$ = 77.0 and 67.4 for $CDCl_3$ and C-2/5 of $[D_8]THF$, and $\delta(^{29}Si)$ = 6.9 for $[(CH_3)_3Si]_2O$. The $\delta(^{119}Sn)$ and $\delta(^{207}Pb)$ values were measured relative to $SnMe_4$ and $PbMe_4$. For the determination of isomer ratios by ^{13}C-NMR spectroscopy only signals of carbon atoms were used which can be expected to have similar relaxation times (e.g. analogous CH_2 and $SnMe_3$ groups).

Bicyclo[3.2.2]nona-2,6,8-triene (**1a**): The method of Tsuji et al.[9] was used with some modifications. 150 g (1.60 mol) of cycloheptatriene and 184 g (1.90 mol) of maleic anhydride were heated under reflux in *o*-xylene for 12 h as described previously[10]. Slow cooling and partial evaporation of the solvent gave 225 g of tricyclo[3.2.2.$0^{2,4}$]non-8-ene-6,7-dicarboxylic anhydride (**3z**). Upon further stripping of the solvent, another 57.1 g of the product was obtained (overall yield 91%). – ^{13}C NMR ([D_6]acetone): δ/^{1}J(C,H) [Hz] = 5.2/162.9, 159.4 (t, C-3), 9.8/170.2 (d, C-2/4), 34.2/144.0 (d, C-1/5), 46.5/143.8 (d, C-6/7), 129.1/168.5 (d, C-8/9), 173.5 (s, C=O); ^{1}J(C,C) [Hz] = 16.6 ($J_{2/3}$), 39.6 ($J_{1/2}$), 39.1 ($J_{1/8}$), 30.1 ($J_{1/7}$), 50.6 ($J_{7/\mathrm{CO}}$).

35.3 g (0.20 mol) of **3z** was dissolved in 250 ml of chlorobenzene and heated in an autoclave to 230°C for ca. 12 h. After cooling the mixture to ambient temperature, the solvent was evaporated under vacuum and the ocher-yellow residue extracted four times with boiling CCl_4. After removing the solvent from the combined extracts, recrystallisation from $CHCl_3$ gave 29.1 g (82%) of bicyclo[3.2.2]nona-2,8-diene-6,7-dicarboxylic anhydride (**1z**). – ^{13}C NMR ($CDCl_3$): δ/^{1}J(C,H) [Hz] = 32.5/126.2 (t, C-4), 33.5/130.6 (d, C-5), 34.7/134.5 (d, C-1), 45.9/139.4 (d, C-6), 49.6/139.4 (d, C-7), 128.9/156.5 (d, C-3), 129.2/159.9 (d, C-2), 129.2/163.9 (d, C-9), 136.0/166.3 (d, C-8), 172.5 (s, C=O next to C-7), 173.7 (s, C=O next to C-6).

We were unable to reproduce the yield[9] of **1a** by oxidative decarboxylation of **1z** in a simple electrolysis apparatus[11a]. In a typical run 4.75 g (25.0 mmol) of **1z** in 85 ml of pyridine, 15 ml of H_2O, and 4 ml of NEt_3 gave 0.23 g (8%) of **1a**. Furthermore, attempts to scale up the reaction decreased the yield. We have therefore used a capillary slit cell[27] [anode: cylindrical platinum plate (230 cm^2); cathode: stainless steel cylinder; slit: 1 mm] incorporated in a continuous-flow apparatus. Reproducible results were obtained as follows: 18.2 g (96.0 mmol) of **1z**, dissolved in 340 ml of pyridine, 60 ml of H_2O and 16 ml of NEt_3, was electrolyzed for 6 h at 10°C, with a current of 1 A and a flow rate of 8 l/min. The black reaction mixture was diluted with 400 ml of a saturated solution of NaCl in H_2O and extracted several times with pentane (4 l). After washing with 400 ml of diluted HCl and 400 ml of H_2O, the organic layer was dried with $MgSO_4$, the solvent was removed under reduced pressure and the residue distilled at 1500 Pa. Collection of the fraction boiling near 65°C gave 1.23 g (11%) of **1a**.

Deprotonation of **1a** *with tBuLi/TMEDA and Quench with Me_3SnCl:* 2.40 ml (3.40 mmol) of a 1.4 M solution of *t*BuLi in hexane was diluted with 30 ml of pentane, cooled to −78°C, and 0.50 ml (3.40 mmol) of TMEDA and 0.40 g (3.40 mmol) of **1a** were added under stirring. The mixture became light yellow and, after raising the temperature to 25°C over ca. 12 h, turned to dark red-brown. After cooling to −78°C, 1.49 g (7.50 mmol) of Me_3SnCl in a few ml of pentane was added whereupon the color disappeared. The mixture was warmed to 25°C, hydrolyzed, and the solvents were removed from the organic layer. Distillation in a short-path apparatus[28] at 0.1 Pa and a heating bath temperature of 30–120°C gave 0.39 g of a mixture that contained 6-trimethylstannylbicyclo[3.2.2]nona-2,6,8-triene (**1b**), 7-trimethylstannylbicyclo[3.2.2]nona-2,6,8-triene (**1c**), and **1a** in a molar ratio of 8:7:8 as determined by ^{13}C-NMR spectroscopy. This corresponds to a yield of 22 and 19% (relative to consumed **1a**) for **1b** and **1c**, respectively. **1a** was removed by repeated distillation as described above. – ^{1}H NMR ($CDCl_3$): **1b**: δ = 0.15 [^{2}J(Sn,H) = 54.6 Hz; s, 9H, CH_3], 2.15 (2H, 4-H*), 3.00 (1H, 5-H*), 3.17 (q, 1H, 1-H), 4.93 (1H, 3-H*), 5.96 (1H, 2-H*), 6.18 (t, 1H, 9-H), 6.57 (t, 1H, 8-H*), 6.73 (d, 1H, 7-H); **1c**: δ = 0.14 [^{2}J(Sn,H) = 54.8 Hz; s, 9H, CH_3], 2.15 (2H, 4-H*), 3.00 (1H, 5-H*), 3.25 (t, 1H, 1-H), 4.93 (1H, 3-H*), 5.96 (1H, 2-H*), 6.18 (t, 1H, 9-H*), 6.32 (d, 1H, 6-H), 6.57 (t, 1H, 8-H*); * indicates signals which may not be distinguished for the two isomers. – ^{13}C NMR ($CDCl_3$): **1b**: δ/^{n}J(Sn,C) [Hz] = −9.8/345.5 (CH_3), 27.3/4.9 (C-4), 37.8/50.6 (C-1), 40.3/43.3 (C-5), 126.0/<1 (C-3), 130.0/20.1 (C-9), 131.7/11.2 (C-2), 137.7/8.3 (C-8), 142.5/not detected (C-6), 146.8/32.5 (C-7); **1c**: δ/^{n}J(Sn,C) [Hz] = −10.1/346.5 (CH_3), 27.6/11.2 (C-4), 36.6/49.9 (C-5), 41.3/44.3 (C-1), 125.9/<1 (C-3), 129.5/8.3 (C-9), 131.9/7.1 (C-2), 138.3/20.8 (C-8), 138.8/31.1 (C-6), 151.3/452.2 (C-7). – ^{119}Sn NMR ($CDCl_3$): δ = −35.9 (**1b**), −38.2 (**1c**).

$C_{12}H_{18}Sn$ (281.0, mixture of isomers **1b** and **1c**)
Calcd. C 51.30 H 6.46
Found C 51.08 H 6.50

Deprotonation of **1a** *with nBuLi/tBuOK and Quench with Me_3SnCl:* In a procedure completely analogous to the previous one, a mixture of 1.47 g (12.0 mmol) of *t*BuOK, 6.80 ml (12.0 mmol) of a 1.77 M solution of *n*BuLi in hexane, and 100 ml of hexane was treated with 0.50 g (4.20 mmol) of **1a**. Very similar color changes were observed, and the distillation of the crude product at 0.07 Pa gave two fractions. Up to a heating bath temperature of 90°C 0.64 g (54%) of NMR-spectroscopically pure 4-trimethylstannylbicyclo[3.2.2]nona-2,6,8-triene (**1d**) was collected as a colorless liquid. By increasing the temperature to 130°C 0.42 g of a yellow viscous liquid was obtained which was a mixture of *endo*-4,7-bis(trimethylstannyl)bicyclo[3.2.2]nona-2,6,8-triene (**1e**), *exo*-4,6-bis(trimethylstannyl)bicyclo[3.2.2]nona-2,6,8-triene (**1f**), and *exo*-4,7-bis(trimethylstannyl)bicyclo[3.2.2]nona-2,6,8-triene (**1g**) in a molar ratio of 2.1:1.6:1.0 (^{13}C NMR); yields 10, 8, and 5% (relative to **1a**) for **1e**, **1f**, and **1g**, respectively.

1d: MS: *m/z* (%) = 282 (2) [M^+], 267 (7) [$M^+ - CH_3$], 227 (13) [$M^+ - CH_3 - C_3H_4$], 197 (5) [$C_6H_5Sn^+$], 165 (100) [Me_3Sn^+], 117 (53) [$C_9H_9^+$], 91 (43) [$C_7H_7^+$]. – ^{1}H NMR ($CDCl_3$): δ = 0.13 [J(Sn,H) = 52.4 Hz; s, 9H, CH_3], 2.28 [J(Sn,H) = 90.3 Hz; dt, $J_{2,4}$ = 2.2 Hz, $J_{3,4}$ = 3.9 Hz, 1H, 4-H], 2.89 (m, $J_{5,6} \approx J_{5,9}$ = 7.2 Hz, 1H, 5-H), 2.98 (dq, $J_{1,7} \approx J_{1,8}$ = 7.2 Hz, $J_{1,6}$ = 1.5 Hz, 1H, 3-H), 5.02 [J(Sn,H) = 23.4 Hz; ddt, $J_{1,3} \approx J_{3,5}$ = 1.0 Hz, $J_{3,4}$ = 3.9 Hz, 1H, 3-H], 5.63 [J(Sn,H) = 22.5 Hz; dt, $J_{2,3}$ = 10.5 Hz, $J_{1,2}$ = 7.8 Hz, $J_{2,4}$ = 2.2 Hz, 1H, 2-H], 5.98 (tm, $J_{5,6} \approx J_{6,7}$ = 7.2 Hz, $J_{6,9}$ = 0.7 Hz, 1H, 6-H*), 6.05 (tm, $J_{8,9}$ = 7.2 Hz, $J_{1,9} \approx J_{6,9}$ = 0.7 Hz, 1H, 9-H*), 6.35 (tt, $J_{5,8} \approx J_{7,8}$ = 1.0 Hz, $J_{1,8} \approx J_{8,9}$ = 7.2 Hz, 1H, 8-H**), 6.51 (t, $J_{6,7} \approx J_{1,7}$ = 7.2 Hz, $J_{7,8}$ = 1.0 Hz, 1H, 7-H**); *, ** pairwise interchange of resonances not excluded. – ^{13}C NMR ($CDCl_3$): δ/^{n}J(Sn,C) [Hz]/^{1}J(C,H) [Hz] = −9.4/313.3/128.6 (CH_3), 29.4/313.9/129.1 (C-4), 35.5/11.9/135.0 (C-1), 37.0/10.1/130.6 (C-5), 123.8/44.9/160.4 (C-2), 127.4/69.3/160.4 (C-9), 128.2/18.1/160.4 (C-6), 129.0/37.7/153.3 (C-3), 135.0/18.3/166.0 (C-7*), 136.0/22.6/163.3 (C-8*); * interchange of signals not excluded. – ^{119}Sn NMR ($CDCl_3$): δ = −1.5.

$C_{12}H_{18}Sn$ (281.0) Calcd. C 51.30 H 6.46
Found C 51.45 H 6.66

1e: ^{13}C NMR ($CDCl_3$): δ/^{n}J(Sn-4,C) [Hz]/^{n}J(Sn-7,C) [Hz] = −10.0/<1/345.5 (7-$SnCH_3$), −9.3/311.0/<1 (4-$SnCH_3$), 30.1/315.7/13.0 (C-4), 38.6/9.0/54.4 (C-5), 40.9/12.0/43.8 (C-1), 124.1/45.5/7.1 (C-2), 127.5/70.4/8.3 (C-6), 129.0/38.4/<1 (C-3), 136.7/21.8/23.0 (C-7), 137.2/15.7/27.9 (C-9), 148.1/15.4/not found (C-8). – ^{119}Sn NMR ($CDCl_3$): δ = −38.5 (Sn-7), −1.5 (Sn-4); ^{5}J(Sn,Sn) = 30.9 Hz.

1f: ^{13}C NMR ($CDCl_3$): δ/^{n}J(Sn-4,C) [Hz]/^{n}J(Sn-6,C) [Hz] = −9.6/<1/342.6 (6-$SnCH_3$), −9.3/311.1/<1 (4-$SnCH_3$), 29.6/314.5/4.2 (C-4), 37.4/12.0/51.1 (C-1), 42.4/11.2/42.1 (C-5), 124.0/45.2/11.5 (C-2), 128.8/21.0/23.0 (C-9), 128.9/37.7/<1 (C-3), 135.0/17.6/8.3 (C-8), 139.9/63.6/not found (C-6), 144.9/20.1/29.8 (C-7). – ^{119}Sn NMR ($CDCl_3$): δ = −37.5 (Sn-6), −2.5 (Sn-4); ^{4}J(Sn,Sn) = 50.5 Hz.

1g: ^{13}C NMR ($CDCl_3$): δ/^{n}J(Sn-4,C) [Hz]/^{n}J(Sn-7,C) [Hz] = −9.8/<1/342.8 (7-$SnCH_3$), −9.4/310.8/<1 (4-$SnCH_3$), 29.8/316.7/9.2 (C-4), 38.8/11.2/49.4 (C-5), 40.9/12.0/44.0 (C-1), 123.9/45.2/6.8 (C-2), 128.1/18.1/8.3 (C-9), 129.1/38.4/<1 (C-3), 135.8/18.1/23.8 (C-8), 136.2/67.0/27.9 (C-6), 149.0/19.6/not found (C-7). – ^{119}Sn NMR

136.2/67.0/27.9 (C-6), 149.0/19.6/not found (C-7). – ^{119}Sn NMR ($CDCl_3$): $\delta = -37.6$ (Sn-7), -1.9 (Sn-4); ^5J(Sn,Sn) = 53.7 Hz.

$C_{15}H_{26}Sn_2$ (443.8, mixture of isomers **1e**, **1f**, and **1g**)
Calcd. C 40.60 H 5.91
Found C 40.92 H 6.19

4-Trimethylstannylbicyclo[3.2.2]nona-2,6,8-triene (**1d**): A deprotonation reaction as described in the previous experiments was carried out with 3.92 g (33.0 mmol) of **1a** and a mixture of 5.60 g (50.0 mmol) of *t*BuOK, 200 ml of pentane, and 22.0 ml (50.0 mmol) of a 2.29 M solution of *n*BuLi in hexane. The red-brown mixture which had formed after warm-up was cooled to –78 °C, and 100 ml of THF was added. After stirring for 30 min, 10.0 g (50.0 mmol) of Me_3SnCl was added. While slowly warming to ambient temperature the mixture became colorless. Workup as described above gave 7.55 g (81%) of **1d** after distillation.

In a parallel experiment the metallation mixture was filtered through a frit, and the red-brown solid material was washed with pentane. Then THF, precooled to –78 °C, was added under vigorous stirring until the solid was dissolved completely. The ^{13}C-NMR spectrum of this solution showed the signals of **1**$^-$**K**$^+$ which were in accord with literature reports[8,29].

Bicyclo[3.2.2]nona-2,6,8-triene-4-yllithium (**1**$^-$**Li**$^+$): Approximately 0.05 g of **1d** was dissolved in 2 ml of THF and cooled to –78 °C. When an equimolar amount of MeLi, dissolved in Et_2O, was added an immediate color change to intense lemon-yellow occurred. The ^{13}C-NMR spectrum of this solution showed no signals of **1d**. – ^{13}C NMR (THF, 0 °C): δ = 35.21 (C-1/5), 58.80 (C-2/4), 112.01 (C-6/9), 119.38 (C-3); the signals are similar to those given for **1**$^-$**Li**$^+$ in the literature[8].

4-Trimethylsilylbicyclo[3.2.2]nona-2,6,8-triene (**1h**): 0.50 g (1.80 mmol) of **1d** was converted into **1**$^-$**Li**$^+$ as described, and Me_3SiCl was added dropwise until the mixture was colorless. The solution was brought to room temperature, the solvent was stripped, and the residue extracted with 200 ml of pentane. After filtering through Na_2SO_4 and removal of the solvent under reduced pressure, 3.00 g (89%) of a colorless liquid was obtained which was pure **1h**. – ^{1}H NMR (C_6D_6): δ = 0.13 (s, 9H, CH_3), 1.55 (br. q, 1H, 4-H), 2.78 (m, 1H, 5-H), 2.82 (br. q, 1H, 1-H), 5.00 (dddd, $J_{1,3}$ = 1.5 Hz, $J_{2,3}$ = 10.6 Hz, $J_{3,4}$ = 3.7 Hz, $J_{3,5}$ = 0.7 Hz, 1H, 3-H), 5.83 (ddd, $J_{1,2}$ = 7.8 Hz, $J_{2,3}$ = 10.6 Hz, $J_{2,4}$ = 2.7 Hz, 1H, 2-H), 5.93 (td, $J_{5,6} \approx J_{6,7}$ = 7.3 Hz, $J_{6,9}$ = 0.7 Hz, 1H, 6-H**), 6.09 (dddd, $J_{8,9}$ = 7.3 Hz, $J_{1,9} \approx J_{6,9}$ = 0.7 Hz, $J_{5,9}$ = 6.1 Hz, 1H, 9-H**), 6.39 (t, $J_{8,9} \approx J_{1,8}$ = 7.3 Hz, 1H, 8-H*), 6.49 (t, $J_{6,7} \approx J_{1,7}$ = 7.3 Hz, 1H, 7-H*); *, ** pairwise interchange of signals not excluded. – ^{13}C NMR ($CDCl_3$): $\delta/^1J$(C,H) [Hz] = –1.9/118.8 (CH_3), 30.1/118.6 (C-4), 35.6/132.8 (C-1*), 35.8/132.8 (C-5*), 127.3/153.3 (C-3), 127.6/161.9 (C-9), 128.9/161.6 (C-6), 129.2/161.6 (C-2), 135.9/163.8 (C-7), 137.5/163.4 (C-8); * interchange of signals not excluded. – ^{29}Si NMR ($CDCl_3$): δ = 1.6.

$C_{12}H_{18}Si$ (190.4) Calcd. C 75.72 H 9.53
Found C 75.58 H 9.63

4-Trimethylplumbylbicyclo[3.2.2]nona-2,6,8-triene (**1i**): 0.50 g (1.80 mmol) of **1d** was converted into **1**$^-$**Li**$^+$ as described, and 0.52 g (1.80 mmol) of Me_3PbCl was added at –78 °C. After workup as described for **1h**, 0.52 g (78%) of pure **1i** was obtained. – MS (70 eV): *m/z* (%) = 370 (3) [M^+], 355 (14) [$M^+ - CH_3$], 325 (4) [$M^+ - 3\ CH_3$], 315 (22) [$C_6H_5Pb(CH_3)_2^+$], 285 (15) [$C_6H_5Pb^+$], 253 (87) [$Pb(CH_3)_3^+$], 223 (32) [$PbCH_3^+$], 208 (44) [Pb^+], 117 (100) [$C_9H_9^+$], 91 (62) [$C_7H_7^+$]. – ^{1}H NMR (C_6D_6, 20 °C): δ = 0.74 [J(Pb,H) = 52.0 Hz; s, 9H, CH_3], 2.89 [J(Pb,H) = 107.7 Hz; m, 1H, 4-H], 3.00 (m, 1H, 5-H*), 3.02 (m, 1H, 1-H*), 5.09 [J(Pb,H) = 45.4 Hz; ddd, $J_{1,3}$ = 0.9 Hz, $J_{2,3}$ = 10.3 Hz, $J_{3,4}$ = 4.2 Hz, 1H, 3-H], 5.54 [J(Pb,H) = 45.8 Hz; ddd, $J_{1,2}$ = 7.8 Hz, $J_{2,3}$ = 10.3 Hz, $J_{2,4}$ = 1.7 Hz, 1H, 2-H], 5.99 (t, $J_{6,7} \approx J_{5,6}$ = 7.1 Hz, 1H, 6-H**), 6.10 (t, $J_{5,9} \approx J_{8,9}$ = 7.0 Hz, 1H, 9-H**), 6.34 (t, $J_{1,8} \approx J_{8,9}$ = 7.0 Hz, 1H, 8-H***), 6.53 (t, $J_{1,7} \approx J_{6,7}$ = 7.1 Hz, 1H, 7-H***); * partially overlapping signals; **, *** pairwise interchange of signals not excluded. – ^{13}C NMR ($CDCl_3$, 20 °C): $\delta/^nJ$(Pb,C) [Hz]/^1J(C,H) [Hz] = –1.3/151.1/135.0 (CH_3), 35.5/23.7/135.0 (C-1), 36.7/276.1/136.7 (C-4), 38.6/11.7/133.5 (C-5), 123.5/88.8/160.2 (C-2), 127.5/120.1/166.0 (C-9), 128.5/35.7/163.1 (C-6), 129.9/59.7/153.1 (C-3), 134.0/37.7/162.6 (C-7), 136.3/46.0/159.9 (C-8). – ^{207}Pb NMR (C_6D_6, 20 °C): δ = 30.2 [J(Pb,CH_3) = 151.8 Hz, $^1\Delta^{207}$Pb(^{13}C) = 85 ppb].

$C_{12}H_{18}Pb$ (369.5) Calcd. C 39.01 H 4.91
Found C 39.00 H 4.66

Tricyclo[3.2.2.0^{2,4}]nona-6,8-diene (**3a**): 18.2 g (96.0 mmol) of **3z** was decarboxylated in the capillary slit cell as described for **1a**. After analogous workup, 1.69 g (15%) of **3a** was obtained. The ^{1}H- and ^{13}C-NMR data were in accord with those given in the literature[18].

6-Trimethylstannyltricyclo[3.2.2.0^{2,4}]nona-6,8-diene (**3b**) *and 8-Trimethylstannyltricyclo[3.2.2.0^{2,4}]nona-6,8-diene* (**3c**): 1.50 g (13.0 mmol) of **3a** was metallated with 2.24 g (20.0 mmol) of *t*BuOK and 8.80 ml of a 2.29 M (20.0 mmol) solution of *n*BuLi in hexane and treated with Me_3SnCl as described for **1d**. After aqueous workup, distillation at 0.1 Pa gave 2.79 g (76%) of **3b** and **3c** in a molar ratio of 2:1 (NMR) as a slightly yellow viscous liquid. The products of a higher boiling fraction were not identified. – ^{1}H NMR ($CDCl_3$): **3b**: δ = 0.18 [J(Sn,H) = 54.7 Hz; s, 9H, CH_3], 0.49 (m, 2H, 3-$H_{syn/anti}$), 1.09 (m, 2H, 2/4-H), 3.68 (quint, 1H, 1-H), 3.82 (q, 1H, 5-H), 5.97 (t, 2H, 8/9-H), 6.81 (dd, 1H, 7-H); **3c**: δ = 0.17 [J(Sn,H) = 54.9 Hz; s, 9H, CH_3], 0.67 (m, 2H, 3-$H_{syn/anti}$), 1.09* (m, 1H, 4-H), 3.69* (m, 1H, 5-H), 3.82* (m, 1H, 1-H), 5.97* (m, 1H, 9-H), 6.59 (m, 2H, 6/7-H); * overlapped by the signals of **3b**. – ^{13}C NMR ($CDCl_3$): **3b**: $\delta/^nJ$(Sn,C) [Hz]/^1J(C,H) [Hz] = –10.1/349.4/128.4 (CH_3), 16.4/162.6 (C-3), 18.0/7.3*/170.2 (C-2/4), 39.8/41.1/141.1 (C-1), 44.0/41.1/140.9 (C-5), 129.9/9.5/170.0 (C-8), 130.5/14.7/167.0 (C-9), 149.1/36.4/168.5 (C-7), 151.1/468.5/– (C-6); * assignment of coupling constants not sure; **3c**: $\delta/^nJ$(Sn,C) [Hz]/^1J(C,H) [Hz] = –10.2/349.4/128.4 (CH_3), 16.5/–/162.6, 155.3 (C-3), 17.4/10.8/169.2 (C-4*), 17.8/8.8/overlapped (C-2*), 40.3/45.5/140.1 (C-5), 43.2/41.3/138.7 (C-1), 138.3/9.0/165.3 (C-6), 139.3/15.9/168.2 (C-7), 140.4/32.5/166.3 (C-9), 142.4/not found/– (C-8); * interchange of resonances not excluded. – ^{119}Sn NMR ($CDCl_3$): **3b**: δ = –37.5 [J(Sn,CH_3) = 349.4 Hz, $^1\Delta^{119}$Sn(^{13}C) = 27 ppb]; **3c**: δ = –38.5 [J(Sn,CH_3) = 349.0 Hz, $^1\Delta^{119}$Sn(^{13}C) = 23 ppb].

$C_{12}H_{18}Sn$ (281.0, mixture of isomers **3b** and **3c**)
Calcd. C 51.30 H 6.46
Found C 51.14 H 6.64

9-Trimethylstannylbarbaralane (**2d**): **3d** was heated in a metal bath to 150–160 °C for 18 h. According to the ^{1}H- and ^{13}C-NMR spectra complete rearrangement to **2d** had taken place. – MS: *m/z* (%) = 282 (5) [M^+], 267 (13) [$M^+ - CH_3$], 165 (100) [$Sn(CH_3)_3^+$], 117 (62) [$C_9H_9^+$], 91 (39) [$C_7H_7^+$], 65 (11) [$C_7H_7^+ - C_2H_2$]. – ^{1}H NMR ($CDCl_3$, 20 °C): δ = 0.02 [J(Sn,H) = 52.0 Hz; s, 9H, CH_3], 0.86 (br. s, 9-H), 2.46 (t, $J_{4,5} \approx J_{5,6}$ = 6.1 Hz, 2H, 1/5-H), 4.04 (m, 2H, 2/4-H), 4.06 (m, 2H, 6/8-H), 5.64 (t, $J_{2,3} \approx J_{3,4}$ = 7.8 Hz, 1H, 3-H*), 5.70 (t, $J_{6,7} \approx J_{7,8}$ = 7.7 Hz, 1H, 7-H*); * interchange of signals not excluded. – ^{13}C NMR ($CDCl_3$, 20 °C): $\delta/^nJ$(Sn,C) [Hz]/^1J(C,H) [Hz] = –10.3/313.7/128.1 (CH_3), 15.2/405.9/133.5 (C-9), 28.2/8.8/153.6 (C-1/5), 74.0/8.8*/168.5 (C-2/4), 75.3/53.1/155.5 (C-6/8), 121.2/7.1/159.4 (C-7), 122.1/2.7/159.4 (C-3); * at 100 °C. – ^{119}Sn NMR (C_6D_6, 20 °C): δ = 2.2.

$C_{12}H_{18}Sn$ (281.0) Calcd. C 51.30 H 6.46
Found C 51.54 H 6.69

9-Trimethylplumbylbarbaralane (**2i**): **1i** was dissolved in toluene and heated to 85–90°C for 12 h. Investigation of the sample by ^{1}H- and ^{13}C-NMR spectroscopy showed that complete rearrangement to 9-trimethylplumbylbarbaralane (**2i**) had occurred. Slow rearrangement was also observed at room temperature. – MS: *m/z* (%) = 370 (4) [M^+], 355 (13) [$M^+ - CH_3$], 325 (3) [$M^+ - 3\ CH_3$], 208 (23) [Pb^+], 117 (100) [$C_9H_9^+$], 91 (45) [$C_7H_7^+$], 65 (12) [$C_7H_7^+ - C_2H_2$], 51 (6) [$C_7H_7^+ - C_3H_4$]. – ^{1}H NMR ($CDCl_3$, 20°C): δ = 0.65 [J(Pb,H) = 54.2 Hz; s, 9H, CH_3], 1.64 (br. s, 1H, 9-H), 2.54 (dt, $J_{4,5} \approx J_{5,6}$ = 6.0 Hz, $J_{5,9}$ = 2.4 Hz, 2H, 1/5-H), 4.06 (m, 2H, 2/4-H*), 4.09 (m, 2H, 6/8-H*), 5.66 (t, $J_{2,3} \approx J_{3,4}$ = 7.7 Hz, 1H, 3-H**), 5.67 (t, $J_{6,7} \approx J_{7,8}$ = 7.7 Hz, 7-H**); *, ** interchange of signals not excluded. – ^{13}C NMR ($CDCl_3$, 20°C): $\delta/^nJ$(Pb,C) [Hz]/^1J(C,H) [Hz] = –3.4/174.6/134.0 (CH_3), 25.4/399.6/140.4 (C-9), 29.9/7.8/153.1 (C-1/5), 74.5/17.4*/164.1 (C-2/4), 76.1/91.9*/165.6 (C-6/8), 121.5/5.1/159.7 (C-3), 121.0/15.4/159.2 (C-7); * at 100°C. – ^{207}Pb NMR (C_6D_6, 20°C): δ = 38.2 [^1J(Pb,CH_3) = 173.9 Hz, $^1\Delta^{207}$Pb(^{13}C) = 102 ppb].

$C_{12}H_{18}Pb$ (369.5) Calcd. C 39.01 H 4.91
Found C 39.05 H 4.69

Reaction of **1^-Li^+** *with $HgCl_2$:* 0.50 g (1.80 mmol) of **1d** was converted into **1^-Li^+** as described. When 0.24 g (0.90 mmol) of dry $HgCl_2$, dissolved in 10 ml of THF, was added at –78°C, the initially dark brown mixture became orange-brown rapidly. After warming to room temperature, all volatiles were removed, and the residue was extracted with pentane. After combining the extracts, filtering through Na_2SO_4 and removal of the solvent, 0.16 g (41%) of a slightly yelllow oil was obtained. The product decomposed at room temperature, particularly in the presence of light, to give metallic mercury. Based on the NMR data and arguments given above it behaves as expected for dibarbaralylmercury **2j**. – ^{1}H NMR ($CDCl_3$, 20°C): δ = 1.30 (br. s, 1H, 9-H), 2.53 (td, $J_{4,5} \approx J_{5,6}$ = 6.7 Hz, $J_{5,9}$ = 1.7 Hz, 2H, 1/5-H), 4.08 (m, 2H, 2/4-H), 4.16 (m, 2H, 6/8-H), 5.56 (t, $J_{2,3} \approx J_{3,4}$ = 7.8 Hz, 1H, 3-H), 5.78 (t, $J_{6,7} \approx J_{7,8}$ = 7.8 Hz, 1H, 7-H). – ^{13}C NMR ($CDCl_3$, 20°C): $\delta/^1J$(C,H) [Hz] = 29.0/151.4 (C-1/5), 47.3/136.0 (C-9), 75.4/162.9 [J(Hg,C) = 16.1 Hz; C-2/4], 76.3/161.4 (C-6/8), 122.3/159.0 (C-3), 121.1/159.0 [J(Hg,C) = 13.0 Hz; C-7].

Reaction of **1^-Li^+** *with $ZnCl_2$:* **1^-Li^+** was treated with $ZnCl_2$ as described for $HgCl_2$ in the previous experiment. A metallic powder (presumably Zn) formed rapidly when standing at room temperature in the presence of light. The NMR spectra showed only signals of the barbaralyl moiety which, by analogy to **2j**, is expected when dibarbaralylzinc **2k** is present. – ^{1}H NMR (C_6D_6, 20°C): δ = 3.64 (br. m, 2H, 1/5-H), 4.06 (br. m, 4H, 2/4/6/8-H), 5.72 (br. m, 1H, 3-H), 5.84 (br. m, 7-H); 1.2–1.3 (9-H, overlapped by residual pentane). – ^{13}C NMR (THF, 20°C): δ = 13.3 (C-9), 29.8 (C-1/5), 75.6 (br. C-2/4/6/8), 120.0 (C-3), 120.1 (C-7).

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