Journal of Organometallic Chemistry 532 (1997) 71–77

Synthesis of novel heterocycles by the reaction of N,C-dilithio-2-allylpyrrole with electrophiles

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Received 27 June 1996; revised 14 August 1996

Abstract

N,C,-dilithio-2-allylpyrrole (1) in THF reacts selectively with various element halides to give Z-isomers, and in the case of element dihalides (Me_2SiCl_2, Me_2SnCl_2, Cp_2ZrCl_2) or $SiCl_4$ to give new heterobicycles [E = Si (7), Sn (8), Zr (12)] or the spirosilane 6. Treatment of 1 with triethoxyborane gives the heterobicyclic borate 9 which reacts with Me_3SiCl to give the heterobicyclic ethoxyborane 10. The synthetic potiential of 8 is shown by its transformation to the heterobicyclic ethylborane 11. All compounds were characterized by multinuclear magnetic resonance, including the application of modified (Hahn-echo extended) polarization transfer pulse sequences for measurement of $^1J(^{29}Si,^{15}N)$, $^1J(^{119}Sn,^{15}N)$ and 2D $^{13}C/^1H$ heteronuclear shift correlations for the determination of signs of coupling constants $^nJ(^{119}Sn,^{13}C)$ and $^{n+1}J(^{119}Sn,^1H)$.

Keywords: Boron; Silicon; Tin; Zirconium; Pyrrole; N,C-dilithio reagent; NMR

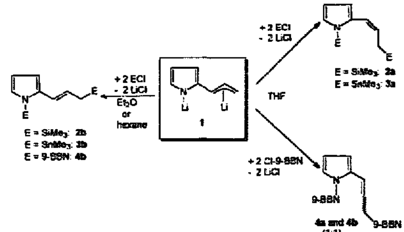
1. Introduction

The synthetic potential of N,C-dilithiated compounds in the synthesis of heterocycles is well documented [1,2]. Recently, we have found that 2-allylpyrrole reacts with two equivalents of n-butyl lithium to give N,C-dilithio-2-allylpyrrole 1 [3]. The stereochemistry of the reactions of 1 with numerous electrophiles is solvent-controlled, leading to Z-isomers in THF and to E-isomers in diethylether or hexane [3]. Taking into account that the conditions leading to the Z-isomers are ideal for heterocyclic synthesis, we have now studied the reactivity of 1 towards some Group 14 element halides (Me_2SiCl_2, Me_2SnCl_2, $SiCl_4$), Cp_2ZrCl_2 and $B(OEt)_3$.

2. Results and discussion

2.1. Synthesis

As shown in Scheme 1, the reaction of 1 in THF with trimethyltin chloride (to give 3a) or Et_2O (to give 3b) proceeds with the same selectivity as in the case of Me_3SiCl [3]. However, the reaction of 1 with 9-chloro-9-borabicyclo[3.3.1]nonane (Cl-9-BBN) in THF affords only a 1:1 mixture of 4a and 4b. It is possible that the borane–THF adduct which is formed in the first step prevents the stereoselective reaction. Thus, the allyllithium function can react with Cl-9-BBN–THF at the 1′-position and the 1:1 mixture of 4a/4b is the result of allylic rearrangement. The pure E-isomer 4b can be obtained by working in hexane. Therefore we have used triethoxyborane rather than boron halides in our attempts to prepare heterocycles containing boron.



Scheme 1.

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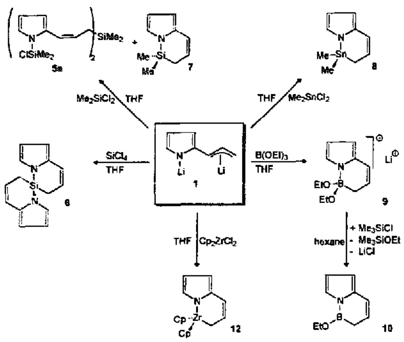
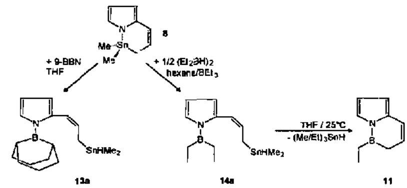
PII S0022-328X(96)06733-2



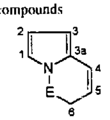
Scheme 2.

The reactions of **1** leading to new heterocycles are summarized in Scheme 2. The reaction of **1** with Me_2SiCl_2 in THF affords the product **5a** together with the desired heterobicycle **7**, which are separated by fractional distillation. The formation of **5a** can be explaned by the greatly differing reactivity of the C- and N-lithiated functions in **1**. The C-lithiated function is expected to react already at low temperature with the SiCl function. Therefore it is important to work at room temperature, to use an excess of Me_2SiCl_2, and to add the THF solution of **1**. For similar reasons the yield of the spirosilane **6** is rather low (36%), and numerous unidentified compounds are formed. Various attempts at the synthesis of the tin analogue of **6** have failed, whereas the compound **8** is readily accessible. The better yield of **8** as compared with **7** is most likely the result of the more labile Sn–C and Sn–N bonds (compared with Si–C and Si–N bonds) which would allow for rearrangement to **8** if a tin compound analogous to **5a** were formed in the reaction of **1** with Me_2SnCl_2. Considering the reactivity of Sn–N and Sn–C bonds, **8** may be useful for further transformation (vide infra). The reaction of **1** with triethoxyborane in THF gives the borate **9** which crystallizes with THF. It is necessary to remove as much of the THF as possible in order to convert **9** to **10** by the reaction with Me_3SiCl. Finally, the dark violet solid zirconium derivative **12** is obtained in good yield via the smooth reaction of **1** with Cp_2ZrCl_2.



Scheme 3.

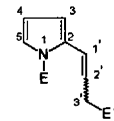
Table 1
^{11}B, ^{13}C, $^{14/15}N$, ^{29}Si and ^{119}Sn NMR data [a] of the bicyclic compounds



		1	6	7	8	9	10	11	12
E			1/2Si	$SiMe_2$	$SnMe_2$	$B(OEt)_2^-$	BOEt	BEt	$ZrCp_2$
$\delta^{11}B$						5.6	34.2	54.7	
$\delta^{29}Si(^1J(^{29}Si^{15}N))$			−10.6 (15.7) [b]	7.9 (12.4) [c]					
$\delta^{119}Sn[J(^{119}Sn^{15}N)]$					28.1 [52.6] [d]				
$\delta^{14/15}N$			−227.2	−227.8	−221.2		−225.0	−196.2	−152.6
$\delta^{13}C$	C-1	132.8	122.4	121.7 (7.8)	125.2 [6.4]	118.7	119.4	120.6	124.5
$(J(^{29}Si^{13}C))$	C-2	98.7	112.7	111.4	110.5 [18.0]	108.6	112.9	114.4	111.8
$[J(^{119}Sn^{13}C)]$	C-3	106.4	112.0	110.7	111.8 [10.2]	106.5	110.2	110.4	110.8
	C-3a	123.2	135.6	135.0	135.9 [< 2]	136.8	136.9	135.4	139.0
	C-4	76.3	122.2	121.8	124.6 [51.0]	121.5	121.1	120.8	121.8
	C-5	146.8	116.5	117.5 (4.5)	115.9 [52.1]	124.4	120.7	123.0	130.0
	C-6	45.3	12.0 (66.5)	13.0 (56.7)	12.2 [398.9]	18.5 [br]	14.0 [br]	19.9 [br]	59.1
	Me/Et/Cp	—	—	−1.2 (57.7)	−5.5 [375.8]	57.4 18.5	58.0 18.8	11.0 [br] 8.6	111.3

[a] Silanes were measured in $CDCl_3$. All other compounds were measured in C_6D_6. [br] Broad signal due to partially relaxed $^1J(^{13}C,^{11}B)$ coupling.
[b] Measured at −30°C.
[c] $^1\Delta^{15/14}N(^{29}Si) = -13.4 \pm 1$ ppb.
[d] $^1\Delta^{15/14}N(^{119}Sn) = -58.0 \pm 4$ ppb.

Table 2
^{11}B, ^{13}C, $^{14/15}N$, ^{29}Si and ^{119}Sn NMR data [a] of the open chain compounds



		2a (Z)	2b (E)	3a (Z)	3b (E)	4a [b] (Z)	4b (E)	5a (Z)	13a (Z)	14a (Z)
N–E		$SiMe_3$	$SiMe_3$	$SnMe_3$	$SnMe_3$	9-BBN	9-BBN	$SiMe_2Cl$	9-BBN	BEt_2
3'-E		$SiMe_3$	$SiMe_3$	$SnMe_3$	$SnMe_3$	9-BBN	9-BBN	$SiMe_2$	Me_2SnH	Me_2SnH
δ ^{11}B	N–B					61.7	61.7		56.8	58.4
	3'-B					85.8	85.8			
δ ^{29}Si	N–Si	11.2	11.1					15.7		
	3'-Si	1.9	1.6					2.9		
δ ^{119}Sn	N–Sn			65.9	66.2					
	3'-Sn			5.6	4.1				−104.0	−103.7
δ ^{13}C	C-2	134.4	137.7	135.3 [18.4] [7.6]	138.4 [19.4] [7.9]	136.0	139.6	135.0	136.3 [19.7]	136.1 [19.5]
($J(^{29}Si^{13}C)$)	C-3	109.6	107.6	110.7 [21.4]	106.3 [11.8]	113.1	114.4	112.8	113.1	112.9
[$J(^{119}Sn^{13}C)$]	C-4	111.3	110.4	110.7 [21.4]	110.7 [20.9] [4.4]	114.5	113.2	111.2	116.6	116.3
	C-5	122.7	123.2	124.2 [15.2]	124.2 [14.5]	126.7	125.1	123.2	124.9	125.7
	C-1'	118.3	120.1	117.5 [51.2] [9.3]	119.5 [53.9] [8.2]	125.5	124.0	118.5	128.8	129.2 [52.8]
	C-2'	125.9	125.9	125.8 [55.4]	126.1 [54.9]	125.5	127.6	127.3	118.4 [55.5]	119.0 [54.7]
	C-3'	19.6 (46.8)	23.9 [47.5]	15.9 [293.6]	17.6 [305.9]	[b]	n.o.	19.4	13.0 [300.6]	12.7 [394.6]
	NE–R	0.2 (58.0)	0.7 (58.1)	−4.6 [396.5]	−4.6 [396.5]	[b]	27.1 [br] (C-1'/5') 34.0 (C2'/4'/6'/8') 23.7 (C-3'/7')	3.4	27.3 [br] (C-1'/5') 34.0 (C2'/4'/6'/8') 23.4 (C-3'/7')	14.3 [br] (CH_2) 8.9 (CH_3)
	3'E–R	−2.0 (51.0)	−1.9 (51.9)	−8.9 [317.5]	−8.9 [317.5]	[b]	32.0 [br] (C-1'/5') 33.5 (C2'/4/1'/6'/8') 23.6 (C-3'/7')	−3.1	−11.7 [335.7]	−11.8 [336.5]

[a] Silanes were measured in $CDCl_3$. The other compounds werde measured in C_6D_6. [br] Broad signal due to partially relaxed $^1J(^{13}C,^{11}B)$ coupling.
[b] ^{13}C (9-BBN) not assigned; 1:1 mixture with **4b**. ^{13}C resonances are similar to those of **4b**.

The tin compound **8** is reactive towards 9-borabicyclo[3.3.1]nonane-dimer (in THF) and tetraethyldiborane (in hexane in the presence of a large excess of triethylborane [4]). As shown in Scheme 3, compound **13a** is formed exclusively by cleavage of the Sn–N bond, and the same type of reaction takes place with tetraethyldiborane, leading to **14a**. If the latter reaction is carried out in THF from the beginning, only unidentified polymeric material is formed. However, if THF is added after the formation of **14a**, a clean cyclization to **11** takes place by elimination of trialkyltin hydride, presumably first as Me_2EtSnH which, after some time in THF, is in equilibrium with Me_3SnH, Et_2MeSnH and Et_3SnH.

2.2. NMR spectroscopic results

^{11}B, ^{13}C, ^{14}N, ^{29}Si and ^{119}Sn NMR data of the heterobicyclic compounds **6–12**, together with the data for **1**, are listed in Table 1, and Table 2 contains the NMR data of the compounds **2a,b–4a,b**, **5a**, **13a** and **14a** for comparison. ^{1}H NMR data are given in Section 4. If ^{1}H NMR data are not fully conclusive with respect to structural assignments, as is the case in **3a,b** owing to overlap of $^{1}H(1')$ and $^{1}H(2')$ signals, ^{13}C NMR data are reliable in all cases. Mutual assignments of ^{1}H and ^{13}C resonances are based on the appropriate 2D $^{13}C/^{1}H$ heteronuclear shift correlations (HETCOR). All sets of NMR data are consistent with the proposed structures.

2.2.1. Chemical shifts $\delta^{11}B$, $\delta^{13}C$ and $\delta^{14}N$

In the series of compounds **6–11**, changes in the $\delta^{13}C$ values of the olefinic carbon atoms are small, indicating only a weak influence of the heteroatoms Si, Sn or B on the bonding situation. The differences in the $\delta^{13}C$ values between the borate **9** and the boranes **10** and **11** can be ascribed to the presence of the trigonal planar boron atom in the latter. The negligible change of the $\delta^{13}C$ values between **10** and **11** excludes any significant N–B(pp)π interactions, in spite of the well suited steric conditions for this type of interaction [5]. The δN values of **6–8** and **10** cover a small range. The reduced nitrogen nuclear shielding in **11** is typical of dialkyl(N-pyrrolyl)boranes [6], and indicates the presence of the unoccupied p_z orbital at the boron atom, but should not be taken as an indication of strong N–B(pp)π bonding. The coordination number of the boron atoms in **9**, **10** and **11** follows from the $\delta^{11}B$ data, which also enable one to distinguish clearly between **10** and **11** [7]. Most $\delta^{13}C$ data and the δN value of **12** show significant changes compared with **6–11**. In general, marked deshielding of $^{14/15}N$ and ^{13}C nuclei is observed which can be traced to the presence of the zirconium atom with its partially unoccupied 4d orbitals [8]. The deshielding effect concerns in particular the nuclei adjacent to Zr [^{14}N,$^{13}C(6)$], and to a lesser extent the ^{13}C nuclei which are separated by two bonds from Zr [$^{13}C(1,3a,5)$], whereas the nuclear shielding of the other ^{13}C nuclei [$^{13}C(2,3,4)$] remains unaffected.

2.2.2. Coupling constants $^{1}J(^{29}Si,^{15}N)$, $^{1}J(^{119}Sn,^{15}N)$ and $^{n}J(^{119}Sn,^{13}C)$

The coupling constants $^{1}J(^{29}Si,^{15}N) = (+)12.4$ Hz and $^{1}J(^{119}Sn,^{15}N) = (-)52.6$ Hz have been measured for **7** and **8** from ^{29}Si and ^{119}Sn NMR spectra (Fig. 1) respectively, using Hahn-echo extended (HEED) [9] polarization transfer pulse sequences, such as INEPT [10]. The value $^{1}J(^{29}Si,^{15}N) = (+)15.7$ Hz for **6** was determined by observing the ^{29}Si satellites in the ^{15}N NMR spectrum. The increase in magnitude of $^{1}J(^{29}Si,^{15}N)$ in **6** compared with **7** is expected [11] [compare $Me_3Si{-}NEt_2$ (+19.2 Hz) and $Me_2Si(NEt_2)_2$ (+23.1 Hz) with regard to $^{1}J(^{29}Si,^{15}N)$], however, the contribution of the N-pyrrolyl group to $^{1}J(^{29}Si,^{15}N)$ appears to be much less positive than that of a dialkylamino group. This trend is even more pronounced in the case of the tin compound **8**, where a negative sign of $^{1}J(^{119}Sn,^{15}N)$ is suggested by comparison with the experimentally determined coupling sign of $^{1}J(^{119}Sn,^{15}N)$ in other N-triorganylstannyl pyrrole derivatives [12]. The corresponding values for the trimethylsilyl and -stannyl derivatives are +13.5 and −37.2 Hz [9]. Owing to the greater polarity of the Sn–N bond, the magnitude of $^{1}J(^{119}Sn,^{15}N)$ is more sensitive to structural changes than $^{1}J(^{29}Si,^{15}N)$. The HEED technique also enables one to measure the isotope induced chemical shifts $^{1}\Delta^{15/14}N(^{29}Si) = -13.4 \pm 1$ ppb and $^{1}\Delta^{15/14}N(^{119}Sn) = -58 \pm 4$ ppb at natural abundance of the nuclei involved. The interpretation and classification of these data must be postponed until a larger data set becomes available.

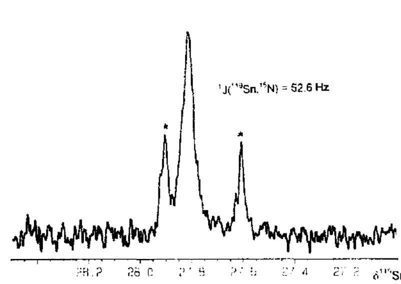


Fig. 1. 186.5 MHz ^{119}Sn NMR spectrum of **8** (ca. 25% in C_6D_6 at 25 ± 1 °C), recorded using the HEED–INEPT pulse sequence [9], refocused with ^{1}H decoupling (Hahn-echo delay 0.05 s; acquisition time 2.5 s; 3000 transients; 140 min spectrometer time). The ^{15}N satellites according to $^{1}J(^{119}Sn,^{15}N) = 52.6$ Hz are shown together with the residual broad parent signal of the ^{119}Sn, ^{14}N isotopomer.

Numerous $^{119}Sn-^{13}C$ coupling constants have been measured for **3a,b** (Table 2) and **8** (Table 1). The signs of $^1J(^{119}Sn,^{13}C(6))$ (< 0), $^2J(^{119}Sn,^{13}C(5))$ (> 0) and $^3J(^{119}Sn,^{13}C(4))$ (< 0) were determined by observing the tilt of the relevant cross-peaks in the 2D $^{13}C/^{1}H$ HETCOR experiments [13] (Fig. 2). The absolute signs of $^nJ(^{119}Sn,^{13}C)$ can be based on the known [14] sign of $^2J(^{119}Sn,^{1}H(6)) > 0$. To the best of our knowledge, this is the first time that signs of $^nJ(^{119}Sn,^{13}C)$ and $^{n+1}J(^{119}Sn,^{1}H)$ have been determined for allylic tin compounds.

The magnitude, and most likely also the sign, of coupling constants $^nJ(^{119}Sn,^{13}C$(pyrrole)) ($n = 2, 3$) in **3a,b** is similar to other N-triorganylstannyl pyrroles (e.g. in Me_3Sn-(2,5-Me_2)NC_4H_2 $^2J(^{119}Sn,^{13}C(2,5)) = -12.5$ Hz, $^3J(^{119}Sn,^{13}C(3,4)) = -19.6$ Hz [12]). However, there are significant differences between $^nJ(^{119}Sn,^{13}C$(pyrrole)) in **3a,b** and **8**, as a consequence of the ring closure. In the case of $^2J(^{119}Sn,^{13}C(3a)) <$ 2 Hz for **8**, the contribution of another coupling pathway according to $^4J(^{119}Sn,^{13}C(3a))$ cannot be neglected, in particular since this coupling constant is observed for **3a,b**. Other changes in $^nJ(^{119}Sn,^{13}C$(pyrrole)) can be attributed to the more rigid structure of **8** as compared with **3a,b**, having an influence on the contribution of the π system in mediating indirect nuclear spin–spin coupling.

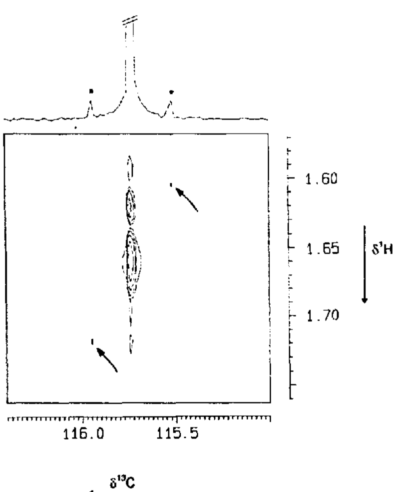


Fig. 2. Contour plot of the 125.8 MHz 2D $^{13}C/^{1}H$ heteronuclear shift correlation [based on $^2J(^{13}C(5),^{1}H(6))$] of **8**. The relevant cross-peaks are marked and their positive tilt indicates alike signs of $^3J(^{119}Sn,^{1}H(6))$ (> 0) and $^2J(^{119}Sn,^{13}C(5))$.

3. Conclusions

The reagent N,C-dilithio-2-allylpyrrole (**1**) is an attractive starting material in heterocyclic synthesis. The products themselves can serve again for further transformations to new heterocycles as shown for the tin/boron exchange (**8/11**). In addition to the synthetic potential of the new heterocycles, they possess interesting NMR spectroscopic properties which can be explored by advanced NMR techniques as shown for some of these compounds.

4. Experimental

All preparative work and handling of samples was carried out under an atmosphere of dry N_2, using oven-dried glassware and dry solvents. Starting materials (^{n}BuLi in hexane, Me_3SnCl, Me_2SnCl_2, $B(OEt)_3$, $SiCl_4$, Cp_2ZrCl_2) were commercial products and used without further purification. Other starting materials were prepared according to literature procedures (NC-dilithio-2-allylpyrrole [3], Cl-9-BBN [15], H-9-BBN [16], "Et_2BH" [17]). Mass spectra (EI-MS; 70 eV) were recorded with a VARIAN-MAT CH 7 instrument with direct inlet. NMR spectra were recorded by using Jeol EX270 (^{1}H, ^{13}C) and Bruker ARX 250 and AM 500 spectrometers (^{1}H, ^{11}B, ^{13}C, ^{14}N, ^{15}N, ^{29}Si, ^{119}Sn). Chemical shifts are given with respect to Me_4Si [$\delta^1H(CHCl_3/CDCl_3)$ 7.24, (C_6D_6) 7.15; $\delta^{13}C(CDCl_3)$ 77.0, (C_6D_6) 128.0], Et_2O-BF_3 [$\delta^{11}B$ with $\Xi(^{11}B) =$ 32.083971 MHz], neat $MeNO_2$ [$\delta^{14}N$ with $\Xi(^{14}N) =$ 7.223656 MHz] and Me_4Sn [$\delta^{119}Sn$ with $\Xi(^{119}Sn) =$ 37.290665 MHz].

4.1. 3a / b and 4a / b

3a/b and **4a/b** were prepared analogously to the procedure described for **2a/b** [3]. **4a** cannot be obtained pure, but only as a 1:1 mixture with **4b**.

4.1.1. N,3'-bis(trimethylstannyl)-2(prop-1'-enyl) pyrrole 3

3a: ^{1}H NMR (C_6D_6; 250 MHz) δ^1H {$J(^1H,^1H)$} [$J(^{119}Sn,^1H)$] = 5.31 (d) {2.6} (H-3); 6.26 (t) {2.6} (H-4); 6.49 (m) (H-5); 5.89 (d) {11.5} (H-1'); 5.55 (dt) {11.5} {9.7} (H-2'); 2.01 (d) {9.7} (H-3'); 0.27 (s) [57.9] (N–$SnMe_3$); 0.05 (s) [52.3] (3'-$SnMe_3$).

3b: ^{1}H NMR (C_6D_6; 250 MHz) δ^1H {$J(^1H,^1H)$} [$J(^{119}Sn,^1H)$] = 6.35 (m) (H-3); 6.20 (t) {2.9} (H-4); 6.47 (m) (H-5); 6.0 (m) (H-1', H-2'); 1.75 (m) [68.0] (H-3'); 0.26 (s) [59.1] (N–$SnMe_3$); 0.03 (s) [52.5] (3'-$SnMe_3$).

4.1.2. N,3'-bis[9'-(9'-borabicyclo[3.3.1]nonyl)]-2(prop-1'-enyl)pyrrole **4**

4a: ^{1}H NMR (C_6D_6; 250 MHz) δ^1H {$J(^1H,^1H)$} = 6.42 (d) {3.2} (H-3); 6.29 (m) (H-4, H-1'); 7.06 (m) (H-5); 5.47 (dt) {11.8} {10.1} (H-2'); 2.32 (d) {10.1} (H-3').

4b: ^{1}H NMR (C_6D_6; 250 MHz) δ^1H {$J(^1H,^1H)$} = 6.41 (m) (H-3); 6.23 (t) {2.6} (H-4); 7.04 (m) (H-5); 6.41 (d) {15.7} (H-1'); 6.08 (dt) {15.7} {7.6} (H-2'); 2.31 (d) {7.6} (H-3'); 1.10–1.30 (m), 1.60–2.00 (m) (9-BBN).

4.2. 7,7'(7aH,7a'H)-spirobi[7a-aza-7-sila-6,7-dihydro-indene] **6**

To a stirred solution of 8.27 ml (70 mmol) $SiCl_4$ in 150 ml of ether, 2.92 g (24 mmol) of **1** in 150 ml of THF was added at room temperature within 30 min. The colour of the reaction mixture turned to orange. After removal of the solvent the residue was extracted with ether. Fractional distillation gave 2.1 g (36%) of **6** as a light brown liquid (b.p. 110 °C/1 Torr). ^{1}H NMR ($CDCl_3$; 250 MHz) δ^1H {$J(^1H,^1H)$} = 6.72 (m) (H-1); 6.30 (m) (H-2); 6.26 (m) (H-3); 6.52 (d) {10.2} (H-4); 5.75 (m) (H-5); 1.90–2.00 (m) (H-6). EI-MS: m/z (%) 238 (100) [M^+]; 133 (10) [$M^+-C_7H_7N$]; 105 (14) [$C_7H_7N^+$].

4.3. Bis[3'-[N-dimethylchlorsilyl-2-prop-(Z)-1'-enyl)pyrrole]]dimethylsilane **5a** *and 7a-aza-7,7-dimethyl-6,7-dihydro-7-sila-7aH-indene* **7**

0.5 g (4.2 mmol) of **1** in 20 ml of THF was added within 10 min to a stirred solution of 1.6 g (12.6 mmol) of Me_2SiCl_2 in 30 ml THF at room temperature. The colour of the reaction mixture turned to brown. The solvent was then removed in vacuo and the residue extracted with hexane. Fractional distillation gave 0.18 g (31%) **7** (b.p. 43 °C/1 Torr) and 0.68 g (36%) **5a** (b.p. 185 °C/1 Torr) as almost colourless liquids.

5a: ^{1}H NMR ($CDCl_3$; 250 MHz) δ^1H {$J(^1H,^1H)$} = 6.66 (d) {2.8} (H-3); 6.54 (t) {2.8} (H-4); 7.04 (d) {2.8} (H-5); 6.71 (d) {11.6} (H-1'); 5.92 (dt) {11.6} {8.9} (H-2'); 2.25 (d) {8.9} (H-3'); 1.04 (s) (N–$SiMe_2$); 0.38 (s) (3'-$SiMe_2$).

7: ^{1}H NMR ($CDCl_3$; 250 MHz) δ^1H {$J(^1H,^1H)$} = 6.89 (m) (H-1); 6.46 (t) {2.9} (H-2); 6.33 (m) (H-3); 6.53 (dt) {10.2} {1.8} (H-4); 5.80 (dt) {10.2} {5.2} (H-5); 1.78 (dd) {5.2} {1.8} (H-6); 0.55 (s) ($SiMe_2$). EI-MS: m/z (%) 163 (100) [M^+]; 148 (92) [M^+–Me]; 133 (6) [M^+–2Me]; 105 (4) [M^+-SiMe_2].

4.4. 7a-Aza-7,7-dimethyl-6,7-dihydro-7-stanna-7aH-indene **8**

To a stirred suspension of 3.6 g (30 mmol) of **1** in 200 ml of ether at −78 °C, a solution of 6.54 g (30 mmol) of Me_2SnCl_2 in 30 ml of THF was added slowly. The mixture was stirred for 15 h while warming up to room temperature. After filtration and removal of the solvent from the filtrate in vacuo, the residue was distilled (94 °C/0.1 Torr). 15 ml of pentane was then added to the raw product and the mixture was left for 20 h at −78 °C. **8** precipitated quantitatively. The precipitate was washed with another portion of pentane cooled to −78 °C and 5.2 g (68%) of **8** was obtained as colourless crystals (m.p. 35 °C; b.p. 94 °C/0.1 Torr). ^{1}H NMR (C_6D_6, 250 MHz) δ^1H {$J(^1H,^1H)$} [$J(^{119}Sn,^1H)$] = 6.53 (m) (H-1); 6.31 (t) {2.6} (H-2); 6.22 (m) (H-3); 6.32 (dt) {11.2} {1.7} [+1.6] (H-4); 5.49 (dt) {11.2} {5.2} [−128.5] (H-5); 1.63 (dd) {5.2} {1.7} [60.3] (H-6); 0.13 (s) [58.3] ($SnMe_2$). EI-MS: m/z (%) 255 (70) [M^+]; 240 (80) [M^+–Me]; 225 (30) [M^+–2Me]; 106 (100) [M^+-SnMe_2].

4.5. Lithium-7a-aza-7,7-diethoxy-7-borata-6,7-dihydro-7aH-indene **9**

To a stirred solution of 5.3 ml (30 mmol) of $B(OEt)_3$ in 50 ml of THF at −78 °C, 4 g (30 mmol) of **1** in 100 ml of THF was added slowly. The colour of the reaction mixture turned to red. Removing the solvent in vacuo left a mixture of **9** and LiOEt which can be directly used for the preparation of **10**. The residue was extracted with hexane. Removal of the hexane in vacuo gave 0.8 g (13%) of **9** as a viscous yellow oil. Colourless crystals of a THF adduct of **9** were obtained from toluene/hexane 1:1 at −78 °C. ^{1}H NMR (C_6D_6; 250 MHz) δ^1H {$J(^1H,^1H)$} = 7.0 (m) (H-1); 6.55 (t) {1.9} (H-2); 6.49 (m) (H-3); 6.66 (d) {9.5} (H-4); 6.11 (dt) {9.5} {4.6} (H-5); 1.53 (d) {4.6} (H-6); 3.54 (q) {7.0} (OCH_2); 1.00 (t) {7.0} (CH_3).

4.6. 7a-Aza-7-ethoxy-7-bora-6,7-dihydro-7aH-indene **10**

To a suspension of 25 mmol of crude **9** in hexane, 3.2 ml (25 mmol) of Me_3SiCl was added at room temperature. The solution was stirred for 15 h. After that the mixture was filtered. Distillation of the filtrate gave 2.3 g (57% with respect to **1**) of **10** as a colourless liquid (b.p. 58 °C/1 Torr). ^{1}H NMR (C_6D_6; 250 MHz) δ^1H {$J(^1H,^1H)$} = 7.37 (d) {2.7} (H-1); 6.41 (t) {2.7} (H-2); 6.29 (m) (H-3); 6.53 (dt) {9.5} {1.8} (H-4); 5.58 (dt) {9.5} {4.5} (H-5); 1.29 (dd) {4.5} {1.8} (H-6); 3.40 (q) {7.1} (OCH_2); 0.92 (t) {7.1} (CH_3). EI-MS: m/z (%) 161 (18) [M^+]; 132 (100) [M^+–Et]; 105 (12) [M^+–BOEt].

4.7. 7a-Aza-7,7-bis(η^5-cyclopentadienyl)-6,7-dihydro-7-zirconia-7aH-indene **12**

To a stirred suspension of 0.6 g (2.1 mmol) of Cp_2ZrCl_2 in 100 ml of ether cooled to −78 °C, 0.24 g (2 mmol) of **1** in 30 ml of THF was added within

10 min. The colour of the reaction mixture became dark brown and changed to dark red while warming up to room temperature. After removing the solvent in vacuo the residue was extracted with ether and filtered. Removal of the ether in vacuo left 0.5 g (73%) of **12** as dark violet crystals. ^{1}H NMR (C_6D_6; 250 MHz) δ^1H {$J(^1H,^1H)$} = 6.51 (m) (H-1); 6.64 (t) {2.7} (H-2); 6.47 (d) {2.7} (H-3); 6.53 (d) {10.5} (H-4); 6.21 (dt) {10.5} {8.1} (H-5); 1.92 (d) {8.1} (H-6); 5.71 (s) (Cp).

*4.8. N-borabicyclo[3.3.1]nonyl-2(prop-(Z)-1'-enyl-3'-dimethylstannyl)pyrrole **13a***

6.2 g (5.1 mmol) of 9-BBN was added in one portion to a solution of 1.3 g (5.1 mmol) of **8** in 20 ml THF at room temperature. The mixture was stirred for 15 h. Removal of the solvent gave 7.3 g (100%) of **13a** as a colourless oil. ^{1}H NMR (C_6D_6, 250 MHz) δ^1H {$J(^1H,^1H)$} [$J(^{119}Sn,^1H)$] = 7.11 (m) (H-1); 6.31 (t) {2.9} (H-2); 6.20 (m) (H-3); 6.48 (d) {10.7} (H-1'); 5.69 (dt) {10.7} {9.1} (H-2'); 2.15 (d) {9.1} [72.4] (H-3'); 5.00 (m) [1744.0] (SnH); overlapping multipletts at 1.82–1.34 (9-BBN group); 0.09 (s) [53.6] (SnMe).

*4.9. N-diethylboryl-2(prop-1'-(Z)-enyl-3'-dimethylstannyl)pyrrole **14a***

To a suspension of 1.3 g (5.1 mmol) of **8** in pentane at 0 °C a mixture of 2.1 mmol of tetraethyldiborane with an excess of BEt_3 was added. After 5 min the suspension became clear. Removal of the volatile material left 1.65 g (100%) of **14a** as a colourless oil. ^{1}H NMR (C_6D_6, 250 MHz) δ^1H {$J(^1H,^1H)$} [$J(^{119}Sn,^1H)$] = 7.01 (m) (H-1); 6.30 (t) {3.1} (H-2); 6.46 (m) (H-3); 6.15 (dt) {11.8} {1.2} (H-1'); 5.65 (dt) {11.8} {9.3} (H-2'); 2.09 (dd) {9.3} {1.2} (H-3'); 5.01 (m) [17.09.6] (SnH); 1.26 (q) {7.6}, 0.95 (t) {7.6} (BEt); 0.06 (d) {1.5} [55.2] (SnMe).

*4.10. 7a-Aza-7-bora-7-ethyl-6,7-dihydro-7aH-indene **11**:*

THF (5 ml) was added to 3.25 g (10 mmol) of **14a**. After 10 min of stirring at room temperature all volatile material was removed in vacuo and the residue was condensed at a pressure of 10^{-3} Torr into a cooled tube (−78 °C). In this way 0.3 g (20%) of **11** was obtained as a colourless oil (b.p. 65 °C/0.1 Torr). ^{1}H NMR (C_6D_6, 250 MHz) δ^1H {$J(^1H,^1H)$} = 6.87 (m) (H-1); 6.35 (t) {3.1} (H-2); 6.19 (m) (H-3); 6.52 (dt) {9.6} {1.7} (H-4); 5.71 (dt) {9.6} {4.2} (H-5); 1.63 (dd) {4.2} {1.7} (H-6); 1.12 (q) {7.6}, 0.85 (t) {7.6} (BEt).

Acknowledgements

Support of this work by the Fonds der Chemischen Industrie and Volkswagen-Stiftung is gratefully acknowledged.

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