Efficient Mono- and Dilithiation of 2-Bromo-1,1-diphenylethene with *n*-Butyllithium/Tetramethylethylenediamine

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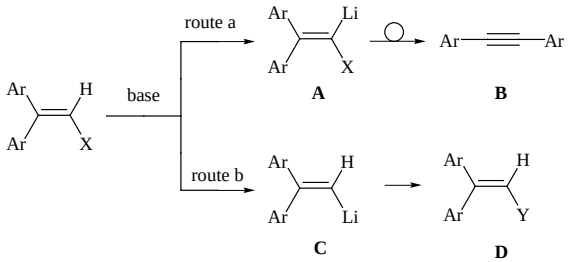
Abstract: Lithiation of 2-bromo-1,1-diphenylethene (**2**) with *n*-butyllithium or *tert*-butyllithium/tetramethylethylenediamine (TMEDA) in pentane at –100 °C effects a halogen–lithium exchange to give 2-lithio-1,1-diphenylethene (**3**) exclusively, which reacts with electrophiles to provide 2-substituted-1,1-diphenylethenes **5**–**8** in high yields. Further lithiation of the monolithium derivative **3** with *n*-butyllithium/TMEDA results in the direct *ortho*-lithiation of *Z*-located phenyl ring to give dilithium derivative **9**, which forms disubstituted ethenes **11**–**13** or heterocycles **15**–**17** on treatment with electrophiles. *tert*-Butyllithium/TMEDA is ineffective for the second lithiation step.

Key words: halides, lithiation, organometallic reagents, complexes, regioselectivity

Two different reaction pathways are known for the lithiation of 2-halo-1,1-diphenylethenes.[2,3] The first path includes proton removal (Scheme 1, route a) under the action of a strong base with the formation of 1-halo-1-lithioethene **A**. In the case of the chloro derivative (X = Cl) this intermediate is sufficiently stable at low temperature (–100 to –85 °C) to react with electrophiles, like CO_2 or Br_2, resulting in the formation of 1-substituted 1-halo-2,2-diphenylethenes in moderate yields.[4–6] At higher temperature or in the cases of bromo and iodo derivatives (X = Br, I), which are significantly more reactive, **A** readily rearranges into diarylacetylene **B.**[5–9] This classical example of the anionic rearrangement was discovered in 1894[10] and recognised as a very suitable way for the synthesis of diarylacetylenes.[7,8]



Scheme 1 X = Cl, Br, I.

The second possibility is halogen–metal exchange (Scheme 1, route b) to give the vinyllithium **C**.[5,11,12] This way is more distinctive for bromo- and iodo-derivatives (X = Br, I) and provides a versatile synthetic tool for the preparation of 2-substituted 1,1-diarylethene **D**. Unfortunately, this halogen-metal exchange is accompanied usually by the formation of acetylenes that reduce the synthetic scope of the reaction.[12,13]

We wish to report here improved conditions for selective and efficient halogen–lithium exchange in 2-bromo-1,1-diphenylethene (**2**) in the presence of TMEDA, which result in the formation of 1,1-diphenylethylene derivatives on treatment of the intermediate vinyllithium compound **3** with electrophiles. Alternatively, the vinyllithium compound **3** can undergo further lithiation of the phenyl ring.

Lithiation of 2-bromo-1,1-diphenylethene (**2**) with 3 equivalents of *n*-BuLi or *t*-BuLi in pentane in the presence of 3 equivalents of TMEDA results in complete halogen-lithium exchange at –100 °C already within 20 minutes (Scheme 2). Product distribution at different temperatures were investigated by treatment of the reaction mixture with iodine (Table 1). At –100 °C the iodide **5** together with a small amount of ethene **1** were identified as the only products along with traces of the starting bromide **2** (<2%). When the reaction was allowed to warm to 0 °C during 1 h, further deactivation of the lithium derivative **3** to ethene **1** was observed. No rearranged tolane **4** was detected not only after instant warming up, but also on keeping the reaction mixture at 20 °C during 10 hours. TMEDA is of great importance for this reaction since only 5% of bromide **2** underwent Br–Li exchange to form lithium derivative **3** and 95% of the starting bromide **2** were recovered in the absence of TMEDA. On the one hand, TMEDA accelerates Br–Li exchange in bromoethene **2**, and on the other hand it stabilises the intermediate vinyllithium compound **3** in a form of a complex up to room temperature and prevents its deactivation to ethene **1**.

Since the yield of the lithium derivative **3** under original conditions was nearly quantitative, it was of interest to examine its reaction with various electrophiles. The lithium derivative **3** was readily converted into substituted ethenes **5**–**8** in high yields (93–96%) by treatment with iodine, methanol-d_4, deuterium oxide, dimethyl sulfate or chlorotrimethylsilane, respectively (Table 2). Products were identified by MS, NMR and IR spectra and by comparison with the data reported in the literature.

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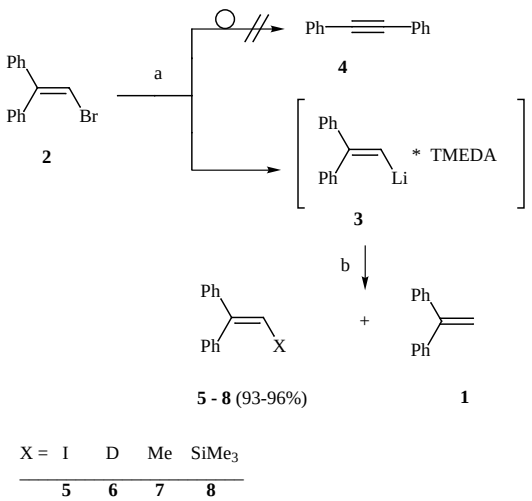


Scheme 2 *Reagents and conditions*: a) *n*-BuLi (3 equiv) or *t*-BuLi (3 equiv), TMEDA (3 equiv), pentane, –100 °C, 20 min; b) electrophile, –90 °C.

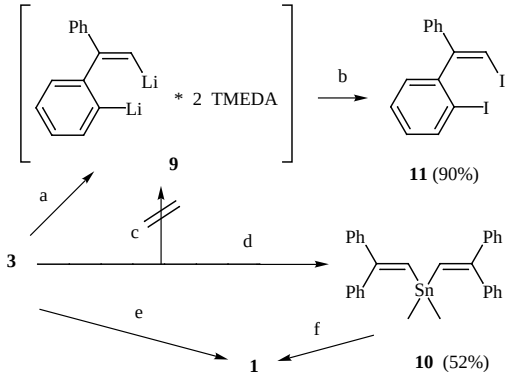
Table 1 Reaction Conditions and Products Distribution from the Lithiation of **2** Followed by I_2-Quench[a]

Base/Reaction Conditions	Products				
	2	**5**	**11**	**1**	**4**
***n*-BuLi**					
–100 °C	<2 (<2)	89 (95)	– (–)	11 (<1)	– (–)
–25 °C	– (–)	84 (95)	5 (–)	11 (4)	– (–)
0 °C	– (–)	70 (95)	20 (–)	7 (3)	– (–)
20 °C, 0.5 h	– (–)	57 (17)	35 (78)	4 (<1)	– (–)
20 °C, 4 h	– (–)	7 (6)	81 (90)	<1 (<1)	– (–)
20 °C, 10 h	– (–)	12 (5)	70 (91)	6 (<1)	– (–)
Reflux, 2 h	– (–)	25 (3)	20 (92)	34 (<1)	– (<1)
20 °C, 10 h	95[b]	4	–	–	–
***t*-BuLi**					
–100 °C	<2	90	–	10	–
–25 °C	–	67	–	28	–
0 °C	–	57	–	39	–
20 °C, 0.5 h	–	51	–	43	–
20 °C, 4 h	–	38	–	55	–
20 °C, 10 h	–	16	–	73	–
Reflux, 2 h	–	5	3	60	11

[a] Ratio *n*-BuLi or *t*-BuLi/TMEDA/**2** = 3:3:1; solvent: pentane–Et_2O (1:1), in parenthesis for pentane only; reaction mixture was quenched with I_2; analysis of the crude reaction mixture by ^1H NMR and GC-MS; yields are determined by GC.
[b] Reaction without TMEDA.

In principle, only 2 equivalents[14] of *n*-BuLi are required for the successful Br–Li exchange under the same conditions, and only traces of the rearranged tolane **4** (<1%) were detected in the reaction mixture by GC in this case. Diethyl ether increases deactivation of the lithium derivative **3** resulting in the formation of 5–10% of ethene **1** when used as a co-solvent to pentane (Table 1).

It is interesting, that further metalation of the lithium derivative **3** in the *ortho*-position of the *Z*-located phenyl ring took place at temperatures higher than 0 °C when 3 equivalents of *n*-BuLi/TMEDA were used. The reaction was monitored by treatment with iodine, as before (Scheme 3, Table 1). More than 90% of vinyllithium **3** turned to the dilithium derivative **9** after 4 hours stirring at 20 °C. Further keeping of the reaction mixture at this temperature or under reflux caused deactivation of **9** with the formation of the vinyllithium derivative **3** and ethene **1**. No rearranged tolane **4** was detected also in this case by GC and ^{13}C NMR analysis.



Scheme 3 *Reagents and conditions*: a) *n*-BuLi, TMEDA, pentane, 20 °C; b) I_2, –100 °C; c) *n*-BuLi, TMEDA, THF, 20 °C; d) Me_2SnCl_2, THF, –100 °C; e) *t*-BuLi, TMEDA, pentane, 20 °C; f) Al_2O_3, chromatography, 100%.

Unexpectedly *t*-BuLi/TMEDA was ineffective for further metalation of **3** to **9**, and formation of ethene **1** was the only process on stirring the reaction mixture at 20 °C over a 4 h period. Upon refluxing the reaction mixture for 2 h, the formation of rearranged tolane **4** became essential (11%), and dilithium derivative **9** was formed only in traces (<3%) together with the formation of ethene **1** (60%). The use of THF as alternative to pentane in the reaction carried out under the standard conditions gave also only mono vinyllithium **3**. Nearly 10% of starting bromide **2** were recovered and traces (5%) of the dilithium derivative **9** in the form of the diiodide **11** were detected together with iodoethene **5** (65%) when the reaction mixture in THF was derivatized by iodine. Alternatively bis(2,2-diphenylethenyl)dimethylstannane (**10**) (52%) was formed in the reaction with dichlorodimethylstannane (DCDMST) (Scheme 3).

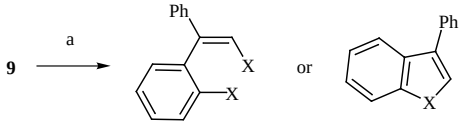
Dilithium derivative **9** obtained by the action of *n*-BuLi/TMEDA on **3** in pentane was treated with methanol-d_4 and dimethyl sulfate and the corresponding bis-deriva-

Table 2 Reaction of Lithium Derivatives **3** and **9** with Electrophiles

Product	X	Electrophile	Yield[a] (%)	Other Products,[b] (%)
5	I	I_2	93	**1** (2)
			82[c]	**1** (10)
			65[d]	**2** (10), **11** (5), **1** (8)
6	D	CD_3OD	96	**1**(5)
		D_2O	88	
7	Me	DMS	93	
8	$SiMe_3$	CTMS	94	
10	$SnMe_2$	DCDMST	52[d]	
11	I	I_2	90	**1** (3), **5** (6)
12	D	CD_3OD	86	**1** (3), **6** (3)
13	Me	DMS	86	**1** (3), **7** (5)
14	$SiMe_3$	CTMS	–	**15** (82),[a] **8** (9), **1** (3)
15	$SiMe_2$	DCDMS	88	
16	$SnMe_2$	DCDMST	74[c]	
17	S	SDC	84	

[a] Yields of analytically pure products.
[b] Yields are determined by GC of the reaction mixture.
[c] Solution of an electrophile in Et_2O was used.
[d] Reaction in THF.

tives **12**–**13** were isolated in a high yields (86%) (Scheme 4, Table 2). Their structures were confirmed by spectral evidence and by comparison with the data known from the literature.



12 -13 (86%)
14 (0%)

15-17 (74-88%)

X =	D	Me	$SiMe_3$	$SiMe_2$	$SnMe_2$	S
	12	**13**	**14**	**15**	**16**	**17**

Scheme 4 *Reaction conditions*: a) electrophile, –100 °C.

The most significant spectral evidence for the *ortho*-substitution in the aromatic ring was provided by the ^1H NMR spectrum of diiodide **11** which showed 4 unequal multiplets from 4 protons in the *ortho*-substituted aromatic ring (experimental part). In order to confirm the lithiation of the *Z*-located phenyl ring in **3,** compound **9** was treated with sulfur dichloride and dichlorodimethylsilane. Products with the correct spectral characteristics for benzothiophene **17** and silaindene **15** were obtained in 84 and 88% yields, respectively. Similarly, treatment of **9** with dichlorodimethylstannane gave stannaindene **16** in 74% yield. It is interesting to note that, the treatment of dilithium derivative **9** with chlorotrimethylsilane results in the formation of cyclic silaindene **15** together with some amount of mono-substituted ethene **8,** and no disilylated ethene **14** was identified by NMR and GC-MS analysis in the reaction mixture. Nearly the same cyclization was reported earlier, when the reaction of 2,2′-bislithiobiphenyl with chlorotrimethylstannane afforded 5,5-dimethyldibenzostannole in 34% yield instead of the expected 2,2′-bis(trimethylstannyl)biphenyl.[15]

In conclusion, TMEDA selectively accelerated Br–Li exchange in bromoethene **2** resulting in the formation of mono- and dilithium derivatives **3** and **9** in high yields. They serve as key intermediates for the facile and convenient preparation of 1-substituted-2,2-diphenylethenes **5**–**8** and disubstituted ethenes **11**–**13** and various heterocyles **15**–**17** in good yields.

All procedures were carried out under N_2. Pentane, Et_2O, THF and TMEDA were dried and distilled consecutively over sodium and NaH under N_2. Commercially available dimethyl sulfate (DMS), chlorotrimethylsilane (CTMS), dichlorodimethylsilane (DCDMS), dichlorodimethylstannane (DCDMST) and sulfur dichloride (SDC) were deoxygenated by a slow streem of N_2 for 10–15 min before use. Standard solutions of *n*-BuLi in hexane (1.6 M) and *t*-BuLi (1.6 M) in pentane were analysed before use by titration with anhyd MeOH using 2,2′-bipyridyl as indicator.[16] Mixture of EtOH and liquid N_2 was used as a cooling bath (–100 to –105 °C). ^1H, ^2H and ^{13}C NMR spectra were recorded on a Bruker ARX 400 instrument at 400.14, 61.42 and 100.62 MHz respectively, chemical shifts are given in δ (ppm). EI mass spectra were determined at 70 eV by using a HP 5989B spectrometer. IR spectra were recorded on a PYE UNICAM SP3-200 spectrometer. Analytical TLC was performed on Kieselgel 60 F 254 and Al_2O_3 60 F 254 neutral (Type E) plates (Merck). Al_2O_3 (Fluka) for chromatography (100–125 mesh, neutral) and silica gel 60 (Merck) for chromatography (63-200 mesh, neutral) were used as sorbents. Melting points are uncorrected.

2-Bromo-1,1-diphenylethen (**2**) was synthesised by the reaction of 1,1-diphenylethene (**1**) with bromine in CCl_4.[2] The crude product was dissolved in CH_2Cl_2, washed with 10% aq $NaHCO_3$ and purified by two consecutive distillations under N_2 in 80% yield as a solid with spectroscopic data identical to those reported in the literature (IR,[17] ^1H NMR,[18] ^{13}C NMR[19]). Bp 100–104 °C/0.1 mbar; mp 40–41 °C (Lit.[2] bp 124–140 °C/1.0 mbar; mp 40–41 °C).

2-Lithio-1,1-diphenylethene (3)

A solution of *n*-BuLi in hexane (1.25 mL, 2 mmol) was added to a solution of TMEDA (0.3 mL, 2 mmol) in pentane (10 mL) at –100 °C (internal temp) during 1 min and the reaction mixture was stirred at –100 °C for 10 min. A solution of the bromide **1** (259 mg, 1 mmol) in pentane (5 mL) was added dropwise at –100 °C over a 3 min period and the mixture was allowed to warm to 0 °C over a 30 min period resulting in the formation of orange-yellow solution of **3**. A solution was again cooled to –90 °C and thus generated suspension of **3** was used for further reactions.

2-Iodo-1,1-diphenylethene (5); General Procedure

Excess of powdered I_2 (493 mg, 2 mmol) was added at –90 °C (internal temp) during 4 min to a stirred suspension of **3** prepared as above. The reaction was allowed to warm to 20 °C over a 1 h period

and was stirred at this temperature for the next 3 h. The mixture was treated with 10% aq $Na_2S_2O_3$ to destroy the excess of I_2, the light yellow organic layer was separated, and the aqueous phase was extracted with Et_2O (3 × 5 mL). The combined organic phases were washed with H_2O, dried (Na_2SO_4), concentrated and the crude product was purified by column chromatography over silica gel (10 g) using hexane as eluent (200–500 mL); yield: 284 mg (93%); mp 39–40 °C (Lit.[2] mp 40–41 °C).

^{13}C NMR ($CDCl_3$): δ = 152.7 (Ph_2C=), 141.8, 141.1, 129.4, 128.3, 128.2, 128.0, 127.9, 127.5, 79.0 (=CHI).

IR (0.2 mol/L, CCl_4): 3107, 3085, 3075, 3029, 2965, 2928, 1966, 1950, 1806, 1600, 1584, 1554, 1494, 1445, 1322, 1201, 1182, 1149, 1074, 1029 cm^{-1}.

NMR and MS data were in agreement with those partially reported.[20,21]

2-Deuterio-1,1-diphenylethene (6)

Excess of CD_3OD (0.16 mL, 4 mmol) was added dropwise to a suspension of **3** at –90 °C followed by the standard warming procedure, neutralised with 5% HCl and worked up as described above for **5**; yield: 174 mg (96%); colourless liquid.

^{1}H NMR ($CDCl_3$): δ = 7.31–7.20 (m, 10 H, 2 × C_6H_5), 5.39 (s, 1 H, =CHD) (<5% of **1** was detected by the signal at 5.40 (s, 2 H, =CH_2).

^{2}H NMR (CH_2Cl_2):[22] δ = 5.47 (s, 1 D, =CDH).

^{13}C NMR ($CDCl_3$): δ = 150.0 (Ph_2C=), 141.5, 128.3, 128.2, 127.7, 114.0 (t, =CHD, J_{CD} = 24.17 Hz).

^{13}C NMR and MS were in agreement to those partially reported.[23]

1,1-Diphenylpropene (7)

Excess of DMS (0.38 mL, 4 mmol) was added dropwise to a suspension of **3** at –90 °C followed by the standard warming procedure. The reaction mixture was treated with 25% aq ammonia to destroy the excess of DMS and worked up as described above for **5** to give the title compound as oily liquid, which solidified up on standing; yield 180 mg (93%); mp 49–50 °C (Lit.[24] mp 49–50 °C).

^{13}C NMR ($CDCl_3$): δ = 142.9, 142.5, 140.3 (Ph_2C=), 130.0, 128.1, 128.0, 127.2, 126.8, 126.7, 124.0 (=CH), 15.7 (CH_3).

IR, MS and ^{1}H NMR data were in a good agreement to those reported.[25,26]

(2,2-Diphenylethenyl)trimethylsilane (8)

Excess of CTMS (0.3 mL, 2.4 mmol) was added dropwise to a suspension of **3** at –90 °C followed by the standard warming procedure. The reaction mixture was carefully treated with 10% aq $NaHCO_3$ and worked up as described above for **5**; yield: 237 mg (94%); oil (Lit.[27] bp 115 °C/0.3 mbar).

MS: *m*/*z* (%) = 252 (47, M^+), 238 (22), 237 (100), 221 (7), 178 (6), 159 (5), 136 (13), 135 (98), 107 (5), 105 (5).

^{1}H and ^{13}C NMR and IR data were in a good agreement to those reported.[27,28]

(*Z*)-2-Lithio-1-(2-lithiophenyl)-1-phenylethene (9)

A solution of **3** prepared according to a standard protocol using *n*-BuLi (384 mg, 6 mmol), TMEDA (696 mg, 6 mmol) and bromide **2** (518 mg, 2 mmol) in pentane (20 mL) was allowed to warm to 20 °C and stirred for further 4 h resulting in the formation of dark-red suspension of **9**.

(*Z*)-2-Iodo-1-(2-iodophenyl)-1-phenylethene (11)

Excess of powdered I_2 (2.02 g, 8 mmol) was added to a suspension of **9** at –100 °C (internal temp) during 4 min, the reaction was allowed to warm up to 20 °C over a 1.5 h period and was stirred at this temperature for the next 3 h. The reaction mixture was worked up as described above for **5**; yield: 778 mg (90%); oily liquid, which solidified at –5 to –2 °C to a low-melting mass.

^{1}H NMR ($CDCl_3$): δ = 7.94 (dd, 1 H, *J* = 8.1, 1.0 Hz, H-3), 7.45 (m, 1 H, H-5), 7.30–7.22 (m, 5 H, C_6H_5), 7.20 (dd, 1 H, *J* = 7.6, 1.5 Hz, H-6), 7.15 (s, 1 H, =CHI), 7.08 (m, 1 H, H-4).

^{13}C NMR ($CDCl_3$): δ = 154.3 (Ph_2C=), 146.8 (C-1), 139.6 (C-3), 138.6 (C-1′), 130.3 (C-6), 129.4 (C-4), 128.6 (C-3′), 128.5 (C-5), 128.3 (C-4′), 127.0 (C-2′), 98.4 (C-2), 82.6 (=CI).

IR (0.3 mol/L, CH_2Cl_2): 3107, 3065, 3037, 3025, 2965, 2927, 1965, 1957, 1948, 1923, 1890, 1805, 1727, 1605, 1585, 1557, 1495, 1465, 1446, 1431, 1405, 1392, 1337, 1320, 1285, 1265, 1255, 1200, 1155, 1100 cm^{-1}.

MS: *m*/*z* (%) = 432 (8, M^+), 306 (15), 305 (92), 179 (15), 178 (100), 177 (12), 176 (22), 152 (14), 151 (10), 150 (6).

Anal. Calcd for $C_{14}H_{10}I_2$: C, 38.92; H, 2.33. Found: C, 39.08; H, 2.17.

(*Z*)-2-Deuterio-1-(2-deuteriophenyl)-1-phenylethene (12)

Excess of CD_3OD (0.32 mL, 8 mmol) was added dropwise to a suspension of **9** at –100 °C followed by the standard warming procedure. The reaction mixture was worked up as described above for **6**; yield: 303 mg (86%); colourless liquid.

^{1}H NMR($CDCl_3$): δ = 7.35–7.31 (m, 9 H, Ar), 5.44 (s, 1 H, =CHD) (**1** (<3%) and **6** (<3%) were detected by signals at 5.39 and 5.40 respectively).

^{2}H NMR (CH_2Cl_2) : δ = 7.33 (s, 1 D, D-Ar), 5.46 (s, 1 D, =CHD).[22]

^{13}C NMR ($CDCl_3$): δ = 150.0 (Ph_2C=), 141.5, 141.4, 128.3, 128.2, 128.0, 127.7 (C_6H_5), 114.0 (t, =CHD, J_{CD} = 24.17 Hz).

MS: *m*/*z* (%) = 182 (100, M^+), 181 (62), 180 (44), 179 (21), 167 (24), 166 (44), 165 (20).

Anal. Calcd for $C_{14}H_{10}D_2$: C, 92.26; H/D, 7.74. Found: C, 92.48; H, 7.52.

***(Z)*-1-(2-Methylphenyl)-1-phenylprop-1-ene (13)**

Excess of DMS (0.86 mL, 9 mmol) was added dropwise to a suspension of **9** at –100 °C followed by the standard warming procedure. The reaction mixture was worked up as described above for **7**; yield: 357 mg (86%); colourless oil.

^{13}C NMR ($CDCl_3$): δ = 141.5, 141.4, 139.3, 136.6, 130.1, 130.0, 128.2, 127.1, 126.6, 126.1, 125.7, 123.8 (=CH), 19.5 (ArCH_3), 15.4 (CH_3C=).

^{1}H NMR and MS were in a good agreement to those partially reported.[25,29]

(*Z*)-2-(2-(Trimethylsilyl)phenyl)-2-phenylethenyl)trimethylsilane (14)

Excess of CTMS (0.38 mL, 3 mmol) was added dropwise to a suspension of **9** at –100 °C followed by the standard warming procedure. The reaction mixture was worked up as described above for **8**. The following compounds were isolated: **8**: 45 mg (9%), **15**: 387 mg (82%) and **1**: 10 mg (3%). No traces of **14** were detected in the reaction mixture by ^{1}H and ^{13}C NMR and GC-MS analysis.

1,1-Dimethyl-3-phenyl-1-silaindene (15)

Excess of DCDMS (0.36 mL, 3 mmol) was added dropwise to a suspension of **9** at –100 °C followed by the standard warming procedure. The reaction mixture was treated with H_2O, the organic layer was separated and filtered through a layer of silica gel (5 cm) using hexane as an eluent and **15** was obtained on concentration of the first fraction (100 mL) to give the title compound as a colourless liquid; yield: 416 mg (88%).

^{1}H NMR ($CDCl_3$): δ = 7.59 (ddd, 1 H, H-7, *J* = 6.6, 1.3, 1 Hz), 7.45–7.21 (m, 8 H, Ar), 6.16 (s, 1 H, =CHSi), 0.37 [s, 6 H, $Si(CH_3)_2$].

^{13}C NMR, IR and MS were in a good agreement to those partially reported.[30]

1,1-Dimethyl-3-phenyl-1-stannaindene (16)

A solution of DCDMST (439 mg, 2 mmol) in Et_2O (5 mL) was added dropwise to a suspension of **9** at –100 °C during 5 min followed by the standard warming procedure. The solvent was removed at reduced pressure (50 mbar) and the residue was extracted with pentane (5 × 5 mL). The combined extracts were concentrated and yellow-orange oil was distilled in a Kugelrohr apparatus at 190–210 °C/0.1 mbar; yield: 483 mg (74%); colourless oil.

^{1}H NMR ($CDCl_3$): δ = 7.64 (dd, 1 H, H-8, *J* = 6.1, 1.5 Hz), 7.41–7.16 (m, 8 H, Ar), 6.57 (s, 1 H, =CHSn), 0.50 (s, 6 H, $Sn(CH_3)_2$, $J_{Sn,H}$ = 60.5, 57.4 Hz).

^{13}C NMR ($CDCl_3$): δ = 161.1 (Ph_2C=, $J_{Sn,C}$ = 38.9 Hz), 149.2 (C-1, $J_{Sn,C}$ = 85.3 Hz), 142.8 (C-1′, $J_{Sn,C}$ = 66.8 Hz), 141.3 (C-8), 135.5 ($J_{Sn,C}$ = 45.5 Hz), 132.5 (=CSn, $J_{Sn,C}$ = 433.9, 414.9 Hz), 128.5, 128.4, 128.1, 127.2, 127.0, 125.9 ($J_{Sn,C}$ = 39.8 Hz), –8.9 [$Sn(CH_3)_2$, $J_{Sn,C}$ = 359.2, 344.1 Hz].

MS: *m*/*z* (%) = 332 (4), 330 (3), 329 (5), 328 (23), 327 (9), 326 (18), 325 (7), 324 (10), 313 (100), 298 (11), 221 (5), 193 (10), 192 (11), 191 (9), 178 (19), 176 (7), 165 (5), 152 (5).

Anal. Calcd for $C_{16}H_{16}Sn$: C, 58.77; H, 4.93. Found: C, 58.49; H, 4.55.

3-Phenyl-1-benzothiophene (17)

Excess of SDC (0.19 mL, 3 mmol) was added dropwise to a suspension of **9** at –100 °C followed by the standard warming procedure. The filtered reaction mixture was concentrated and the crude product was purified by column chromatography on silica gel using hexane as an eluent (200 mL); yield: 353 mg (84%); colourless liquid; n_D^{20} 1.6797 (Lit.[31] n_D^{25} 1.6789).

^{1}H NMR ($CDCl_3$): δ = 7.94–7.89 (m, 2 H), 7.60–7.57 (m, 2 H), 7.50–7.46 (m, 2 H), 7.42–7.32 (m, 4 H).

^{1}H, ^{13}C NMR, MS and IR spectrum were in agreement to those partially reported.[31,32]

Bis-(2,2-diphenylethenyl)dimethylstannane (10)

A solution of **3** was prepared according to a standard protocol in THF (15 mL) as an alternative to pentane starting from 3 mmol of *n*-BuLi (192 mg, 3 mmol), TMEDA (348 mg, 3 mmol) and bromide **2** (259 mg, 1 mmol). A solution of DCDMST (110 mg, 0.5 mmol) in THF (5 mL) was added dropvise at –100 °C during 5 min followed by the standard warming procedure. The solvent was removed at reduced pressure (50 mbar), the rest was extracted with pentane (5 × 5 mL) and the combined extracts were concentrated. Unreacted bromide **2**, ethene **1** and byproducts were distilled off in vacuum (75–150 °C/0.7 mbar); yield: 132 mg (52%); light-yellow oil.

^{1}H NMR($CDCl_3$): δ = 7.36–7.15 (m, 10 H, 2 × C_6H_5), 6.46 (s, 2 H, =CHSn, J_{SnH} = 69.2, 66.1 Hz), –0.34 (s, 6 H, 2 CH_3, J_{SnH} = 57.4, 55.6 Hz).

^{13}C NMR($CDCl_3$): δ = 158.1 (Ph_2C=), 144.1, 142.9, 132.1 (=CSn), 129.5, 128.2, 128.0, 127.5, 127.4, –7.7 [$Sn(CH_3)_2$].

IR (0.3 mol/L, CCl_4): 3107, 3085, 3055, 3027, 2967, 2927, 2877, 2863, 1965, 1950, 1900, 1885, 1810, 1765, 1735, 1665, 1655, 1600, 1585, 1550, 1493, 1446, 1385, 1370, 1353, 1327, 1312, 1280, 1245, 1194, 1158, 1145, 1125 cm^{-1}.

Anal. Calcd for $C_{30}H_{28}Sn$: C, 71.04; H, 5.56. Found: C, 70.61; H, 5.19.

An attempt was made to use column chromatography on alumina for the purification of **10**, but only ethene **1** in nearly quantitative yield was eluted with Et_2O.

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