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Synthesis of 1-Benzometalloles Containing Group 14, 15, and 16 Heavier Elements *via* a Common Dilithiostyrene Intermediate

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The Group 14 (Si, Ge, and Sn), Group 15 (P, As, Sb, and Bi), and Group 16 (Se and Te) 2-trimethylsilyl-1-benzometalloles (7) were prepared by the reaction of the corresponding metal reagents with β,*o*-dilithio-β-trimethylsilylstyrene intermediate (6), which was derived from phenylacetylene or *o*-bromoiodobenzene *via* three steps. The trimethylsilyl group in 7 could be readily removed by treatment with tetrabutylammonium fluoride to give the *C*-unsubstituted 1-benzometalloles (10).

Keywords 1-benzometallole; dilithiostyrene; benzarsole; benzostibole; benzobismole; benzostannole

Five-membered heterocyclic dienes (heteroles) such as pyrroles, furans, and thiophenes represent an important domain of heterocyclic chemistry and many of their derivatives serve as useful functional compounds in various chemical fields. Recently, the synthesis of monocyclic (**1**) and benzo-fused heteroles (**2**) containing a Main Group heavier element other than nitrogen, oxygen, or sulfur (also called metalloles, due to the metallic nature of the elements) has received increasingly intensive study and a variety of metalloles have been prepared.[1] However, their synthetic routes are not always versatile, in addition, most of known metalloles are highly substituted and only a few examples of *C*-unsubstituted metalloles have been reported. Therefore, we were interested in the synthesis of simple metalloles and report here two versatile synthetic routes to Group 14 (Si, Ge, and Sn), Group 15 (P, As, Sb, and Bi), and Group 16 (Se and Te) 1-benzometalloles, all of which can be obtained easily from a common key 1,4-dilithiostyrene intermediate, and the synthesis for the first time of several *C*-unsubstituted benzometalloles.[2]

Phenyl(trimethylsilyl)acetylene (**4**),[3] prepared from phenylacetylene (**3**) by successive treatment with butyllithium and trimethylsilyl chloride (TMSCl) in a high yield, was hydraluminated[3,4] with diisobutylaluminum hydride (DIBAL-H) in hexane followed by bromination with *N*-bromosuccinimide (NBS) to give (*Z*)-β-bromo-β-trimethylsilylstyrene (**5**)[5] regio- and stereo-selectively in *ca.* 80% yield. The key starting compound (**5**) was treated with 2.2 molar eq of butyllithium in anhydrous ether under an argon atmosphere, then with a metal reagent (M or MX$_2$: see Table I), resulting in ring closure to afford the desired 2-trimethylsilyl-1-benzometalloles (**7a**—**j**) in moderate to high yileds (Table I) *via* the dilithiostyrene intermediate (**6**).[6] When deuterium oxide was used instead of the metal reagents, the dideuteriostyrene (**8**) was formed. This result clearly gives evidence for the intermediacy of the 1,4-dianion species (**6**), which is formed by dilithiation of **5** with butyllithium but could not be isolated.


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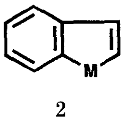
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M : Main Group heavier elements

It should be emphasized that the trimethylsilyl (TMS) group is essential in the present synthetic route since it has an important role. Namely, the presence of the TMS group causes the regio- and stereo-selective formation of the (*Z*)-β-bromostyrene (**5**) in the bromination of **4** through hydralumination. Replacement of the TMS group by an alkyl or aryl group did not lead to such selective bromination, affording a mixture of four olefinic isomers. In addition, (*Z*)-β-bromostyrene (**9**)[7] having no other substituent on the vinyl function, on treatment with butyllithium, underwent only elimination to give the parent phenylacetylene (**3**). Finally, the TMS group in **7** can be readily removed, forming the *C*-unsubstituted benzometalloles (**10**).

The Group 16 *C*-unsubstituted benzometalloles (**10a**—**c**) were obtained in high yields by treatment of **7a**—**c** with aqueous potassium hydroxide in methanol, but similar alkaline treatment of the other group metalloles (**7d**—**j**) resulted partially or mainly in decomposition to afford **10** in poor yields. However, treatment of **7a**—**j** with tetrabutylammonium fluoride (TBAF) in tetrahydrofuran containing water afforded the corresponding *C*-unsubstituted benzometalloles (**10**) in high yields (Table II), except for the benzosilole (**7h**) and benzostannole (**7j**), which decomposed to give no characterizable products.

Another route for the formation of the key 1,4-dilithium intermediate (**6**) was also examined. *o*-Bromoiodobenzene (**11**) was coupled with trimethylsilylacetylene in diethylamine in the presence of a catalytic amount of a mixture of bis(triphenylphosphine)palladium dichloride and copper(I) iodide[8] to give (*o*-bromophenyl)trimethylsilylacetylene (**12**) in *ca.* 90% yield. Treatment of **12** with DIBAL-H followed by bromination with NBS give (*Z*)-β,*o*-dibromo-β-trimethylsilylstyrene (**13**) in 76% yield. The dibromostyrene (**13**) also afforded the benzometalloles (**7a**—**j**) on successive treatment with butyllithium and the metal reagents, in the yields shown in Table I, *via* the intermediate (**6**). Although there is little to choose between the two routes in regard and number of steps, the former route starting from commercially easily available phenylacetylene (**3**) is less costly than the latter *via* **13**.

The benzoselenole (**10b**),[9] benzotellulole (**10c**),[10] benzophosphole (**10d**),[11] and benzosilole (**10h**)[12] are known, but the other *C*-unsubstituted benzometalloles

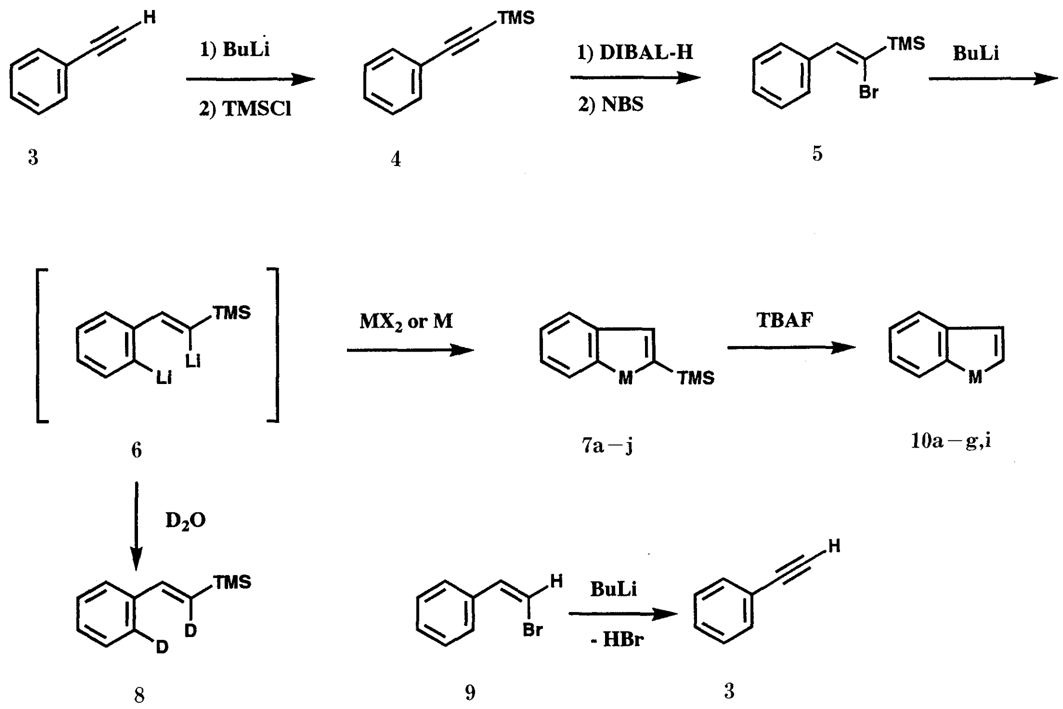


Chart 1

TABLE I. 2-Trimethylsilyl-1-benzometalloles (10)

Compd. No.	M	Reagent (M or MX$_2$)	Yield (%) From **5**	Yield (%) From **13**	bp (mmHg)$^{a)}$ or mp$^{b)}$ (°C)	Formula	HRMS$^{c)}$ or Analysis Calcd C	Calcd H	Found C	Found H
7a	S	$(PhSO_2)_2S$	62	51	bp 92—95 (3)	$C_{11}H_{14}SSi$	206.0586		206.0594	
7b	Se	Red Se	67	63	bp 101—104 (2)	$C_{11}H_{14}SeSi$	254.0030		254.0064	
7c	Te	Te powder	90	89	bp 117—118 (2)	$C_{11}H_{14}SiTe$	303.9927		303.9893	
7d	PPh	$PhPCl_2$	83	82	mp 76—77	$C_{17}H_{19}PSi$	72.31	6.78	72.27	6.83
7e	AsPh	$PhAsCl_2$	90	86	mp 66—67	$C_{17}H_{19}AsSi$	62.57	5.87	62.58	5.80
7f	SbPh	$PhSbCl_2$	82	85	mp 59—60	$C_{17}H_{19}SbSi$	54.72	5.13	54.64	5.14
7g	BiPh	$PhBiBr_2$	78	80	mp 73—75	$C_{17}H_{19}BiSi$	44.34	4.16	44.13	4.09
7h	$SiMe_2$	Me_2SiCl_2	80	83	bp 129—131 (8)	$C_{13}H_{20}Si_2$	232.1104		232.1103	
7i	$GeMe_2$	Me_2GeCl_2	85	87	bp 112—114 (6)	$C_{13}H_{20}GeSi$	278.0546		278.0544	
7j	$SnMe_2$	Me_2SnCl_2	88	85	bp 110—112 (2)	$C_{13}H_{20}SiSn$	324.0357		324.0367	

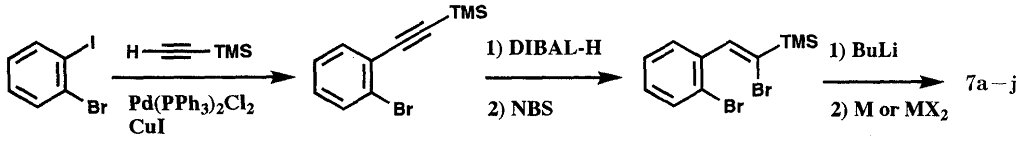
a) Bath temperature. *b*) Recrystallization from MeOH or EtOH. *c*) High-resolution MS *m*/*z*: M$^+$.

TABLE II. 1-Benzometalloles (10)

Compd. No.	M	Yield (%)	mp (°C)	Recryst. solv.	Formula	HRMS (*m*/*z*: M$^+$) Calcd	Found
10a	S	83	29—32	Pentane	C_8H_6S	134.0190	134.0181
10b	Se	88	48—50	Hexane$^{a)}$	C_8H_6Se	181.9634	181.9630
10c	Te	92	67—69	Pentane$^{d)}$	C_8H_6Te	231.9532	231.9513
10d	PPh	96	66—68	MeOH$^{c)}$	$C_{14}H_{11}P$	210.0598	210.0615
10e	AsPh	97	61—63	MeOH	$C_{14}H_{11}As$	254.0077	254.0071
10f	SbPh	97	28—29	MeOH–Et$_2$O	$C_{14}H_{11}Sb$	299.9899	299.9905
10g	BiPh	82	55—58	MeOH–Et$_2$O	$C_{14}H_{11}Bi$	388.0665	388.0700
10i	$GeMe_2$	92	bp 93—95	20 mmHg	$C_{10}H_{12}Ge$	206.0151	206.0144

a) Lit.[8] 51 °C. *b*) Lit.[9] 68—69 °C. *c*) Lit.[10] 66—68 °C.

(**10e**—**g**, **i**) and all the 2-trimethylsilylmetalloles (**7a**—**j**) are new compounds, and were characterized mainly on the basis of their mass and ^{1}H-NMR spectral analyses. The ^{1}H-NMR spectral data for **7** and **10**, summarized in Tables III and IV, show that the chemical shifts of the olefinic 2- and 3-protons are sensitive to a change in the heteroatom, and some regularities exist. In the same group metalloles, both olefinic protons of the metalloles con-



11 12 13

Chart 2

Table III. ^{1}H-NMR Spectral Data for **7** (400 MHz, $CDCl_3$: δ)

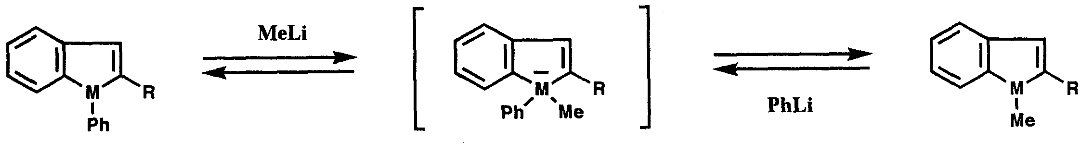
Compd. No.	3-H (s)	$SiMe_3$ (s)	Ar-H (m)	$M\text{-}Me_2$ (s)
7a (S)	7.52	0.40	7.1—8.1	
7b (Se)	7.80	0.38	7.1—8.2	
7c (Te)	8.26	0.32	7.0—8.1	
7d (P)	7.63[a]	0.08	7.1—7.3	
7e (As)	7.72	0.07	7.2—7.8	
7f (Sb)	8.16	0.07	7.0—7.8	
7g (Bi)	10.67	0.08	7.0—8.0	
7h (Si)	7.54	0.16	7.2—7.7	0.31
7i (Ge)	7.57	0.18	7.1—7.7	0.51
7j (Sn)	7.79	0.18	7.2—7.8	0.46

a) Doublet, $J_{P,3}=15.5$ Hz.

Table IV. ^{1}H-NMR Spectral Data for **10**[a] (400 MHz, $CDCl_3$: δ)

Compd. No.	2-H (d)	3-H (d)	$J_{2,3}$ (Hz)	Ar-H (m)
10a (S)	7.39	7.30	5.5	7.3—7.9
10b (Se)	7.93	7.54	5.9	7.2—8.0
10c (Te)	8.75	8.00	7.0	7.0—8.1
10d (P)	6.82[b]	7.36[c]	7.7	7.2—7.7
10e (As)	7.16	7.49	7.7	7.1—7.7
10f (Sb)	7.42	7.89	9.3	7.0—7.6
10g (Bi)	9.30	9.93	8.5	7.1—8.1
10i (Ge)	6.54	7.34	9.5	7.1—8.1[d]

a) The assignment of the 2- and 3-protons was based on the chemical shifts of the 3-protons of the corresponding 2-deuteriobenzometalloles prepared from **7** by treatment with TBAF in THF containing D_2O instead of H_2O. *b*) Double doublet, $J_{P,2}=39.6$ Hz. *c*) Double doublet, $J_{P,3}=15.0$ Hz. *d*) $GeMe_2$: 0.52 (s).



7e−g
10e−g

14

15e−g : **R=TMS**
16e−g : **R=H**

Chart 3

taining elements in higher horizontal order-rows of the periodic table resonate at lower fields than those containing elements in lower order-rows. For example, the values of the chemical shifts of both 2- and 3-protons of the Group 15 metalloles (**10d**—**g**) increase in the order **10d** (P) < **10e** (As) < **10f** (Sb) < **10g** (Bi). This tendency is similar to that observed for the Group 16 metalloles (**10a**—**c**). Furthermore, in the cases of the Group 14 (**10i**) and Group 15 metalloles (**10d**—**g**), the 3-protons resonate at lower fields than the 2-protons, in contrast to the Group 16 metalloles (**10a**—**c**), 1-benzofuran,[13] and 1-phenylindole,[14] of which the 3-protons resonate at higher fields than the 2-protons. This implies a lower ring current in the Groups 14 and 15 metalloles, which appear to be nonaromatic heteroles, in contrast with the Group 16 heteroles (**10a**—**c**) and indoles, which are known to be aromatic.[15]

It is known that siloles,[16,17] germoles,[17] and phospholes[18] undergo substitution of alkyl or phenyl groups bonded to the heteroatoms by organolithium reagents. Therefore, we examined the behavior of the new Group 15 1-phenylbenzometalloles toward organolithium reagents with the aim of obtaining 1-alkylbenzometalloles. The reaction of the 1-phenylmetalloles (**7e**—**g**) with a 2.5-fold excess of methyllithium in tetrahydrofuran (THF) at −20 °C resulted in substitution to give the desired 1-methylmetalloles (**15e**—**g**) in 75—90% yields, probably *via* the intermediate (**14**). Similarly, the *C*-unsubstituted 1-methylmetalloles (**16e**—**g**) were obtained in 70—80% yields from **10e**—**g** by treatment with methyllithium. The methyl group in **15** and **16** could be converted back to the parent phenyl group by treatment with phenyllithium, but the yields were low (10—20%) and 65—80% of the starting 1-methyl compounds were recovered even when a five-fold or more excess of phenyllithium was used. It is known that a thermodynamically more stable organolithium compound is preferentially released in the *S*N2-like exchange reactions involving such intermediates as **14**.[17,19] In the present case, the phenyl group may be released from **14** in preference to the methyl group to form phenyllithium, which is more stable than methyllithium.

Experimental

Melting points were measured on a Yanagimoto micro melting point hot stage apparatus and are uncorrected. IR spectra were determined with a Hitachi 270-30 spectrometer. Mass spectra (MS) and high-resolution mass spectra (HRMS) were recorded on a JEOL DX-300 instrument. ^{1}H-NMR spectra were determined with a JEOL PMX-60-SI (60 MHz) or JEOL JNM-GSX-400 (400 MHz) spectrometer in $CDCl_3$ using tetramethylsilane as an internal standard unless otherwise stated, and spectral assignments were confirmed by spin-decoupling experiments. Microanalyses were performed in the Microanalytical Laboratory of this Faculty by Mrs. Igarashi and Miss Yakubo.

Phenyl(trimethylsilyl)acetylene (4) A commercially available butyllithium hexane solution (concentration: 1.6 M; 270 ml, 0.44 mol) was added dropwise to a magnetically stirred solution of phenylacetylene (**3**) (40.8 g, 0.4 mol) in anhydrous ether (200 ml) at a rate such that the temperature was maintained below −65 °C under a nitrogen atmosphere. The mixture was stirred for 1.5 h at −78 °C, then trimethylsilyl chloride (TMSCl) (61 ml, 0.48 mol) was added dropwise with stirring. The mixture was stirred for 1.5 h at −78 °C, allowed to warm to room temperature, and stirred for an additional 10 h. After cooling in an ice bath, ether (200 ml) and water (80 ml) were added to the mixture with stirring. The layers were separated and the aqueous layer was extracted with ether (100 ml). The combined organic layer was washed with saturated aqueous NaCl, dried over $MgSO_4$, and evaporated *in vacuo*. The residue was vacuum-distilled to give **4**: 64 g, 91% yield, colorless oil, bp 61—65 °C (6 mmHg) [lit.[3] bp 64—67 °C (7 mmHg)].

(*Z*)-*β*-Bromo-*β*-trimethylsilylstyrene (5) A DIBAL-H hexane solution (0.93 M, 385 ml, 0.36 mol) was added dropwise with stirring to a solution of **4** (56.6 g, 0.33 mol) in hexane (200 ml) under a nitrogen atmosphere at room temperature. The mixture was stirred for an additional 10 h, then NBS (60.9 g, 0.34 mol) was added in small portions over a 0.5 h period with stirring in an ice bath. The reaction mixture was diluted with hexane (200 ml), and water (50 ml) was added to the mixture with stirring. The resulting hexane layer was separated, washed with saturated aqueous NaCl, dried, and evaporated *in vacuo*. The residue was vaccum-distilled to give **5**: 68 g, 81% yield, colorless oil, bp 95 °C (2 mmHg). ^1H-NMR (60 MHz, $CDCl_3$) δ: 0.30 (9H, s, $SiMe_3$), 7.27 (1H, s, α-H), 7.31—7.86 (5H, m, Ph-H). HRMS *m*/*z*: M^+ Calcd for $C_{11}H_{15}BrSi$: 254.0127. Found: 254.0122. IR (neat): 1576 (C=C) cm^{-1}.

2-Trimethylsilyl-1-benzometalloles (7a—j) from 5 Geneal Procedure: A butyllithium hexane solution (1.6 M, 6.8 ml, 11 mmol) was added to a solution of **5** (1.3 g, *ca.* 5 mmol) in anhydrous ether (50 ml) with stirring under an argon atmosphere in an ice bath, and then the reaction mixture was stirred for 2 h at room temperature. A solution of a metal reagent ($PhPCl_2$, $PhAsCl_2$, Me_2SiCl_2, Me_2GeCl_2, or Me_2SnCl_2: 1.1—1.2 mol eq) in ether (30 ml) or a metal reagent [$(PhSO_2)_2S$, Red Se, Te powder, $PhSbCl_2$, $PhBiBr_2$: 1.2—1.3 mol eq; they are insoluble in ether] was added dropwise or in small portions over a 1 h period to the solution with stirring in an ice bath. The reaction mixture was stirred for a further 20 h at room temperaure, then ether (100 ml) and saturated aqueous $NaHCO_3$ (15 ml) were added to it with stirring. The layers wre separated and the organic layer was washed with saturated aqueous NaCl, dried, and evaporated *in vacuo*. The residue was chromatographed on silica gel using hexane as an eluent to give the products (**7**), which were further purified by vacuum distillation or recrystallization.

The 1-benzometalloles (**7**) obtained are listed together with their yields, melting or boiling points, and elemental or HRMS analytical data in Table I. ^1H-NMR spectral data are collected in Table III.

***β*,*o*-Dideuterio-*β*-trimethylsilylstyrene (8)** A butyllithium hexane solution (1.6 M, 18 ml, 29 mmol) was added to a solution of **5** (2.7 g, 10.6 mmol) in anhydrous ether (50 ml) with stirring under an argon atmosphere in an ice bath, and then the reaction solution was stirred for 3 h at room temperature. D_2O (99.8%, 2 ml) was added to the solution with stirring in an ice bath and the mixture was stirred for a further 1.5 h at room temperature. The mixture was diluted with hexane (150 ml), washed with water, dried, and evaporated *in vacuo*. The residue was chromatographed on silica gel using hexane as an eluent to give **8**: 1.62 g, 87% yield, colorless oil, bp 83—84 °C (13 mmHg). MS *m*/*z*: 178 (M^+ for $C_{11}H_{14}D_2Si$: **8**) and 176 (M^+ for $C_{11}H_{16}Si$) (95 : 5). ^1H-NMR δ: 0.17 (9H, s, $SiMe_3$), 6.88 (1H, t, $J_{H,D}=2.9$ Hz, α-H), 7.26—7.5 (4H, m, Ph-H).

1-Benzometalloles (10a—g,i) General Procedure: A TBAF THF solution (1.0 M, 7.5 ml, 7.5 mmol, containing *ca.* 5% H_2O) was added dropwise to a solution of **7** (5 mmol) in THF (5 ml) with stirring under an argon atmosphere at room temperature, and then the reaction mixture was refluxed for 2 h. After addition of ether (50 ml) and saturated aqueous $NaHCO_3$ (10 ml), the reaction mixture was stirred for 10 min, and then the organic layer was separated, washed with saturated aqueous NaCl, dried, and evaporated *in vacuo*. The residue was chromatographed on silica gel using hexane as an eluent to give the corresponding **10**, which was further purified by recrystallization or vacuum distillation.

The benzometalloles (**10**) obtained are listed together with their yields, melting or boiling points, and HRMS data in Table II. ^1H-NMR spectral data are collected in Table IV. The 2-trimethylsilylmetalloles (**7h**) and (**7j**), on treatment with TBAF, underwent decomposition to give no characterizable products.

(*o*-Bromophenyl)trimethylsilylacetylene (12) Bis(triphenylphosphine)palladium dichloride (330 mg, 0.47 mmol), copper(I) iodide (360 mg, 1.9 mmol), and trimethylsilylacetylene (17.0 ml, 120 mmol) were successively added to a solution of *o*-bromoiodobenzene (**11**) (28.3 g, 100 mmol) in diethylamine (90 ml) and the mixture was vigorously stirred for 3.5 h at room temperature. The mixture was evaporated *in vacuo* and the residue was dissolved in hexane (300 ml). After removal of the resulting insoluble precipitates by filtration, the filtrate was washed with water, dried, and evaporated *in vacuo*. The residue was chromatographed on silica gel using hexane as an eluent to give **12**: 23 g, 91% yield, colorless oil, bp 96—98 °C (2.5 mmHg). IR (neat): 2164 (C≡C) cm^{-1}. ^1H-NMR (60 MHz) δ: 0.31 (9H, s, $SiMe_3$), 7.1—7.8 (4H, m, Ph-H). HRMS *m*/*z*: M^+ Calcd for $C_{11}H_{13}BrSi$: 251.9970. Found: 251.9959.

(*Z*)-*β*,*o*-Dibromo-*β*-trimethylsilylstyrene (13) A diisobutylaluminum hydride hexane solution (1.0 M, 75 ml, 75 mmol) was added dropwise to a solution of **12** (17.92 g, 70.8 mmol) in hexane (45 ml) with stirring under an argon atmosphere and the reaction solution was stirred for 3 d at room temperature. *N*-Bromosuccinimide (13.7 g, 77 mmol) was added in small portions over a 20 min period to the above solution with stirring at −20 °C and stirring was continued for 30 min, then for an additional 1 h at room temperature. The mixture was diluted with hexane (300 ml), and water (20 ml) was added to it with stirring in an ice bath. The resulting precipitates were filtered off and the filtrate was washed with water, dried, and evaporated *in vacuo*. The residue was chromatographed on silica gel using hexane as an eluent to give **13**, which was further purified by vacuum distillation. **13**: 18.5 g, 76% yield, colorless oil, bp 110—120 °C (3 mmHg). ^1H-NMR (60 MHz) δ: 0.30 (9H, s, $SiMe_3$), 7.43 (1H, s, α-H), 7.1—8.0 (4H, m, Ph-H). HRMS *m*/*z*: M^+ Calcd for $C_{11}H_{14}Br_2Si$: 331.9233. Found: 331.9238.

2-Trimethylsilyl-1-benzometalloles (7a—j) from 13 General Procedure: A butyllithium hexane solution (1.6 M, 6.8 ml, 11 mmol) was added to a solution of **13** (1.7 g, *ca.* 5 mmol) in anhydrous ether (50 ml) with stirring under an argon atmosphere in an ice bath, and then the reaction mixture was stirred for 2 h at room temperature. The metal reagents were added, and the whole was worked up as described for the synthesis of **7** from **5** to give **7a**—**j**; the yields are shown in Table I, together with those from **5**.

1-Methyl-2-trimethylsilyl-1-benzometalloles (15e—g) General Procedure: A methyllithium ether solution (1.06 M, 2.36 ml, 2.5 mmol) was added dropwise to a solution of **7e**—**g** (1.0 mmol) in THF (5 ml) with stirring under an argon atmosphere at −20 °C (room temperature for **7e**) and the solution was stirred for an additional 20 min (5 h for **7e**). After addition of hexane (10 ml) and water (0.5 ml), the reaction mixture was stirred for 10 min at −20 °C, allowed to warm to room temperature, dried, and evaporated *in vacuo* below 20 °C. The residue was chromatographed on silica gel using hexane as an eluent to give **15** as a colorless oil.

1-Methyl-2-trimethylsilyl-1-benzarsole (**15e**): 75% yield. ^1H-NMR (60 MHz) δ: 0.24 (9H, s, $SiMe_3$), 1.23 (3H, s, As-Me), 7.62 (1H, s, 3-H), 7.1—7.8 (4H, m, Ph-H). HRMS *m*/*z*: M^+ Calcd for $C_{12}H_{17}AsSi$: 264.0317. Found: 264.0298.

1-Methyl-2-trimethylsilyl-1-benzostibole (**15f**): 85% yield. ^1H-NMR δ: 0.21 (9H, s, $SiMe_3$), 0.94 (3H, s, Sb-Me), 8.00 (1H, s, 3-H), 7.0—7.8 (4H, m, Ph-H). HRMS *m*/*z*: M^+ Calcd for $C_{12}H_{17}SbSi$: 310.0137. Found: 310.0131.

1-Methyl-2-trimethylsilyl-1-benzobismole (**15g**): 87% yiled. ^1H-NMR δ: 0.21 (9H, s, $SiMe_3$), 1.12 (3H, s, Bi-Me), 10.21 (1H, s, 3-H), 6.9—7.8 (4H, m, Ph-H). HRMS *m*/*z*: M^+ Calcd for $C_{12}H_{17}BiSi$: 398.0904. Found: 398.0855.

1-Methyl-1-benzometalloles (16e—g) 1-Phenylbenzometalloles (**10e**—**g**) (0.3—0.5 g) were treated with methyllithium and worked up as described for **15** to give **16** as colorless oils.

1-Methyl-1-benzarsole (**16e**): 80% yield. ^1H-NMR (60 MHz) δ: 1.25 (3H, s, As-Me), 7.18 (1H, d, $J=7.7$ Hz, 2-H), 7.39 (1H, d, $J=7.7$ Hz, 3-H), 7.2—7.7 (4H, m, Ph-H). HRMS *m*/*z*: M^+ Calcd for C_9H_9As: 191.9920. Found: 191.9944.

1-Methyl-1-benzostibole (**16f**): 82% yield. ^1H-NMR δ: 0.97 (3H, s, Sb-Me), 7.46 (1H, d, $J=9.2$ Hz, 2-H), 7.74 (1H, d, 9.2 Hz, 3-H), 7.2—7.8 (4H, m, Ph-H). HRMS *m*/*z*: M^+ Calcd for C_9H_9Sb: 237.9743. Found: 237.9746.

1-Methyl-1-benzobismole (**16g**): 72% yield. ^1H-NMR δ: 1.14 (3H, s, Bi-Me), 9.32 (1H, d, $J=8.8$ Hz, 2-H), 9.53 (1H, d, $J=8.8$ Hz, 3-H), 7.1—7.4 (4H, m, Ph-H). HRMS *m*/*z*: M^+ Calcd for C_9H_9Bi: 326.0508. Found: 326.0522.

Treatment of 16e—g with Phenyllithium A phenyllithium cyclohexane–ether (7:3) solution (1.8 M, 1.39 ml, 2.5 mmol) was added to a solution of **16** (0.5 mmol) in THF with stirring at −27 °C under a nitrogen atmosphere, and then the mixture was stirred for a further 20 min. After addition of hexane (10 ml) and water (0.5 ml), the reaction mixture was stirred for 10 min at −20 °C and dried over anhydrous Na_2SO_4. The mixture was filtered and the filtrate was evaporated *in vacuo*. The residue was chromatographed on silica gel using hexane to give the starting **16e—g** and the 1-phenylmetalloles (**10e—g**) successively, in 65—80% and 10—20% yields, respectively.

References and Notes

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