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A Versatile Synthetic Route to 1-Benzometalloles involving the First Examples of Several C-Unsubstituted Benzometalloles

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The group 14 (Si, Ge, Sn), group 15 (P, As, Sb, Bi) and group 16 (S, Se, Te) (2-trimethylsilyl)-1-benzometalloles **5** have been prepared from phenylacetylene *via* three steps and converted into the corresponding C-unsubstituted benzometalloles **7** by detrimethylsilylation.

A variety of fully unsaturated monocyclic and fused five-membered heterocyclic rings containing an element other than nitrogen, oxygen or sulfur (metalloles) have been prepared.[1] However, their synthetic routes are not always versatile, in addition, most of known metalloles are highly substituted and only few examples of C-unsubstituted metalloles have been reported. We report here a versatile synthetic route to group 14 (Si, Ge, Sn), group 15 (P, As, Sb, Bi) and group 16 (Si, Se, Te), 1-benzometalloles, all of which can be obtained easily from a common starting material, and the synthesis of the first examples of several C-unsubstituted benzometalloles.

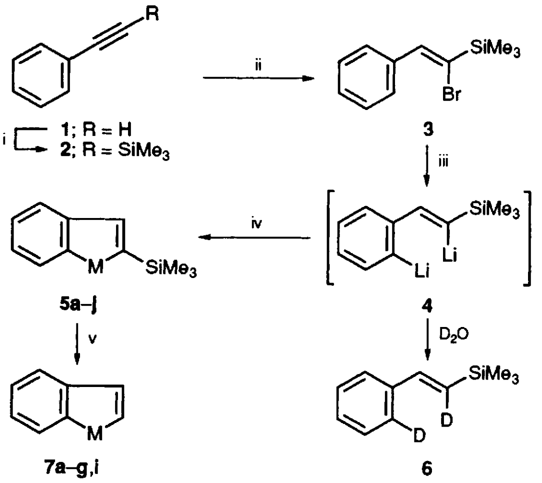
Phenyl(trimethylsilyl)acetylene **2** prepared from phenylacetylene **1** was hydraluminated[2] with diisobutylaluminium hydride (DIBAL-H) in hexane followed by bromination with *N*-bromosuccinimide (NBS) to give (*Z*)-β-bromo-β-(trimethylsilyl)styrene **3** in *ca.* 80% yield from **1**. The key starting compound **3** was treated with n-butyllithium in dry diethyl ether under argon atmosphere, then with a metal reagent to result in ring closure giving rise to the desired 2-trimethylsilyl-1-benzometalloles **5a–j** in 60–90% yields (Table 1),† *via* the dilithium intermediate **4**.[3] When deuterium oxide was used instead of the metal reagents, the dideuteriostyrene **6** was formed. This result clearly gives evidence for the intermediacy of the 1,4-dianion species **4** in the reaction process.

Table 1 2-(Trimethylsilyl)benzometalloles **5**

Compound	M	Reagent	Yield (%)
5a	S	$(PhSO_2)_2S$	62[b]
5b	Se	Red Se	67[b]
5c	Te	Te powder	90[b]
5d[a]	POPh	$PhPCl_2$	83[c]
5e	AsPh	$PhAsCl_2$	90[d]
5f	SbPh	$PhSbCl_2$	82[e]
5g	BiPh	$PhBiBr_2$	78[f]
5h	$SiMe_2$	Me_2SiCl_2	80[b]
5i	$GeMe_2$	Me_2GeCl_2	85[b]
5j	$SnMe_2$	Me_2SnCl_2	87[b]

[a] 1-Phenyl-2-(trimethylsilyl)benzophosphole was initially formed, but it was readily oxidised to be isolated as **5d**. [b] Oil. [c] M.p. 146–147 °C. [d] M.p. 66–67 °C. [e] M.p. 59–60 °C. [f] M.p. 73–75 °C.

It is to be emphasized that the trimethylsilyl (TMS) group is essential for the present synthetic route since it plays an important role in the route. Namely, the presence of the TMS group in **2** causes the regio- and stereo-selective formation of the (*Z*)-β-bromostyrene **3** in a high yield. 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, and (*Z*)-β-bromostyrene having no other substituent on the vinyl function, on treatment with n-butyllithium, underwent only elimination to give phenylacetylene **1**. Finally, the TMS group in **5** can be readily removed forming the C-unsubstituted benzometalloles **7** in high yields. The group 16 metalloles **7a–c** were obtained almost quantitatively by treatment of **5a–c** with aqueous potassium hydroxide in methanol. However, similar alkaline treatment of the other group metalloles **5d–j** resulted mainly in decomposition to



Scheme 1 *Reagents and conditions*: i, Bu^{n}Li, diethyl ether, Me_3SiCl, −78 °C, 1.5 h, 85%; ii, DIBAL-H, hexane, room temp., 20 h, NBS, −20 °C to room temp., 3 h, 92%; iii, Bu^{n}Li, diethyl ether, argon, reflux, 2 h; iv, reagents (see Table 1), diethyl ether, 0 °C to room temp., 1–2 h, 60–90%; v, 30% KOH, MeOH, 65–75 °C, 2–3 h, quant., for **7a–c**; CsF, THF–H_2O (5%), 65 °C, 2 h, 90%, for **7d**; TBAF, THF–H_2O(5%), 60 °C, 2 h, 85–97%, for **7e–g, i**

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† Satisfactory elemental analyses and spectroscopic (^1H NMR and mass) data were obtained for all new benzometalloles **5a–j** and **7e–g, i**.

give **7** in very poor yields, but treatment with a fluoride reagent such as caesium fluoride and tetrabutylammonium fluoride (TBAF) in tetrahydrofuran (THF) containing water afforded the corresponding C-unsubstituted benzometalloles **7** in high yields, except for the benzosilole **5h** and benzostannole **5j**, which decomposed to give no products.

Although the benzoselenole **7b**,[4] benzotellulole **7c**[5] and benzophosphole **7d**[6]‡ are known, the other C-unsubstituted benzometalloles **7e–g,i** are new compounds.§ It should be noted in the ^{1}H NMR spectra of new group 15 benzometalloles **7e–g** that the 3-protons (δ **7e**, 7.49; **7f**, 7.89; **7g**, 9.93) resonate at lower field than the 2-protons (δ **7e**, 7.16; **7f**, 7.42; **7g**, 9.30) by analogy with 1-phenylbenzophosphole[6] (δ 3-H, 7.36; 2-H, 6.82), but in contrast to 1-phenylindole[7] and group 16 (O, S, Se, Te) benzoheteroles,[8] of which 3-protons resonate at higher field than the 2-protons. The values of the chemical shifts of the olefinic protons are in the order **7d** (P) > **7e** (As) > **7f** (Sb) > **7g** (Bi); this tendency is similar to that observed for the group 16 benzometalloles **7a–c**.[8]

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‡ The benzophosphole 1-oxide **7d** was readily deoxygenated by treatment with trichlorosilane in benzene to give 1-phenyl-1-benzophosphole.

§ Selected data (m.p. and ^{1}H NMR) for new N-unsubstituted benzometalloles **7**; **7e**: m.p. 61–63 °C; δ 7.16 (1H, d, 2-H), 7.49 (1H, d, 3H), 7.1–7.7 (9H, m, Ar-H) and $J_{2,3}$ 7.7 Hz; **7f**: m.p. 28–29 °C; δ 7.42 (1H, d, 2-H), 7.89 (1H, d, 3-H), 7.0–7.6 (9H, m, Ar-H) and $J_{2,3}$ 9.3 Hz; **7g**: m.p. 55–58 °C; δ 9.30 (1H, d, 2-H), 9.93 (1H, d, 3-H), 7.1–7.7 (9H, m, Ar-H) and $J_{2,3}$ 8.8 Hz; **7i**: b.p. 93–95 °C (20 mmHg); δ 0.52 (6H, s, $GeMe_2$), 6.54 (1H, d, 2-H), 7.34 (1H, d, 3-H), 7.2–7.6 (4H, m, Ar-H) and $J_{2,3}$ 9.5 Hz. The assignment of the olefinic protons of these compounds was based on the chemical shifts of 3-protons of the corresponding 2-deuterio-1-benzometalloles prepared from **5** by treatment with TBAF in THF containing D_2O.

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