

Synthesis, Structure, and Reaction of 1-Alkynyl(aryl)- λ^3 -bromanes

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Hypervalent 1-alkynyl(aryl)- λ^3 -iodanes enjoy their rich chemistry in modern organic synthesis:¹ in addition to the well-established methods for their syntheses, this is mostly due to the powerful electron-withdrawing nature of the aryl- λ^3 -iodanyl groups² as well as their very high leaving-group ability.³ In marked contrast, the closely related group 17 1-alkynyl(aryl)- λ^3 -bromanes **2** have never been synthesized or characterized. A greater Hammett substituent constant ($\sigma_p = 1.63$ for PhBrBF₄) of λ^3 -bromanyl group compared to that ($\sigma_p = 1.37$ for PhIBF₄) of λ^3 -iodanyl group suggests that the 1-alkynyl- λ^3 -bromanes **2** probably serve as more efficient Michael acceptors.⁴ We report herein for the first time the synthesis and characterization of 1-alkynyl(aryl)- λ^3 -bromanes **2**, which undergo tandem Michael–carbene rearrangements by the reaction with a very weak nucleophile.¹

Lewis acid-catalyzed ligand exchange on iodine(III) of aryl- λ^3 -iodanes ArIX₂ with 1-alkynylsilanes, stannanes, and boranes constitutes an efficient general method for the synthesis of 1-alkynyl(aryl)- λ^3 -iodanes.¹ The attempted ligand exchange of *p*-trifluoromethylphenyl(difluoro)- λ^3 -bromane **1**, prepared from *p*-trifluoromethylphenyl(trimethyl)silane by the reaction with bromine trifluoride at -78 to -25 °C in dichloromethane in 72% yield,^{5,6} with 1-trimethylsilyl-1-decyne in the presence of BF₃–Et₂O gave poor results, and only traces of 1-decynyl(aryl)- λ^3 -bromane **2b** were obtained; however, by using a trimethylstannyl derivative, the alkynylbromane **2b** was produced in 82% yield by the reaction with difluorobromane **1** (1.5 equiv) and BF₃–Et₂O (3 equiv) at -78 °C (Scheme 1).

The ligand exchange with primary, secondary, and tertiary alkylethynylstannanes afforded a good yield of the 1-alkynyl- λ^3 -bromanes **2a–f**, but not with phenylethynylstannane that gave tarry matter (Table 1). Selective stannane– λ^3 -bromane exchange of trimethyl(trimethylsilylethynyl)stannane resulted in the formation of silylethynylbromane **2g** (78%). These oily λ^3 -bromanes **2** are always contaminated with a small amount (4–9%) of (*E*)- β -fluorovinyl- λ^3 -bromanes (*E*)-RFC=CHBr(Ar)BF₄. These λ^3 -bromanes **2** are highly moisture-sensitive: the half-life times ($t_{1/2}$) of 13 days for **2b** and 31 days for **2f** in CD₂Cl₂ at room temperature decrease to 25 min and 1.5 h, respectively, in the presence of a small amount of water.

¹H NMR spectra of λ^3 -bromanes **2** showed that the ortho (δ 8.21–8.26 ppm), meta (δ 7.91–7.94 ppm), and propargylic (δ 2.56–2.59 ppm) protons are considerably deshielded compared to those of the corresponding bromides, similarly to those observed for 1-alkynyl(aryl)- λ^3 -iodanes.¹ ¹³C NMR chemical shifts of acetylenic carbon atoms of **2b** and λ^3 -iodane **3** are shown in Figure 1 and compared with those of 1-decynylbromide and iodide. Compared to that in bromodecyne, the β -carbon in **2b** is much more

Scheme 1

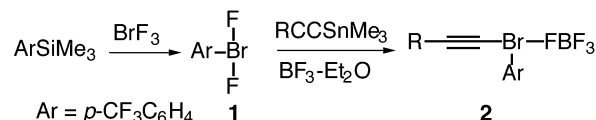


Table 1. Synthesis of Alkynylbromanes via Ligand Exchange^a

entry	1-alkynylstannane	2	yield (%) ^b
1	<i>n</i> -BuCCSnMe ₃	2a	76
2	<i>n</i> -C ₈ H ₁₇ CCSnMe ₃	2b	82
3	Me ₂ CHCH ₂ CCSnMe ₃	2c	83
4	Me ₂ CH(CH ₂) ₂ CCSnMe ₃	2d	79
5	<i>cyclo</i> -C ₆ H ₁₁ CCSnMe ₃	2e	83
6	<i>t</i> -BuCCSnMe ₃	2f	89
7	Me ₃ SiCCSnMe ₃	2g	78
8	PhCCSnMe ₃	2h	-

^a Conditions: 1:1.5:3 1-alkynylstannane:I:BF₃–Et₂O, dichloromethane, -78 °C, 3 h, Ar. ^b Isolated yields after purification by repeated decantation with hexane.

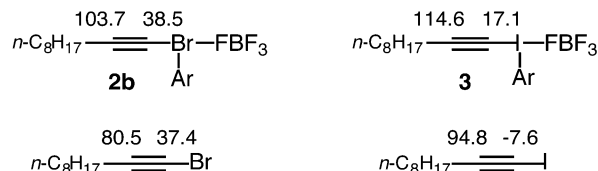


Figure 1. ¹³C NMR chemical shifts of acetylenic carbons: δ values in ppm in CDCl₃. Ar: *p*-CF₃C₆H₄.

deshielded than the α -carbon, while **3** showed a larger deshielding of the α -carbon (relative to iododecyne). The spin–orbit-induced heavy atom effects, which increase in going from bromine to iodine, are responsible for strong shielding of α -carbon (δ -7.6 ppm) in 1-decynyl iodide.⁷ The large deshielding of the α -carbon in λ^3 -iodane **3** is mostly due to the diminishing spin–orbit effects, probably evoked by partial removal of lone pair electrons on the iodine upon the change of the oxidation state.⁸ On the other hand, negligibly small increase of the ¹³C shift of the α -carbon in λ^3 -bromane **2b** is in part due to small heavy atom effects of bromine compared to those of iodine. Positive charge that developed on the less electronegative I(III) in **3** larger than that on the Br(III) in **2b** will be also responsible for these chemical shift differences.^{9,10}

The structure of *tert*-butylethynyl- λ^3 -bromane **2f** was firmly established by a single-crystal X-ray analysis of its crown ether complex **4**.¹¹ Slow evaporation of a dichloromethane–diethyl ether (1:1) solution of a 2:1 mixture of λ^3 -bromane **2f** and 18-crown-6 (18C6) at 4 °C under argon afforded colorless single crystals of the 2:1 complex **4** that were suitable for X-ray crystallography (Figure 2).¹²

The two ethynyl- λ^3 -bromanyl groups in **4** protrude both faces of the host to provide a perching type of host–guest relationship.¹¹

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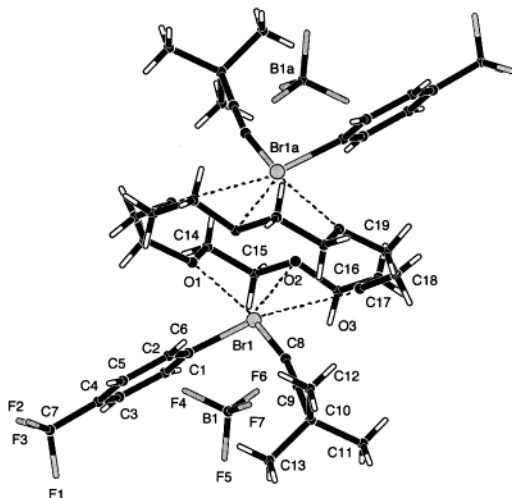
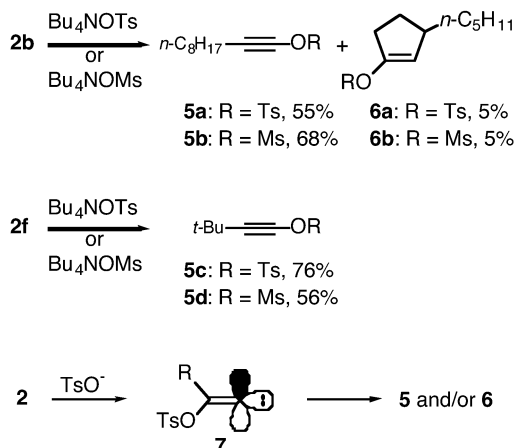


Figure 2. Structure of the 2:1 complex **4**. Selected bond lengths (Å) and angles (deg): Br(1)–C(1) 1.961(4), Br(1)–C(8) 1.808(5), C(8)–C(9) 1.211(6), Br(1)⋯O(1) 2.854(4), Br(1)⋯O(2) 3.077(4), Br(1)⋯O(3) 2.939(5), C(1)–Br(1)–C(8) 94.3(2), Br(1)–C(8)–C(9) 167.3(4).

Scheme 2



The complex adopts a distorted pentagonal planar coordination about the bromines, in which each bromine atom makes contact with the three adjacent oxygen atoms (O1–O3) of 18C6. The rms deviation of the six atoms (Br1, C1, C8, and O1–O3) from their least-squares planes is 0.236 Å with the sums of the bromine-centered bond angles $\Sigma^\circ\text{Br} = 362.8^\circ$. Interestingly, the *tert*-butylethynyl ligand is not bound linearly to the Br(III) with the Br1–C8–C9 angle of 167.3(4) $^\circ$.¹³ It is noted that the C8–C9 distance of 1.211(6) Å in **4** is considerably longer than the average triple bond length (1.181 Å),¹⁴ which probably reflects an effective polarization of π -electrons of the triple bond caused by the positive partial charge on bromine(III).¹⁵ The long carbon–carbon triple bond length, combined with the strong electron-withdrawing nature of phenyl- λ^3 -bromanyl group,⁴ makes the alkyne bromanes **2** highly electron-deficient Michael acceptors.

In fact, even a weakly nucleophilic sulfonate anion, which cannot undergo Michael addition toward alkyne- λ^3 -iodanes,¹⁶ attacks the β -acetylenic carbon of **2** to generate alkylidene carbenes **7**. Thus, reaction of **2b** with Bu₄NOTs in dichloromethane at room temperature afforded the alkyne tosylate **5a** (55% yield) as a major

product, along with formation of the cyclic alkenyl tosylate **6a** (5% yield). Bu₄NOMs gave a similar result (Scheme 2). Isolation of **6a** clearly indicates that the reaction involves the intermediacy of alkylidene carbene **7**, produced by Michael addition of tosylate anion and the subsequent reductive elimination of the aryl- λ^3 -bromanyl group. 1,2-Shift of tosyloxy group in **7** produces **5**, while intramolecular 1,5-carbon–hydrogen insertion affords **6**.¹ *tert*-Butylethynylbromane **2f** that cannot undergo 1,5-carbon–hydrogen insertion afforded the alkyne tosylate **5c,d** selectively.

In conclusion, we have synthesized 1-alkynyl(aryl)- λ^3 -bromanes via ligand exchange on Br(III) of aryl(difluoro)- λ^3 -bromane. The alkyne- λ^3 -bromanes undergo tandem Michael–carbene rearrangements by the reaction with sulfonate anions.

Supporting Information Available: Experimental procedures, compound characterization data for **2**, and **4–6** (PDF). X-ray crystallographic data in CIF format for **4**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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