Phenylboration of Monoalkyn-1-yltin Compounds

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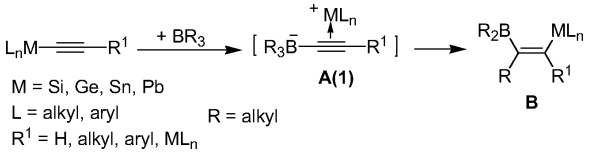
The 1 : 1 reactions of triphenylborane **1** with monoalkyn-1-yltin compounds $Me_3Sn–C{\equiv}C–R^1$ **2** [R^1 = ^{t}Bu (**a**), Ph (**b**), ferrocenyl (**c**), Si(H)Me_2 (**d**), $SnMe_3$ (**e**)] afford mainly (> 80 %) the corresponding alkene derivatives **3** by 1,1-phenylboration. Exchange B-Ph/Sn–C≡C–R^1 takes place as a side reaction. The corresponding 1 : 2 reaction with **2b** leads to the dialkenylborane **4b** (R^1 = Ph), of which the molecular structure could be determined by X-ray analysis. In contrast, the 1 : 2 reaction with **2e** gave an allene derivative **5e**. The solution-state structures of compounds **3** – **5** have been confirmed by ^{1}H, ^{11}B, ^{13}C and ^{119}Sn NMR spectroscopy.

Key words: Triphenylborane, Organoboration, Alkynes, Organotin, NMR, X-Ray

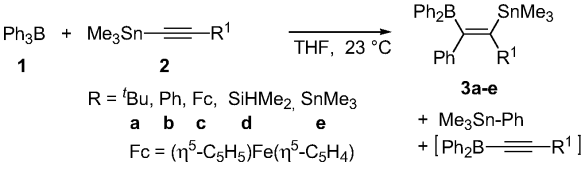
Introduction

1,1-Alkylboration of various alkyn-1-yl metal compounds as a versatile method for forming new carbon-carbon bonds has been extensively studied [1, 2]. The products are attractive for various catalysed carbon-carbon coupling reactions, making use *e. g.* of the Sn–C(sp^2) [3, 4] or the B–C(sp^2) bond [5]. The 1,1-alkylboration proceeds by cleavage of the M–C (alkyne) bond *via* an alkyn-1-ylborate-like intermediate **A(1)** [1] towards an alkene **B**, in which usually the boryl group and the metal fragment are in *cis* positions at the C=C bond [1] (Scheme 1). In contrast with numerous trialkylboranes, triphenylborane **1** has not been studied in a systematic way in this context. Except for qualitative experiments with alkyn-1-yltin compounds [1], this borane **1** has been used only occasionally in reactions with some alkyn-1-ylsilanes [6 – 8].



Scheme 1. 1,1-Alkylboration of alkyn-1-ylmetal compounds.

It is known that the formation of alkenes of the type **B** is reversible, depending on the substituents R and R^1 [1]. Since **B** is also a triorganoborane, it may compete, once it is formed, with BR_3 in the reaction with $L_nM–C{\equiv}C–R^1$. Moreover, considering the intermediate **A(1)**, other reaction pathways are conceivable, depending mainly on R, *e. g.* exchange reactions leading to R–ML_n and alkyn-1-ylboranes $R_2B–C{\equiv}C–R^1$. In this work, we report on the reaction of triphenylborane **1** with several monoalkyn-1-yltin compounds **2**, carried out in a 1 : 1 or 1 : 2 ratio.



Scheme 2. 1,1-Phenylboration of monoalkyn-1-yltin compounds **2**.

Results and Discussion

*Reaction of triphenylborane **1** with monoalkyn-1-yltin compounds **2** (1 : 1 ratio)*

In all cases studied, the reaction shown in Scheme 2 proceeds mainly to the alkenes **3**. The formation of **3**, monitored by ^{119}Sn NMR spectroscopy, was accompanied by side reactions (*ca.* 10 – 15 %). Since $Me_3Sn–Ph$ (δ^{119}Sn = −28.4 [9]) was identified as one of the side products from the beginning in the reaction solutions, Ph/C≡C–R^1 exchange competes with the 1,1-phenylboration. The alkyn-1-ylborane $Ph_2B–C{\equiv}C–R^1$ could not be detected, since it is probably even more reactive towards **2** than BPh_3, and therefore

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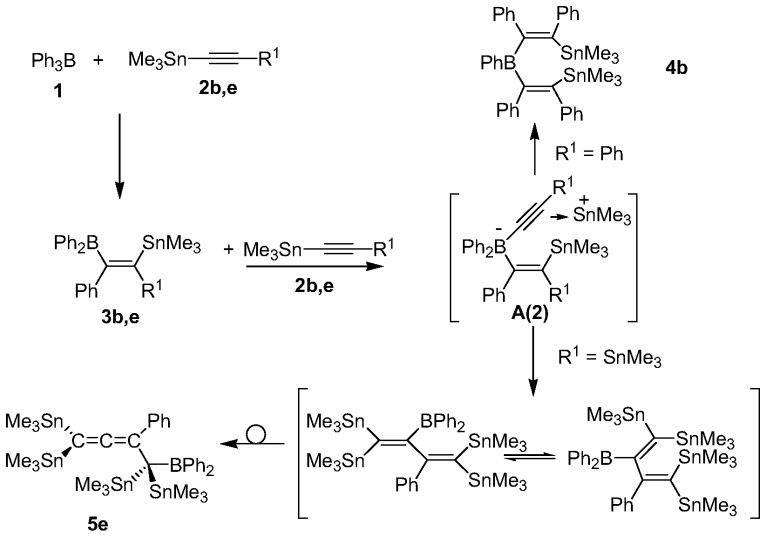

Scheme 3. Reactions of triphenylborane **1** with two equivalents of **2b** and **2e**.

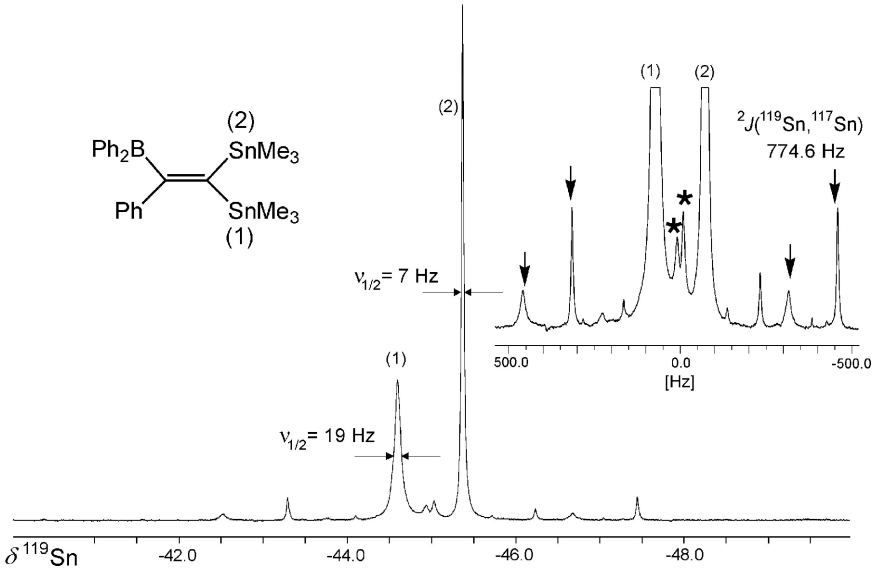

Fig. 1. 186.5 MHz $^{119}Sn\{^1H\}$ NMR spectrum (refocused INEPT, based on $^2J(^{119}Sn, ^1H)$ = 55 Hz) of the alkene derivative **3e** showing ^{117}Sn (arrows) and ^{119}Sn (asterisks) satellites. In contrast to the ^{117}Sn satellites (AX spin system), only the inner lines of the ^{119}Sn satellites (AB spin system) are visible. Note the broad and sharper lines for Sn(1) and Sn(2), respectively, owing to *trans* and *cis* positions with respect to the ^{11}B nucleus.

may be the source of numerous other side products. After several hours unassigned ^{119}Sn NMR signals began to grow. The results for the reaction of **1** with **2d** were reported previously [8]. In the case of **3e**, some of the new growing ^{119}Sn NMR signals were in the region typical of allenyltin compounds [10 – 12] (*vide infra*).

*Reaction of triphenylborane **1** with monoalkyn-1-yltin compounds **2** (1 : 2 ratio)*

The alkenylboranes **3** are likely to react with a second equivalent of **2**, and this can be achieved stepwise or in one reaction. Two major reaction pathways are conceivable, considering again an alkyn-1-ylborate-like intermediate **A(2)** as shown in Scheme 3. Migration of one of the remaining B-phenyl groups from boron to the neighbouring alkynyl-carbon atom in **A(2)** affords the dialkenylborane **4b** (R^1 = Ph). This compound crystallised readily from the reaction mixture, and its molecular structure could be determined by X-ray analysis (*vide infra*). The analogous reaction starting from triethylborane and two equivalents of trimethyl(propyn-1-yl)tin led to a substituted borol-3-ene [13]. A dialkenylborane, comparable with **4b**,

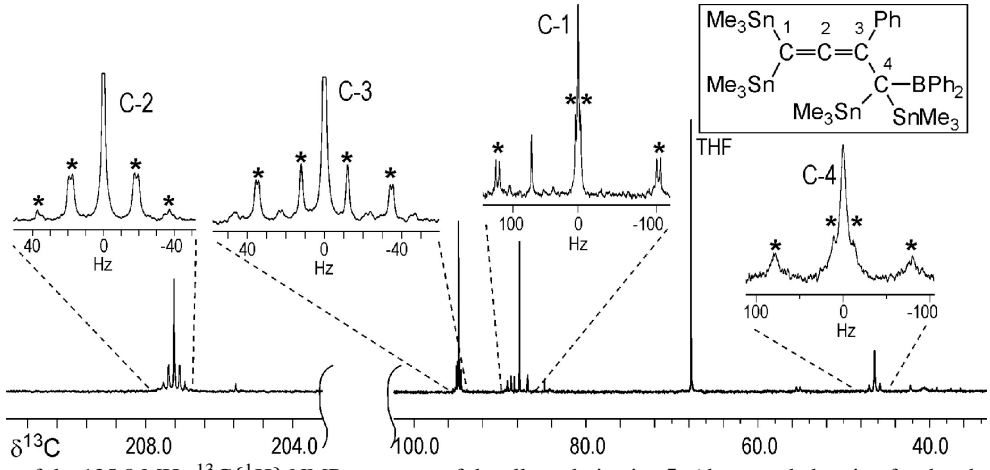

Fig. 2. Parts of the 125.8 MHz $^{13}C\{^1H\}$ NMR spectrum of the allene derivative **5e** (the crowded region for the phenyl groups is not shown). The expansions for the $^{13}C(1\text{-}4)$ signals show the $^{117/119}Sn$ satellites corresponding to the respective coupling constants.

Table 1. ^{119}Sn, ^{11}B and ^{13}C NMR data[a] for the alkene derivatives **3a – e**, **4b** (Schemes 2, 3).

	$\delta^{119}Sn$	$\delta^{11}B$	$\delta^{13}C_{(=C-Sn)}$, [$^1J(^{119}Sn, ^{13}C)$, Hz]	$\delta^{13}C_{(=C-B)}$, [$^2J(^{119}Sn, ^{13}C)$, Hz]
3a[b]	−56.9	64.6	163.2 [514.8]	160.4 (br)
3b[c]	−41.3	66.4	153.1 [455.2]	162.0 (br) [61.0]
3c[d]	−52.4	66.1	149.9 [525.2]	161.9 [65.4]
3d[e]	−47.0	71.0	153.4 [323.3], [$^1J(^{29}Si, ^{13}C)$ = 52.6 Hz]	182.3 (br) [29.3]
3e[f]	−46.5	65.0	159.3 [314.9], [274.9]	184.1 (br)
4b[g]	−38.7	67.3	156.3 [454.9]	160.0 (br) [57.1]

[a] In C_6D_6 at 296 K; coupling constants $J(^{119}Sn,^{13}C)$ are given in brackets [±0.3 Hz]; (br) denotes broad ^{13}C NMR signals owing to partially relaxed scalar ^{13}C-^{11}B spin-spin coupling; [b] other ^{13}C NMR data: δ [$J(^{119}Sn, ^{13}C)$ = −2.0 [317.9] (Me_3Sn); 34.1 [23.5], 43.0 [51.8] (^{t}Bu); 126.3, 128.2, 131.0 [7.6], 144.6 [106.4] (Ph); 128.4, 132.1, 139.6, 141.8 (br) (BPh_2); [c] other ^{13}C NMR data: δ [$J(^{119}Sn, ^{13}C)$] = −3.7 [327.4] (Me_3Sn); 68.6, 70.9 [26.2], 91.2 [51.6] (C_5H_4); 69.4 (C_5H_5); 126.0, 128.6, 129.9, 145.9 [88.6] (Ph); 128.0, 132.0, 139.3, 141.8 (br) (BPh_2); [d] other ^{13}C NMR data: δ [$J(^{119}Sn, ^{13}C)$] = −6.7 [335.5] (Me_3Sn); 125.2, 126.0, 128.2, 128.4, 128.6, 130.2, 143.1 [79.2], 146.8 [37.4] (Ph); 128.5, 132.8, 139.6, 141.9 (br) (BPh_2); [e] other ^{13}C and ^{29}Si NMR data, ref. [8]; [f] other ^{13}C NMR data: δ [$J(^{119}Sn, ^{13}C)$] = −5.0 [314.9], −4.9 [318.7] (Me_3Sn); 127.4, 128.5, 129.3, 149.9 [128.6] [86.9] (Ph); 128.6, 132.7, 139.7, 141.6 (br) (BPh_2); other ^{119}Sn NMR data: δ = −45.7 ($^2J(^{119}Sn, ^{117}Sn)$ = 774.6 Hz); [g] other ^{13}C NMR data: δ [$J(^{119}Sn, ^{13}C)$] = −7.6 [338.5] (Me_3Sn); 124.9 [8.0], 128.2, 142.2, [76.3], 147.2 [36.8] (Ph); 128.8, 130.6, 141.0, 141.2 (br) (BPh_2).

although not detected, was considered as an intermediate [13]. Heating of **4b** for prolonged times at 110 °C in toluene caused decomposition instead of rearrangement into a borol-3-ene.

Alternatively (R^1= $SnMe_3$), the B-alkenyl group may be transferred from the boron to the neighbouring alkynyl-carbon atom leading to a buta-1,3-diene derivative as shown. Such boranes are known to undergo a fast and in these cases irreversible allylic rearrangement [14] to give organometallically substituted allenes [10 – 12] such as **5e**.

NMR spectroscopic studies

The proposed solution-state structures of compounds **3**, **4** and **5** are consistent with the set of NMR data (Table 1 and Experimental Section). The ^{11}B NMR signals are rather broad, typical of phenylboranes, with characteristic $\delta^{11}B$ values [15]. The olefinic ^{13}C NMR signals of **3** and **4** are broad (B–C=; scalar relaxation of the second kind [16]), and sharp (Sn–C=), and the latter are accompanied by $^{117/119}Sn$ satellites corresponding to $^1J(Sn, ^{13}C)$ [9, 17]. Other satellites for $^nJ(Sn, ^{13}C)$ ($n > 1$) support the assignments. The ^{119}Sn NMR signals for **3** are broadened as a result of partially relaxed three-bond ^{119}Sn-^{11}B spin-spin coupling. This is most particularly evident for **3e**, where the stannyl groups are in *trans* and *cis* positions with respect to the boryl group (Fig. 1). The greater line width of one of the ^{119}Sn NMR signals indicates the *trans* position of this Me_3Sn group relative to the boryl group, since $|^3J(^{119}Sn, ^{11}B)_{trans}| > |^3J(^{119}Sn, ^{11}B)_{cis}|$ [9, 17]. In the case of **4b**, the data correspond to structural features determined for the solid-state structure (*vide infra*).

The allene derivative **5e** provides a large set of ^{13}C and ^{119}Sn NMR data, all of which support the proposed structure. The ^{13}C NMR spectrum (Fig. 2) shows the

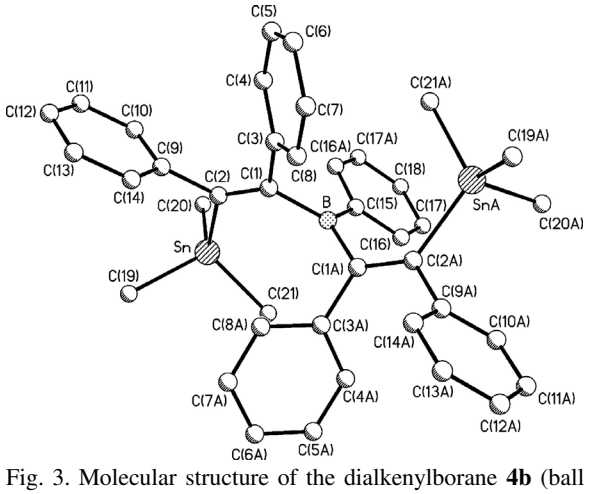

Fig. 3. Molecular structure of the dialkenylborane **4b** (ball and stick model; hydrogen atoms omitted for clarity). Selected bond lengths (pm) and angles (°): B–C1 157.4(4), B–C15 156.2(6), C1–C2 134.4(4), C1–C3 150.4(5), C2–C9 150.1(4), Sn–C2 217.9(3), Sn–C19 213.8(5), Sn–C20 215.5(5), Sn–C21 212.9(3); C1–B–C1A 119.0(4), C1–B–C15 120.5(2), B–C1–C2 124.2(3), B–C1–C3 113.9(2), C2–C1–C3 121.8(3), C1–C2–C9 122.0(3), C1–C2–Sn 126.0(2); B–C1–C2–Sn 2.2(5), C3–C1–C2–C9 −8.2(5), C15–B–C1–C2 65.4(3).

typical signals for the C=C=C–C unit together with the required $^{117/119}$Sn satellites. The ^{13}C NMR signals of the Ph_2B group are broad as a result of restricted rotation about B–C bonds. This is confirmed by the broad and featureless ^{119}Sn NMR signals in the region typical of allenyltin compounds. The $^{13}C(p)$ resonance of the C(3)-phenyl group reveals $^{117/119}$Sn satellites with an integral intensity corresponding to the four tin atoms present, indicating a long-range coupling across six and seven bonds, respectively, with $^{6,7}J(Sn,^{13}C)$ = 7.7 Hz. These and other long-range coupling constants are typical of the allene system.

*X-Ray structural study of the dialkenylborane **4b***

The molecular structure of **4b** is shown in Fig. 3 together with selected structural parameters. The surroundings of the boron atom are trigonal planar within the experimental error, which is also true for all three-coordinate carbon atoms in this molecule. All bond lengths and angles are in the expected range. Although the plane of the B-phenyl group is only slightly twisted against the B,C1,C15,C1A plane, ideal for BC(pp)π interactions, the C–C(B–Ph) distances show the usual pattern, similar to that of the C-Ph groups in **4b**. The orientation of the C-Ph and the alkenyl groups minimises steric interactions between phenyl groups and Me_3Sn groups.

Experimental Section

General

The preparative work and the handling of samples were carried out observing necessary precautions to exclude traces of air and moisture. Carefully dried solvents and oven-dried glassware were used throughout. Triphenylborane **1** [18] and the alkyn-1-yltin compounds (**2a** [19], **2b** [20], **2c** [21], **2e** [20]) were prepared following literature procedures. NMR measurements (5 mm o. d. tubes, 23 °C; *ca.* 5 – 10 % in C_6D_6): Bruker ARX 250 and DRX 500: ^{1}H, ^{11}B, ^{13}C, and ^{119}Sn NMR (refocused INEPT [22] based on $^2J(^{119}Sn,^1H)$ = 55 Hz); Varian INOVA 400: ^{1}H, ^{13}C NMR; chemical shifts are given with respect to Me_4Si [δ^1H (C_6D_6) = 7.15; δ^{13}C (C_6D_6) = 128.0]; δ^{11}B = 0 for BF_3-OEt_2 with $\Xi(^{11}B)$ = 32.083971 MHz; and δ^{119}Sn = 0 for $SnMe_4$ with $\Xi(^{119}Sn)$ = 37.290665 MHz. The melting point (uncorrected) was determined using a Büchi 510 melting point apparatus.

*1,1-Phenylboration of the alkyn-1-yltin compounds **2a – e** with triphenylborane **1** (general procedure)*

To the solution of triphenylborane **1** (1.0 – 1.5 mmol) in 5 mL of THF a solution of 1 or 2 eqvivalents of the respective alkyn-1-yltin compound **2** in THF (5 – 10 mL) was added at r. t. After 30 – 60 min the solvent was removed in a vacuum, and a pale yellow or dark red (**3c**) oil remained. According to NMR spectra, the alkenes **3** and the allene **5e** were pure (*ca.* 85 – 95 %). The dialkenylborane **4b** [m. p. 199 – 203 °C (decomp.)] was purified by crystallisation from benzene.

3a: ^{1}H NMR (500 MHz): δ^1H [$J(^{119}Sn,^1H)$] = 0.21 [49.8] (s, 9H, $SnMe_3$); 1.34 (s, 9H, ^{t}Bu); 6.86 (t, 1H, Ph, $^3J(H,H)$ = 7.5 Hz); 6.98 (t, 2H, Ph, $^3J(H,H)$ = 7.5 Hz); 7.18 (d, 2H, Ph, $^3J(H,H)$ = 7.5 Hz); 7.3 – 8.1 (m, 10H, BPh_2). **3b:** ^{1}H NMR (500 MHz): δ^1H [$J(^{119}Sn,^1H)$] = −0.49 [52.9] (s, 9H, $SnMe_3$); 7.1 – 7.3, 7.6 – 7.8, 8.55 (m, 15H, Ph, BPh_2). **3c:** ^{1}H NMR (500 MHz): δ^1H [$J(^{119}Sn,^1H)$] = 0.26 [51.8] (s, 9H, $SnMe_3$); 4.08 (m, 2H, C_5H_4); 4.14 (m, 2H, C_5H_4); 4.24 (s, 5H, C_5H_5); 6.9, 8.1 (m, 15H, Ph, BPh_2). **3e:** ^{1}H NMR (500 MHz): δ^1H [$J(^{119}Sn,^1H)$] = 0.17 [50.7], 0.25 [53.0] (s, 18H, $SnMe_3$); 6.97, 7.07, 7.77 (t, t, d, 5H, Ph); 7.3, 8.1 (m, 10H, BPh_2). **4b:** ^{1}H NMR (500 MHz): δ^1H [$J(^{119}Sn,^1H)$] = −0.28 [52.3] (s, 18H, $SnMe_3$); 7.1 – 8.3 (m, 15H, Ph, BPh_2). **5e:** ^{1}H NMR (500 MHz): δ^1H [$J(^{119}Sn,^1H)$] = 0.28 [50.8], 0.43 [53.1] (s, s, 36H, $SnMe_3$); 7.0 – 8.4 (m, 15H, Ph, BPh_2). ^{13}C NMR (125.8 MHz): δ^{13}C [$J(^{119}Sn,^{13}C)$] = −4.9 [326.5], [4.6] ($SnMe_3$); −1.9 [321.3], [5.6] ($SnMe_3$); 46.4 (br) [160.9], [22.4] (C-B); 87.8 [253.2], [7.9] (=C-Sn); 94.8 [71.0], [24.1] (=C-Ph); 124.7 [7.7] (*p*), 126.6 [9.6] (*o*), 127.6 (*m*), 142.4 [31.5], [28.1] (*i*) (Ph); 128.5 (br) (*m*), 129.4

(*p*), 134.9 (br) (*o*), 147.0 (br) (*i*) (BPh_2); 207.2 [39.4], [35.1] (=C=). ^{119}Sn NMR (186.5 MHz): δ^{119}Sn = −3 to −7 (br).

Crystal structure determination of the dialkenylborane ***4b***

A crystal of appropriate size was sealed under argon in a Lindemann capillary, and the data collection was carried out at 20 °C. The reflection intensities were collected on a Siemens P4 diffractometer (MoK_α radiation, λ = 71.073 pm, graphite-monochromated). Structure solution and refinement were carried out with the program package SHELXTL-PLUS V.5.1. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were placed in calculated positions and refined by applying a riding model with fixed isotropic displacement parameters. $C_{40}H_{43}B_1Sn_2$: Colourless irregular crystal with dimensions 0.16 × 0.12 × 0.12 mm^3, monoclinic space group *C*2/*c* with the lattice parameters *a* =1332.3(3), *b* = 1762.2(4), *c* =1590.2(3) pm, β = 90.29(3)°, *V* = 3733.2(13) × 10^6 pm^3, *Z* = 4, μ = 1.362 mm^{-1}; a total of 13065 reflections collected in the range 2.30° ≤ θ ≤ 28.05°, 4164 independent reflections, 2280 assigned to be observed [$I \geq 2\sigma(I)$]; full-matrix least squares refinement on F^2 with 196 parameters converged at *R*1/*wR*2 values of 0.037/0.083; the max./min. residual electron density was 0.73/−0.32 × 10^{-6} e pm^{-3} [23].

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[23] CCDC 658105 (**4b**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk /data_request/cif.