

Hydroboration of Bis(trimethylsilyl)ethyne. New Aspects of Hydroboration

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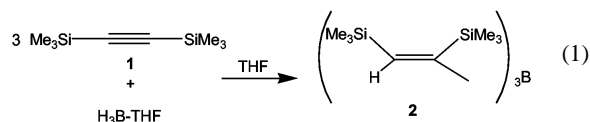
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The hydroboration of bis(trimethylsilyl)ethyne, $\text{Me}_3\text{Si-C}\equiv\text{C-SiMe}_3$ **1**, with 9-borabicyclo [3.3.1] nonane (9-BBN) gives first the expected (*Z*)-alkene **5** which rearranges, without UV irradiation, after several days quantitatively into the (*E*)-alkene **6**. Heating of **6** in the presence of a further equivalent of **1** leads, again almost quantitatively, to an allene, the 1,1,4,4-tetrakis(trimethylsilyl)-4-[9-(9-borabicyclo[3.3.1]nonyl)]buta-1,2-diene **8**. Reactive structures arising from π - σ delocalisation involving the boryl group are proposed to be responsible both for the *cis/trans*-isomerisation and the allene formation. It is suggested that analogous structures may explain the previously observed formation of allenes **9** and **10**, tin-analogues of **8**. The structures of **5**, **6** and **8** in solution follow from a consistent set of NMR data (^1H , ^{11}B , ^{13}C , ^{29}Si NMR), and the solid-state structure of **8** was confirmed by X-ray analysis.

Key words: Alkynes, Alkenes, Allenes

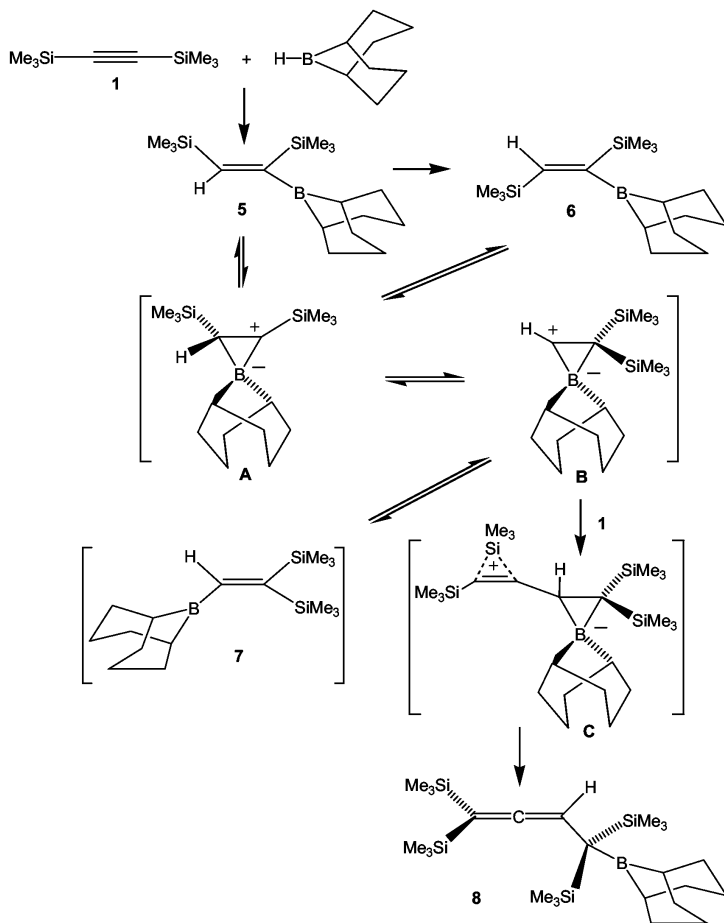
Introduction

Various alkyn-1-ylsilanes have been used in hydroboration reactions, and it appears that the prediction of potential products is much less straightforward when compared with hydroboration of simple alkynes. Depending on the bulkiness of the borane, on the second substituent at the $\text{C}\equiv\text{C}$ bond(s), on the nature of the silyl group, and also on reaction conditions, a wide range of different types of products has been obtained [1–4]. Among other readily available alkyn-1-ylsilanes bis(trimethylsilyl)ethyne, $\text{Me}_3\text{Si}-\text{C}\equiv\text{C}-\text{SiMe}_3$ **1**, is an attractive, widely used reagent in organometallic chemistry. It has been reported [5] that three equivalents of **1** react with $\text{BH}_3\cdot\text{THF}/\text{THF}$ in the usual way by *cis*-1,2-hydroboration to give the expected tris(alkenyl)borane **2** [eq. (1)], and this has been confirmed by a detailed NMR study [6].



In contrast, the reaction of **1** with an excess of Et₂BH [7] proceeds in a more complex way, since C≡C bonds are converted into C-C bonds and.

in the course of condensation reactions, triethylborane, Et₃B, is eliminated to give cyclic products [8]. Other hydroborating reagents such as HBCl₂ [9] or 1,2,4,3,5-trithiadiborolane [10] have been used to give alkenylboranes with the expected stereochemistry, although it has been noted [9] that the alkenylboranes, after methanolysis of the B-Cl bonds, undergo photo-induced *Z-E*-isomerisation. The reaction of **1** with *nido*-pentaborane(9) gives 2,3-bis(trimethylsilyl)-2,3-dicarba-*nido*-hexaborane(8) [5], whereas in the Me₂S-assisted reaction of **1** with *nido*-decaborane(14) only one carbon atom of **1** becomes part of a carborane cage [11]. 6-Aza-*nido*-decaborane reacts with **1** by 1,1-hydroboration as a result of 1,2-migration of one Me₃Si group [12]. Surprisingly, to the best of our knowledge, the hydroboration of **1** using 9-borabicyclo[3.3.1]nonane, 9-BBN, one of the most popular hydroborating reagents, has not been investigated in detail. Therefore, in the present work we have studied this reaction, and in the light of the results, we attempt to interpret previous findings [13–15] for analogous reactions of bis(trimethylstannyl)ethyne, Me₃Sn-C≡C-SnMe₃ (**3**), and trimethylsilyl(trimethylstannyl)ethyne, Me₃Si-C≡C-SnMe₃ (**4**), with 9-BBN.



Scheme 1.

Results and Discussion

Reaction of bis(trimethylsilyl)ethyne, $\text{Me}_3\text{Si}-\text{C}\equiv\text{C}-\text{SiMe}_3$ (**1**), with 9-borabicyclo[3.3.1]nonane, 9-BBN

The reaction of equimolar amounts of **1** and 9-BBN in toluene, pentane or THF at room temperature is slow, and it leads selectively to the expected hydroboration product **5** with *Z*-configuration. After 4 d at room temperature, much faster upon heating at 60 to 110 °C, at day light or in the dark, **5** isomerises into **6** with *E*-configuration (see Table 1 for NMR data). At 60 to 110 °C, in the presence of an excess of **1**, **6** is converted almost quantitatively (there are small amounts, < 10%, of unidentified alkenes and allenes) into the allene derivative **8** (see Table 2 for NMR data). A potential intermediate **7**, formally the product of 1,1-hydroboration, could not be detected. The allene **8** is also formed to a significant amount by heating the products of the 1:1 reaction; then some 9-BBN is left

Table 1. ^{11}B , ^{13}C and ^{29}Si NMR data^a of the alkenes **5** and **6**.

	$\delta^{13}\text{C}$ (SiCH=)	$\delta^{13}\text{C}$ (BC=)	$\delta^{13}\text{C}$ (SiMe ₃)	$\delta^{13}\text{C}$ (BBN)	$\delta^{11}\text{B}$	$\delta^{29}\text{Si}$
5	151.7 (65.7)	178.8 (br)	0.9 (51.6) 1.8 (50.7)	31.6 (br) 34.6, 23.6	+82.6	-10.34 -10.39
7b	146.1 (65.2)	178.7 (br) (42.2)	0.9 (50.9) 1.0 (51.5)	32.4 (br) 34.0, 23.5	+85.5	-10.6(12.7) -1.5(12.7)

^a In C₆D₆; coupling constants ¹*J*(²⁹Si, ¹³C) are given in parentheses, and *J*(²⁹Si, ²⁹Si) in $\langle \rangle$ (all accurate to at least ± 0.5 Hz); (br) denotes the broadened ¹³C NMR signal of a carbon atom linked to boron.

in the reaction mixture. The results are summarised in Scheme 1.

Scheme 1 also shows the proposed zwitterionic structures **A** and **B** related to the alkenes **5**, **6** and **7**. These structures are the result of π - σ delocalisation and take into account the stabilising effect of trimethylsilyl groups on a positively charged centre in β -position [16]. Assuming a contribution of **A**, the

Table 2. ^{11}B , ^{13}C , ^{29}Si and ^{119}Sn NMR data^a of the allenes **8**, **9**, **10** and **11**.

	$\delta^{13}\text{C}$ ($\text{M}_2\text{C}=\text{C}=\text{C}$)	$\delta^{13}\text{C}$ ($=\text{C}=\text{C}$)	$\delta^{13}\text{C}$ ($=\text{C}(\text{H})$)	$\delta^{13}\text{C}$ (MMe_3)	$\delta^{13}\text{C}$ (BBN)	$\delta^{13}\text{C}$ C-BBN	$\delta^{11}\text{B}$	$\delta^{29}\text{Si}$ ^{119}Sn
8	87.7 (51.8)	212.3 (< 2)	77.6 (< 2)	1.3 (52.4) 3.3 (51.6)	30.9 (br) 33.9, 23.6	36.0 (br) (33.3; 1J)	+84.8	−3.4 (=CSi ₂) < 1.9; 5J > −0.6 (CSi ₂) < 1.9; 5J >
9 ^b	80.4 [280.0] [8.3]	207.5 [38.0]	75.9 [68.0] [21.7]	−7.6 [333.6] −4.9 [314.3]	29.5 (br) 33.9, 23.8	33.3 (br) [149.0; 1J] [22.7; 4J]	+78.2	−9.6 (=CSn ₂) {335.7; 2J } {243.9, 233.4; 5J } 9.0 (CSn ₂) {477.7; 2J } {243.9, 233.4; 5J }
10 ^c	85.3 [271.0] 85.0 [271.8]	209.0 [40.5] 208.95 [40.5]	76.7 [33.4] 68.1 [33.4]	0.7, 0.6 3.1, 3.03 −7.1 [331.4] −7.14 [332.1] −4.45 [315.1] −4.53 [315.8]	29.7 (br) 33.93, 33.87, 33.63, 23.6 ^d	37.3 (br) [108.0; 1J]	+80.5	−3.6, −3.7 (=CSi) [30.0; 2J] [22.0, 24.9; 5J] −0.2, −0.4 (CSi) [51.5, 51.3; 2J] [19.5, 21.7; 5J] −12.6, −12.8 (=CSn) {268.0, 255.0; 5J } 2.6, 1.7 (CSn) {268.0, 255.0; 5J }

^a In C_6D_6 ; coupling constants $J(^{29}\text{Si}, ^{13}\text{C})$ are given in parentheses, $J(^{119}\text{Sn}, ^{13}\text{C})$ and $J(^{119}\text{Sn}, ^{29}\text{Si})$ in brackets, $J(^{29}\text{Si}, ^{29}\text{Si})$ in $\langle \rangle$, and $J(^{119}\text{Sn}, ^{119}\text{Sn})$ in braces (all ± 1 Hz or more accurate, as in the case of **8**: ± 0.1 Hz); (br) denotes the broadened ^{13}C NMR signal of a carbon atom linked to boron; ^b data from Ref. [11]; in CDCl_3 ; ^c data from Ref. [10]; in CDCl_3 ; ^d some ^{13}C NMR signals were not resolved.

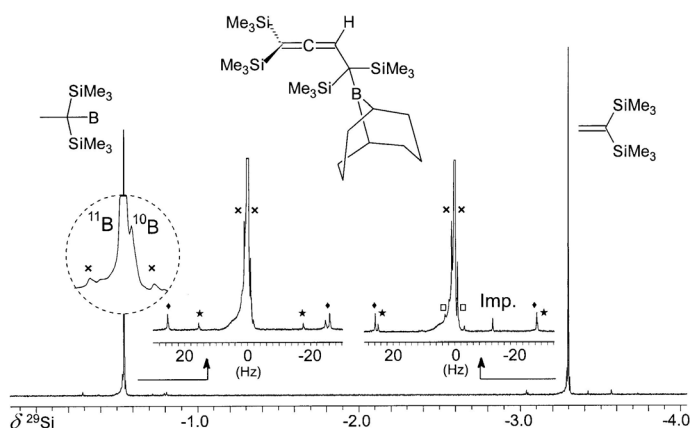


Fig. 1. 99.4 MHz ^{29}Si NMR spectrum (re-focused INEPT with ^1H decoupling [20]) of the allene **8** showing satellites due to $^1J(^{29}\text{Si}, ^{13}\text{C})$ (marked by asterisks for C(1) and C(4), and by filled rhombs for SiMe₃ groups), $^3J(^{29}\text{Si}(1), ^{13}\text{C}(3)) = 6.2$ Hz (marked by open squares) and $^5J(^{29}\text{Si}, ^{29}\text{Si}) = 1.9$ Hz (marked by crosses). There are noteworthy isotope-induced chemical shifts $^1\Delta^{12/13}\text{C}(4)(^{29}\text{Si}) = -11.0$ ppb (see Ref. [21,22]), and $^2\Delta^{10/11}\text{B}(^{29}\text{Si}(4)) = +2.7$ ppb (see Ref. [23, 24]).

cis/trans-isomerisation of **5** into **6** is readily explained. In principle, such an isomerisation could also be explained by assuming a canonic structure of **5** with CB(pp) π interactions which is often discussed in the case of vinylboranes. However, the geminal positions of the bulky boryl and Me₃Si groups at the C=C bond in **5** do not favour a coplanar arrangement of the C₂B plane of the boryl group and the C=C—B plane, a prerequisite of efficient CB(pp) π interactions.

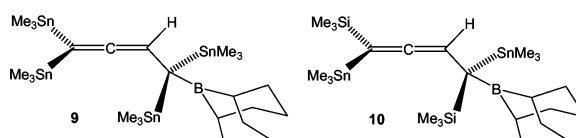
Migration of one Me₃Si group in **A** leads to the structure **B**, in which the positively charged centre is stabilised by two Me₃Si groups in β -positions. One could now envisage the formation of the alkene **7** which however, is not detected in the reaction solutions using NMR spectroscopy. An alternative is shown by the reaction of **B** with **1**, leading at first to **C** and finally to the allene **8**. Since **1** does not react with other triorganoboranes such as triethylborane or 9-Et-9-BBN,

even on prolonged heating at 100 °C, it is difficult to conceive that **7** will react with **1** without considering **B**, a structure much more reactive than that of **7**. The carbocationic centre in **B** should interact with **1** by cleavage of one of the Si—C≡ bonds, in a similar way as described for 1,1-organoboration of alkyn-1-ylmetal compounds [17], leading to **C** which then rearranges irreversibly into the allene **8**. If **A** also reacts with **1**, the formation of a different allene is expected. Indeed, a small amount of at least one other allene is present in the reaction mixtures. However, the NMR data set is insufficient for reliable structural assignments.

The ^{29}Si NMR spectrum of **8** is shown in Figure 1. The magnitude of $^5J(^{29}\text{Si}, ^{29}\text{Si}) = 1.9\text{ Hz}$ is small when compared with $^5J(^{119}\text{Sn}, ^{119}\text{Sn})$ in **9** (243.9, 233.4 Hz). Similarly, $^5J(^{119}\text{Sn}, ^{29}\text{Si})$ values in **10** (22.0, 24.9; 19.5, 21.7 Hz [14]) are small with respect to $^5J(^{119}\text{Sn}, ^{119}\text{Sn})$ in **9**, even by considering the smaller gyromagnetic ratio $\gamma(^{29}\text{Si})$ [$0.53 \cdot \gamma(^{119}\text{Sn})$] and the smaller valence s electron density of silicon $\Psi_{\text{Si}}(0)^2$ [approximately $0.25 \Psi_{\text{Sn}}(0)^2$]. This indicates that in **8** and **10** certain conformations of the C(4)(9-BBN)(SiMe₃)₂ or C(4)(9-BBN)(SiMe₃)(SnMe₃) moieties are more populated than those of the C(4)(9-BBN)(SnMe₃)₂ unit in **9**. The dependence of the magnitude of $^5J(^{119}\text{Sn}, ^{119}\text{Sn})$ on the respective dihedral angle [Sn—C(1)···C(4)—Sn] has been demonstrated previously [13b].

*Comparison of the reactivity of Me₃Si—C≡C—SiMe₃ (**1**) with that of Me₃Sn—C≡C—SnMe₃ (**3**) and Me₃Si—C≡C—SnMe₃ (**4**) towards 9-BBN*

It has been reported that the reactions of **3** and **4** with 9-BBN afford the allenes **9** [13a] and **10** (two diastereomers in a 1:1 molar ratio; only one diastereomer is shown) [14], respectively, and the molecular structure of **9** has been determined by X-ray analysis [15]. We have repeated the reaction of **3** with 9-BBN using different molar ratios (2:1, 1:1), and it was confirmed that **9** is formed irrespective of the molar ratio. In the 1:1 reaction, 9-BBN was left in the reaction mixture. Intermediates analogous to the alkenes **5** or **6** have not been detected using low-temperature (−50 to 25 °C) ^{119}Sn NMR, and although the intermediacy of an alkene analogous to **7** has been proposed, NMR spectroscopic evidence was not found. The stabilising effect of a Me₃Sn group in β -position to a positively charged centre should exceed that of a Me₃Si group. This points towards the role of the zwitterionic structures **A** and **B** (Scheme 1), and it suggests that the anal-



ogous structures, in particular analogous to **B**, must be considered in the course of the formation of the allenes **9** and **10**. The Sn—C≡ bond is known to be much more reactive than the Si—C≡ bond [17] which means that the conversion of the tin-analogues of **B** into the tin-analogues of **C** proceeds under very mild conditions, and that the allenes **9** and **10** are the sole products.

*X-Ray structural analysis of the allene **8***

The molecular structure of **8** is shown in Fig. 2. The quality of the single crystals was inadequate for collecting a data set which allows the calculation of precise data of bond lengths and angles. However, the proposed structure of **8** is confirmed. The crystals are triclinic, space group $P\bar{1}$, while those of the tin analogue **9** are monoclinic; space group $P2_1/n$ [15].

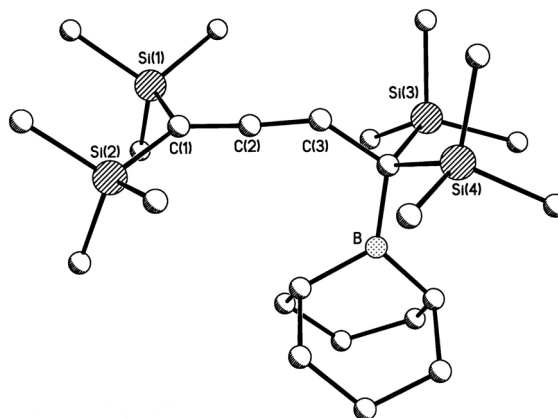


Fig. 2. Molecular structure of the allene **8** (see text and Experimental Section).

Conclusion

Hydroboration of alkynes with organometallic substituents appears to proceed initially in the expected way (*cis*-1,2-hydroboration) to give alkenylboranes. In contrast with simple non-terminal alkynes, *cis/trans*-isomerisation may take place already after a few days without UV irradiation, followed by further rearrangements [18] which in the case of **1**, studied in this work, lead to the allene **8**. The proposed reactive zwitterionic structures (Scheme 1), as a result of π - σ delocalisation, may also explain the straightforward formation

of the previously obtained allenes **9** and **10**, the tin-analogues of **8**.

Experimental Section

Handling of samples for NMR measurements as well as all preparative work was carried out by observing necessary precautions to exclude traces of oxygen and moisture. All solvents were dried by standard methods; starting materials (**1** and 9-BBN) were used as commercial products without further purification, and **3** was prepared following a literature procedure [19].

NMR spectra were recorded at 25 °C on Bruker ARX 250 or DRX 500 spectrometers, all equipped with multinuclear units, using saturated C₆D₆ solutions in 5 mm tubes. Chemical shifts are given with respect to Me₄Si [$\delta^1\text{H}$ (C₆D₅H) = 7.15, $\delta^{13}\text{C}$ (C₆D₆) = 128.0, $\delta^{29}\text{Si}$ = 0 for Me₄Si with $\Xi(^{29}\text{Si})$ = 19.867187 MHz]. ^{29}Si NMR spectra were measured using the refocused INEPT pulse sequence with ^1H decoupling [20]. It proved advantageous to use optimised low power levels for ^1H decoupling, fairly long acquisition times (6 to 10 s) and repetition delays (10–15 s) in order to obtain the sharp signals undisturbed by truncation of the FID and artificial broadening induced by temperature gradients within the sample. IR spectra were recorded using a Perkin Elmer instrument Spectrum 2000 FT IR, and EI-MS was measured with a Finnigan MAT 8500 spectrometer (Ionisation energy 70 eV) with direct inlet.

(*Z*)-1,2-Bis(trimethylsilyl)-1-(9-borabicyclo[3.3.1]nonyl)-ethene **5**

A solution of **1** (0.615 g, 3.6 mmol) in pentane, THF or toluene (15 ml) was prepared, and 9-BBN (0.437 g, 3.58 mmol) was added as a solid in one portion at room temperature. The mixture was kept stirring for 6–12 h, and quantitative formation of **5** was indicated by NMR spectra (Table 1). After removing all volatile material, pure (> 90%) **5** was left as a colourless, oily liquid. ^1H NMR (250.13 MHz; C₆D₆): δ ($J(^{29}\text{Si}, ^1\text{H})$) = 0.23 (6.6) (s, 9 H, SiMe₃), 0.26 (6.5) (s, 9 H, SiMe₃), 1.20–2.00 (m, 14 H, 9-BBN), 7.13 (20.7; 3J) (8.0; 2J) (s, 1 H, =CH).

(*E*)-1,2-Bis(trimethylsilyl)-1-(9-borabicyclo[3.3.1]nonyl)-ethene **6**

The reaction solutions containing **5** were left for several days at room temperature, either at day light or in the dark, and the rearrangement of **5** into **6** was monitored by ^{29}Si

NMR spectroscopy. After 4 days, when the ^{29}Si NMR signals of **5** were no longer detected, the solvent was removed in a vacuum to give a colourless, oily liquid which was identified by NMR (Table 1) as pure (> 90%) **6**. ^1H NMR (250.13 MHz; C₆D₆): δ ($J(^{29}\text{Si}, ^1\text{H})$) = 0.09 (6.5) (s, 9 H, SiMe₃), 0.13 (6.4) (s, 9 H, SiMe₃), 1.20–2.00 (m, 14 H, 9-BBN), 6.65 (17.0; 3J) (6.7; 2J) (s, 1 H, =CH).

1,1,4,4-Tetrakis(trimethylsilyl)-4-[9-(9-borabicyclo[3.3.1]nonyl)]buta-1,2-diene **8**

A mixture of **1** (1.128 g, 6.6 mmol) and 9-BBN (0.437 g, 3.58 mmol) in toluene (15 ml) was heated at 110 °C for 24 h. After removing all volatile material in a vacuum, the residue was dissolved in pentane. This solution was kept for 7 d at –78 °C, and a colourless precipitate was obtained. Recrystallisation from pentane at –20 °C gave pure (Table 2), crystalline (m.p. 55–57 °C) **8** (1.85 g, 60%). IR (hexane): ν = 1895 (C=C_{asym}) cm^{–1}. ^1H NMR (250.13 MHz; C₆D₆): δ ($J(^{29}\text{Si}, ^1\text{H})$) = 0.16 (6.4) (s, 18 H, SiMe₃), 0.17 (6.4) (s, 18 H, SiMe₃), 1.40–2.00 (m, 14 H, 9-BBN), 4.70 (4.80; 4J) (s, 1 H, =CH).

Crystal structure determination of the allene **8**

A single crystal of **8**, recrystallised from pentane at –20 °C, was sealed under argon in a Lindemann capillary. Intensity data collection was carried out on a Siemens P4 diffractometer with Mo-K α -radiation (λ = 71.073 pm; graphite monochromator) at room temperature. The hydrogen atoms were put in calculated positions. All non-hydrogen atoms were refined with anisotropic temperature factors. The hydrogen atoms were refined applying the riding model with fixed isotropic temperature factors.

8: C₂₄H₅₀BSi₄, colourless, irregular shape: 0.12 × 0.10 × 0.07 mm³; triclinic space group $P\bar{1}$; a = 9.5486(19), b = 17.040(3), c = 18.941(4) Å, α = 82.98(3), β = 89.74(3), γ = 89.25(3)°, Z = 4, μ = 0.203 mm^{–1}; 28,214 reflections collected in the range 2°–28° in ϑ , 13,639 independent reflections ($I > 2\sigma(I)$); full matrix least squares refinement on F^2 with 523 parameters, $R1/wR2$ -values 0.1385 / 0.3895, max. / min. residual electron density 0.42 / –0.41 · 10^{–6} e[–] pm^{–3}.

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