Monocarbaborane Chemistry: Cage Opening of *nido*-1-CB_8H_{12} by Tertiary Bases − an Example of a Straightforward *nido* → *arachno* Transformation; Isolation of a New Series of 4-L-*arachno*-5-CB_8H_{12} Compounds (L = NMe_3, NEt_3, and Quinoline)

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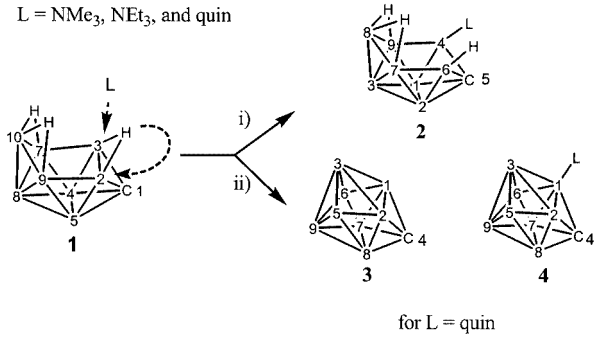
Room-temperature reactions between the carborane *nido*-1-CB_8H_{12} (**1**) and selected tertiary Lewis bases [L = NMe_3, NEt_3, and quinoline (quin)] in CH_2Cl_2 at room temperature for 24 h resulted in the isolation of a series of 4-L-*arachno*-5-CB_8H_{12} compounds (**2**; L = NMe_3, **2a**, L = NEt_3, **2b** and L = quin, **2c**). This main reaction mode can be classified as a straightforward *nido* → *arachno* transformation and was characterized by a cage opening of the original pentagonal face in **1** by L at the bridging site adjacent to the carbon apex with the formation of a hexagonal open face. The formation of **2a** was clean, whereas that of **2c** was accompanied by formation of the *closo*-[4-CB_8H_9]$^-$ (**3**) anion as a side-product. The first representative of the zwitterionic 1-L-*closo*-4-CB_8H_8 (**4**) series, 1-quin-*closo*-4-CB_8H_8 (**4c**), was isolated as another side product from the quinoline reaction. The structure of compound **2b** was determined by an X-ray diffraction analysis and the constitution of all compounds is consistent with the results of mass spectrometry. Multinuclear (^1H, ^{11}B, and ^{13}C), two-dimensional [^{11}B-^{11}B]-COSY, and $^1H\{^{11}B$(selective)$\}$ magnetic resonance measurements lead to complete assignments of all resonances and are in excellent agreement with the structures proposed.

Introduction

Although the *nido*-1-CB_8H_{12} (**1**) carborane has been known since 1977,[1] not much chemistry of this interesting compound has so far been reported. Carborane **1** was employed as a starting material for the preparation of the smaller monocarbaborane anions [2-CB_6H_7]$^-$, [1-CB_7H_8]$^-$, and [4-CB_8H_9]$^-$ (**3**), completing a series of the parent seven,[2] eight,[2,3] and nine-vertex[4] *closo* monocarbaboranes. The sole example of metallacarborane chemistry based on carborane **1** so far, has been the synthesis of the platinacarborane [6,6-$(PPh_3)_2$-*arachno*-6,4-$PtCB_7H_{11}$].[5] In the present work, we have extended the rather undeveloped chemistry of carborane **1** by its room-temperature reactions with selected tertiary amines (L = NMe_3, NEt_3, and quin). We would like to demonstrate that these reactions lead to a simple opening of the *nido* cage in **1** and the formation of a series of corresponding 4-L-*arachno*-5-CB_8H_{12} compounds. Numbering systems for the nine-vertex *closo*, *nido*, and *arachno* skeletons used in this work are given in Scheme 1. Structures are presented in a simplified manner; unmarked vertices in Scheme 1 stand for cluster BH units, while C denotes the CH vertex.



Scheme 1. Simplified scheme for the cluster opening in *nido*-1-CB_8H_{12} (**1**) by selected tertiary Lewis bases (L = NMe_3, NEt_3, and quinoline) and the formation of side products; i) L, ambient temperature, main reaction mode; ii) side reaction mode

Results and Discussion

As shown in path i) of Scheme 1, room-temperature reactions of the *nido*-1-CB_8H_{12} (**1**) monocarbaborane with

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selected tertiary amines (L = Me_3N, Et_3N, and quin) in dichloromethane afforded a series of Lewis-base adducts of general formula 4-L-*arachno*-5-CB_8H_{12} (**2**) (**2a** for L = Me_3N, **2b** for L = Et_3N, and **2c** for L = quin) as the main reaction products in yields of 96, 36, and 35 %, respectively.

The formation of compounds of type **2** in this reaction can be classified as a clean *nido* → *arachno* transformation, in which the base L adds two more cluster electrons to the original 22-electron *nido* system of **1** to form 24-electron *arachno* ligand derivatives of structure **2**. As also outlined in Scheme 1, the most likely mechanism of this reaction involves an attack by L at the B4 site in **1**, followed by transfer of the 4,6-μ-H bridging hydrogen onto the B6 vertex with the formation of the cage BH_2 group. The reaction with Me_3N is very clean, while in the case of quinoline the formation of the *closo*-[4-CB_8H_9]$^-$ (**3**) anion in small yields was also observed. As shown in path ii) of Scheme 1, the quinoline reaction also produced small amounts of anion **3** (yield 12%) and 1-quin-*closo*-4-CB_8H_8 (**4c**) (yield 15%), compound **4c** being the first representative of the zwitterionic L-*closo*-CB_8H_8 series. The anion **3** and compound **4c** are most probably formed by air oxidation of compound **2c** during chromatography on silica gel.

The structure of **2b** was determined by an X-ray diffraction analysis and is depicted in Figure 1.

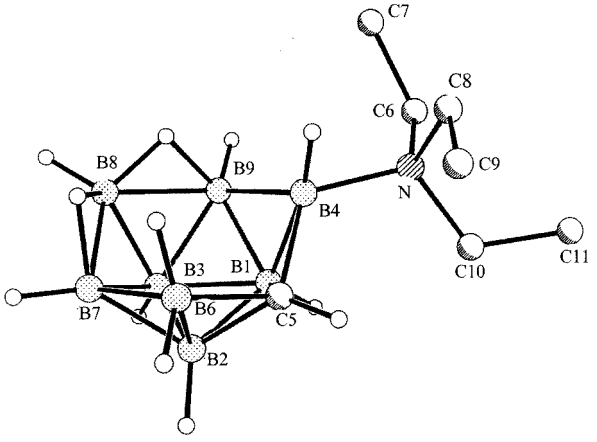

Figure 1. ORTEP representation of the molecular structure of 4-Et_3N-*arachno*-5-CB_8H_{12} (**2b**); selected bond lengths (Å) and angles (°): B1−B2 1.768(6), B1−B3 1.795(7), B1−B4 1.795(6), B1−C5 1.660(6), B1−B9 1.715(7), B2−B3 1.794(7), B2−C5 1.644(6), B2−B6 1.762(8), B2−B7 1.716(8), B3−B7 1.781(8), B3−B8 1.699(8), B3−B9 1.767(7), B4−C5 1.632(6), B4−B9 2.074(7), B4−N 1.639(5), C5−B6 1.673(7), B6−B7 1.991(8), B7−B8 1.805(8), B8−B9 1.789(8), C5−B4−B9 99.6(3), B4−C5−B6 111.8(4), B7−B6−C5 99.8(3), B7−B8−B9 104.6(4), and B8−B9−B4 112.0(4)

The molecule contains one BH_2 and one LBH group, one CH vertex and two non-equivalent BHB bridges within an open hexagonal face. A significant feature is that the cage CH group does not occupy the position of lowest connectivity 4, but the vertex of connectivity 5. The Et_3N substituent is attached at the B4 site in an asymmetric manner. The compounds are thus isomeric with the 6-L-*arachno*-4-CB_8H_{12} species reported previously by one of our groups.[6,7] The longest B−B separations (in Å) can be found in the open face for B4−B9 [2.074(7)] and B6−B7 [1.991(8)], followed by the "bridging" B7−B8 [1.805(8)] and B8−B9 [1.789(8)] distances. The shortest B−B distance can be seen for B3−B8 [1.699(8)], and all other B−B distances fall within the usual limits. In the open-face, the C5−B4 bond [1.632(6)] is shorter than C5−B6 [1.673(7)], and the other two C−B cage distances are in the usual range.

The constitutions of the *arachno* compounds of type **2** and that of the *closo* compound **4c** are in agreement with the results of NMR spectroscopy. All ^{11}B resonances were interrelated by [^{11}B-^{11}B]-COSY spectroscopy,[8] which, in combination with $^1H\{^{11}B(selective)\}$ measurements,[9] led to complete assignments of the resonances to individual cluster BH vertices for all compounds. Simplified stick diagrams interrelating the ^{11}B chemical shifts are given in Figure 2.

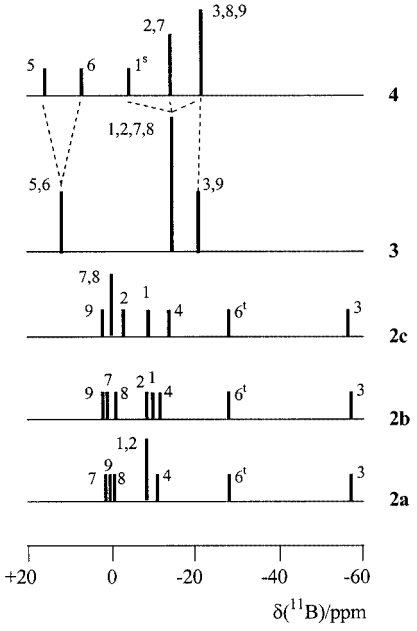

Figure 2. Simplified stick diagrams showing comparison of the ^{11}B NMR shifts and relative intensities for the 4-L-*arachno*-5-CB_8H_{12} compounds (**2**) (**2a** for L = NMe_3, **2b** for L = NEt_3, and **2c** for L = quin) (bottom traces), *closo*-[4-CB_8H_9]$^-$ (**3**) anion (data from reference[4]), and 1-quin-*closo*-4-CB_8H_8 (**4c**) (upper diagrams)

In accord with the crystallographic structure of **2b**, the ^{11}B NMR spectra of all compounds of type **2** (see bottom traces in Figure 2) consist of seven different doublets for BH vertices and one triplet due to the $B(6)H_2$ unit. Apart from resonances of the ligand L, the $^1H\{^{11}B\}$ NMR spectra of these compounds consist of thirteen singlets attributable to eight different *exo*-BH units, one *endo*-BH group, two signals of the *exo* and *endo* components of the cage CH_2 vertex, and to two different B−H−B bridges. The $^{13}C\{^1H\}$ NMR spectra of compounds of type **2** contain a broad singlet assigned to the cluster CH_2 group, the shifts for **2a** and **2b** being essentially the same. The mass spectrum of **2c** shows the expected molecular cut-off, whereas the spectra of **2a** and **2b** indicate fragmentation to [CB_8H_{10}] and L un-

der the conditions of the MS experiment as the main fragmentation mode.

Although crystals of 1-quin-*closo*-4-CB_8H_8 (**4c**) were not suitable for an X-ray diffraction analysis, its structure in solution can be elucidated on the basis of NMR spectroscopy. As demonstrated in Figure 2 (upper traces), the ^{11}B NMR spectrum of **4c** shows straightforward similarities to that of the parent *closo*-[4-CB_8H_9]$^-$ anion (**3**).[4] It consists of seven different doublets, of which those assigned to B2,7 and B3,8,9 overlap, and one singlet assigned to the ligand-substituted boron B1. The $^1H\{^{11}B\}$ NMR spectrum of **4c** shows a set of low-field quinoline resonances of integral intensity 7 and seven resonances (integral intensity 9) due to the cage BH units, of which those attributed to 3-H, 8-H, and 9-H overlap. Moreover, the mass spectrum of **4c** shows the expected molecular cut-off, and the 1-quin-*closo*-4-CB_8H_8 constitution is the only asymmetric possibility among the 1-, 3- and 5-substituted isomers of the L-*closo*-4-CB_8H_8 series.

Conclusion

The room-temperature reactions between tertiary amines and compound **1** discussed in this work, especially that with trimethylamine, represent a straightforward *nido* → *arachno* transformation in the nine-vertex series of monocarbaboranes. Of similar character is the previously reported[10] conversion of the *nido*-[B_9H_{12}]$^-$ anion into 4-C_5H_5N-*arachno*-4-B_9H_{13} by treatment with C_5H_5N·HCl in the nine-vertex borane series. It is highly probable that compound **2b** acts as an intermediate in the formation of the *closo* anions [1-CB_7H_8]$^-$ and [1-CB_8H_9]$^-$,[4] and we are currently investigating this assumption in more detail together with the possibility of heteroatom insertion into the open face of compounds of type **2**. The 1-quin-*closo*-4-CB_8H_8 (**4c**) is the first representative of the zwitterionic 1-L-*closo*-4-CB_8H_8 (**4**) series and work aimed at a more effective preparation of these or similar compounds is in progress.

Experimental Section

General Remarks: All reactions were carried out with use of standard vacuum or inert-atmosphere techniques as described by Shriver[11] although some operations, such as column LC, were carried out in air. The starting carborane **1** was prepared according to the literature.[1] Dichloromethane and hexane (Fluka) were dried with CaH_2 and freshly distilled before use. Other chemicals were reagent or analytical grade and were used as purchased. The analytical TLC and column chromatography, melting points, mass spectrometry, and NMR spectroscopy were essentially carried out as described in other work from our laboratories.[12]

4-(Me_3N)-*arachno*-5-CB_8H_{12} (2a): A stream of anhydrous Me_3N was bubbled through a solution of compound **1** (111 mg, 1 mmol) in CH_2Cl_2 (20 mL) for 10 min at 0 °C and the mixture was then left stirring for 24 h at ambient temperature. Volatiles were then evaporated and the residue was subjected to chromatography on a silica gel column (30 × 2.5 cm) yielding a pure fraction of R_f (CH_2Cl_2) 0.64 which was identified by NMR spectroscopy as **2a** (162 mg, 96%). An analytical sample of **2a** was obtained by crystallization from a saturated CH_2Cl_2 solution, which was carefully covered by the same volume of hexane. **For 2a:** R_f (CH_2Cl_2) 0.64; m.p. >350 °C (dec.). ^{11}B NMR ($CDCl_3$): δ = 2.4 (d, $^1J_{B,H}$ ≈145 Hz, 1 B, B7), 1.6 (d, $^1J_{B,H}$ = 147 Hz, 1 B, B9), 0.15 (d, $^1J_{B,H}$ ≈150 Hz, 1 B, B8), −8.5 (d, $^1J_{B,H}$ ≈160 Hz, 2 B, B1,2), −10.6 (d, $^1J_{B,H}$ = 149 Hz, 1 B, B4), −27.6 (t, $^1J_{B,H}$ = 122/119 Hz,1 B, B6), −58.4 (d, $^1J_{B,H}$ = 150 Hz, 1 B, B3) ppm, all theoretical [^{11}B-^{11}B]-COSY cross-peaks observed, except for B6-B7, B7-B8, and B8-B9. $^1H\{^{11}B\}$ NMR ($CDCl_3$): δ = 3.35 (s, 1 H, 8-H), 3.22 (s, 1 H, 9-H), 3.12 (s, 1 H, 7-H), 2.86 (s, 9 H, Me_3N), 2.43 (s, 1 H, 1-H or 2-H), 2.38 (s, 1 H, 1-H or 2-H), 1.32 (s, 1 H, *endo*-4-H), 1.23 (s, 1 H, *exo*-6-H), 0.80 (s, 1 H, 5-H), 0.60 (s, 1 H, *endo*-6-H), −0.72 (s, 1 H, 3-H), −1.96 (s, 1 H, 7,8-μ-H), −2.06 (s, 1 H, 8,9-μ-H,) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 10.6 (br. s, 1 C, C5) ppm. MS (70 eV, EI): *m*/*z* (%) = 110 (9) [M − Me_3N − 2H]$^+$, 107 (100) [M − Me_3N − 5H]$^+$, 59 (48) [M − CB_8H_{12}]$^+$. $C_4H_{21}B_8N$ (169.76): calcd. C 28.29, H 12.47; found C 30.15, H 11.80.

4-(Et_3N)-*arachno*-5-CB_8H_{12} (2b): A solution of compound **1** (111 mg, 1 mmol) in CH_2Cl_2 (20 mL) was treated with triethylamine (303 mg, 3 mmol) and the mixture was then left stirring for 24 h at ambient temperature. Volatiles were then evaporated and the residue was subjected to chromatography on a silica gel column (30 × 2.5 cm) yielding a pure fraction of R_f (CH_2Cl_2) 0.5 which was identified by NMR spectroscopy as **2b** (76 mg, 36%). An analytical sample of **2b** was obtained by crystallization from a saturated CH_2Cl_2 solution that was covered by the same volume of hexane. **For 2b:** R_f (CH_2Cl_2) 0.5; m.p. >350 °C (dec.). ^{11}B NMR ($CDCl_3$): δ = 3.1 (d, $^1J_{B,H}$ ≈ 140 Hz, 1 B, B9), 2.2 (d, $^1J_{B,H}$ ≈ 145 Hz, 1 B, B7), −0.1 (d, $^1J_{B,H}$ = 155 Hz, 1 B, B8), −7.9 (d, $^1J_{B,H}$ = 155 Hz, 1 B, B2), −9.7 (d, $^1J_{B,H}$ = 158 Hz, 1 B, B1), −11.4 (d, $^1J_{B,H}$ = 156 Hz, 1 B, B4), −27.3 (t, $^1J_{B,H}$ = 116/119 Hz,1 B, B6), −58.2 (d, $^1J_{B,H}$ = 149 Hz, 1 B, B3) ppm, all theoretical [^{11}B-^{11}B]-COSY cross-peaks observed, except for B6-B7, B7-B8, and B8-B9. $^1H\{^{11}B\}$ NMR ($CDCl_3$): δ = 3.31 (s, 2 H, 8,9-H), 3.06 (s, 1 H, 7-H), 3.06 (s, 6 H, CH_3CH_2N), 2.39 (s, 1 H, 2-H), 2.30 (s, 1 H, 1-H), 1.34 (s, 9 H, CH_3CH_2N), 1.15 (s, 1 H, *exo*-6-H), 1.04 (s, 1 H, *endo*-4-H), 0.80 (s, 1 H, 5-H), 0.63 (s, 1 H, *endo*-6-H), −0.72 (s, 1 H, 3-H), −1.94 (s, 1 H, 7,8-μ-H), −2.04 (s, 1 H, 8,9-μ-H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 10.6 (br. s, 1 C, C5) ppm. MS (70 eV, EI): *m*/*z* (%) = 213 (0.1) [M]$^+$, 110 (5) [M − Et_3N − 2H]$^+$, 101 (10) [M − CB_8H_{12}]$^+$. $C_7H_{27}B_8N$ (211.85): calcd. C 39.68, H 12.85; found C 40.25, H 11.92.

4-quin-*arachno*-5-CB_8H_{12} (2c), (quinH)$^+$*closo*-[4-CB_8H_9]$^-$ (3), and 1-quin-*closo*-4-CB_8H_8 (4c): A solution of compound **1** (111 mg, 1 mmol) in CH_2Cl_2 (20 mL) was treated with quinoline (303 mg, 3 mmol) and the mixture was then left stirring for 24 h at ambient temperature. Volatiles were then evaporated and the residue was subjected to chromatography on a silica gel column (30 × 2.5 cm) using CH_2Cl_2 as the mobile phase yielding pure fractions of R_f (CH_2Cl_2) 0.71 and 0.20 which were identified by NMR spectroscopy as **2c** (83 mg, 35%) and **4c** (35 mg, 15%). Further elution with MeCN/CH_2Cl_2 (1:2, v/v) gave a fraction of R_f = 0.23, which was identified by NMR spectroscopy[4] as **3** (28 mg, 12%). **For 2c:** R_f (CH_2Cl_2) 0.71; m.p. 245 °C. ^{11}B NMR ($CDCl_3$): δ = 3.5 (d, $^1J_{B,H}$ = 157 Hz, 1 B, B9), 0.5 (d, $^1J_{B,H}$ ≈ 150 Hz, 2 B, B7,8), −3.4 (d, $^1J_{B,H}$ = 147 Hz, 1 B, B2), −7.9 (d, $^1J_{B,H}$ = 151 Hz, 1 B, B1), −14.6 (d, $^1J_{B,H}$ = 150 Hz, 1 B, B4), −27.4 (t, $^1J_{B,H}$ = ≈115 Hz, 1 B, B6), −57.3 (d, $^1J_{B,H}$ = 151 Hz, 1 B, B3) ppm, all theoretical [^{11}B-^{11}B]-COSY cross-peaks observed, except for B3-B9, B6-B7, B4-B9, B7-B8, and B8-B9. $^1H\{^{11}B\}$ NMR ($CDCl_3$): δ = 3.45 (s, 2 H, 7-

H,8), 3.30 (s, 1 H, 9-H), 2.76 (s, 1 H, 2-H), 2.45 (s, 2 H, 1-H, *endo*-4-H), 1.41 (s, 1 H, *exo*-6-H), 1.18 (s, 1 H, 5-H), 0.50 (s, 1 H, 3-H), 0.80 (s, 1 H, C*H*5), 0.63 (s, 1 H, *endo*-6-H), −0.72 (s, 1 H, 3-H), −1.69 (s, 1 H, 7,8-μ-H), −1.73 (s, 1 H, 8,9-μ-H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 30.0 (br. s, 1 C, C5) ppm. MS (70 eV, EI): *m*/*z* (%) = 241 (32) $[M]^+$, 239 (100) $[M - 2H]^+$. $C_{10}H_{19}B_8N$ (239.82): calcd. C 50.08, H 7.99; found C 52.10, H 8.32. **For 4c:** R_f (CH_2Cl_2) 0.20; m.p. > 350 °C. ^{11}B NMR ($CDCl_3$): δ = 16.5 (d, $^1J_{B,H}$ = 141 Hz, 1 B, B5), 7.2 (d, $^1J_{B,H}$ = 140 Hz, 1 B, B6), −6.5 (s, 1 B, B1), −15.7 (d, $^1J_{B,H} \approx$ 135 Hz, 2 B, B2,7), −21.0 (d, *J* = 150 Hz, 3 B, B3,8,9) ppm, all theoretical [^{11}B-^{11}B]-COSY cross-peaks observed, except for B1-B2, B1-B7, B3-B5, B5-B8, and B5-B9. $^1H\{^{11}B\}$ NMR ($CDCl_3$): δ = 9.65−7.06 (m, 7 H, quin-H), 5.90 (s, 1 H, 4-H), 4.83 (s, 1 H, 5-H), 4.32 (s, 1 H, 6-H), 1.99 (s, 1 H, 2-H or 7-H), 1.47 (s, 1 H, 2-H or 7-H), 0.87 (s, 3 H, 3,8,9-H,) ppm. MS (70 eV, EI): *m*/*z* (%) = 237 (40) $[M]^+$, 236 (48) $[M - H]^+$.

X-ray Crystallographic Study: Crystals of **2b** were grown by slow diffusion of hexane vapors into a CH_2Cl_2 solution. The reflection intensities for compound **2b** were collected on a Siemens P4 diffractometer (graphite-monochromated Mo-K_α radiation, λ = 71.073 pm). The structure solution and refinement was carried out with the program package SHELXTL-PLUS V.5.1. The collection temperature for the structure determination was 296 K. All non-hydrogen atoms were refined with anisotropic temperature factors. The hydrogen atoms in **2b** were located by difference Fourier maps and the remaining hydrogen atoms were placed in calculated positions. All hydrogen atoms were refined applying the riding model with fixed isotropic temperature factors. Crystal data: $C_7H_{27}B_8N$, a colorless irregular block with dimensions 0.22 × 0.18 × 0.16 mm crystallizes in the monoclinic space group $P2_1/c$ with the lattice parameters *a* = 1119.06(19), *b* = 765.84(8), *c* = 1723.10(18) pm, β = 97.576(9)°, *V* = 1463.8(3) 10^6 pm^3, *Z* = 4, μ = 0.046 mm^{-1}; 3447 reflections collected in the range 2° ≤ 2ϑ ≤ 50°, 2554 reflections independent, 1238 assigned to be observed [$I > 2\sigma(I)$], full-matrix least-squares refinement against F^2 with 161 parameters converged at *R*1/*wR*2-values of 0.084/0.225; the max./min. residual electron density was 0.38/−0.39 10^{-6} e·pm^{-3}. CCDC-223376 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Center, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

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