

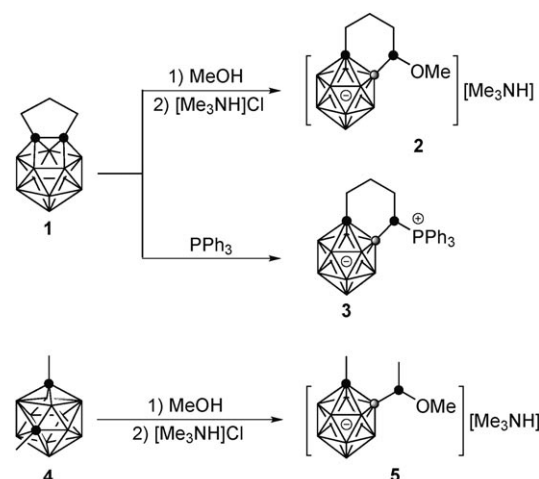
Reaction of 13-Vertex Carboranes with Nucleophiles: Unprecedented Cage-Carbon Extrusion and Formation of Monocarba-*closo*-dodecaborate Anions**

Jian Zhang, Hoi-Shan Chan, and Zuowei Xie*

Only in recent years has significant progress been made in the chemistry of supercarboranes (carboranes with more than 12 vertices).^[1] A number of 13- and 14-vertex carboranes have been prepared and structurally characterized since 2003.^[2–7] They are readily reduced by Group 1 metals to give the corresponding *nido*-supercarborane dianions.^[3–7] The carbon-atoms-adjacent (CAD) carborane 1,2-(CH₂)₃-1,2-C₂B₁₁H₁₁ can even undergo single-electron reduction to generate a stable carborane radical anion with $2n + 3$ framework electrons.^[8] It can also react with various electrophiles to afford hexasubstituted CAD 13-vertex carboranes 8,9,10,11,12,13-X₆-1,2-(CH₂)₃-1,2-C₂B₁₁H₅ (X = Me, Br, I).^[4] We are interested in the reaction of supercarboranes with nucleophiles. We now report that unprecedented products of cage-carbon extrusion are isolated instead of the expected deborated species after treatment of 13-vertex carboranes with nucleophiles.

A solution of 1,2-(CH₂)₃-1,2-C₂B₁₁H₁₁ (**1**)^[3] in methanol was stirred at room temperature for one day to give, after addition of [Me₃NH]Cl, Me₃NH[1,2-(CH₂)₃CH(OMe)-1-CB₁₁H₁₀] (**2**), which was isolated in 75 % yield (Scheme 1). This reaction can be monitored by ¹¹B NMR spectroscopy. Whereas **1** reacted with MeOH/NaOH to afford a mixture of inseparable products, its icosahedral cousin 1,2-(CH₂)₃-1,2-C₂B₁₀H₁₀ is stable in refluxing MeOH and is converted to the *nido* species (CH₂)₃C₂B₉H₁₀[–] in refluxing MeOH/NaOH solution.^[9] When PPh₃ was used as nucleophile, the zwitterionic compound [1,2-(CH₂)₃CH(PPh₃)-1-CB₁₁H₁₀]-CH₂Cl₂ (**3**) was isolated in 80 % yield after recrystallization from CH₂Cl₂. Similarly, the carbon-atoms-apart (CAP) 13-vertex carborane 1,6-Me₂-1,6-C₂B₁₁H₁₁ (**4**)^[7] reacted with MeOH to afford, on addition of [Me₃NH]Cl, Me₃NH[1-Me-2-CH(OMe)Me-1-CB₁₁H₁₀] (**5**) in 55 % yield.

The ¹¹B NMR spectra of **2** and **5** show similar 1:1:6:3 patterns, whereas that of **3** displays a 1:3:7 pattern. The signal of the substituted B2 atom in both **2** and **5** is clearly distinguished from others at $\delta = -7.7$ and -5.0 ppm as a singlet in the proton-coupled ¹¹B NMR spectra. However, the resonance of B2 in **3** overlaps with other cage B peaks, and is hardly resolved. The α -C atom bonded to B2 is unambigu-



Scheme 1. Reaction of CAD and CAP 13-vertex carboranes with nucleophiles.

ously identifiable, as it appears as a broad signal in the ¹³C NMR spectra due to coupling to a ¹¹B nucleus, at $\delta = 74.2$ ppm in **2**, $\delta = 72.2$ ppm in **5**, and $\delta = 17.2$ ppm in **3**. The ³¹P NMR spectrum of **3** exhibits one sharp peak at $\delta = 32.7$ ppm, supportive of a tertiary phosphonium salt.^[10]

Single-crystal X-ray analyses confirm the molecular structures of **2**, **3**, and **5**, as shown in Figures 1–3, respectively.^[11] The icosahedral cages in the three compounds have the same structural features of a monocarba-*closo*-dodecaborate anion.^[12]

Cage-carbon extrusion from carborane clusters is very rare but not unknown. Two examples have been reported. A recent *closo*-to-*closo* example is the transformation of [1-H₂N-*closo*-CB₁₁F₁₁][–] into [3-NC-*closo*-B₁₁F₁₀]^{2–}, which is limited to highly fluorinated boron clusters.^[13] The other is the conversion of [7-R- μ -(9,10-HR'C)-7-*nido*-CB₁₀H₁₁][–] to [1-R-6-CH₂R'-1-*closo*-CB₉H₈][–], in which cage-carbon extrusion is suggested to proceed after removal of one BH vertex.^[14] In this regard, a plausible pathway for formation of monocarba-*closo*-dodecaborate anions is proposed in Scheme 2. Attack of the nucleophile on one of the cage carbon atoms of the 13-vertex carborane^[15] leads to cleavage of the C_{cage}–C_{cage} bond and formation of new C_{cage}–B bonds to preserve cluster integrity. Hydrogen migration then generates the final icosahedral product. This behavior is significantly different from that of *o*-carboranes, in which a cage boron atom is attacked by nucleophiles to give deboration products.^[16,17] Although the reasons are not yet clear, comparison of the ¹³C chemical shift of the cage carbon atoms of 136 ppm in **1** with

[*] J. Zhang, H.-S. Chan, Prof. Dr. Z. Xie
Department of Chemistry, The Chinese University of Hong Kong
Shatin, NT, Hong Kong (China)
Fax: (+852) 2603-5057
E-mail: zxie@cuhk.edu.hk

[**] This work was supported by grants from the Research Grants Council of the Hong Kong Special Administration Region (Project No. 403906) and The Chinese University of Hong Kong.

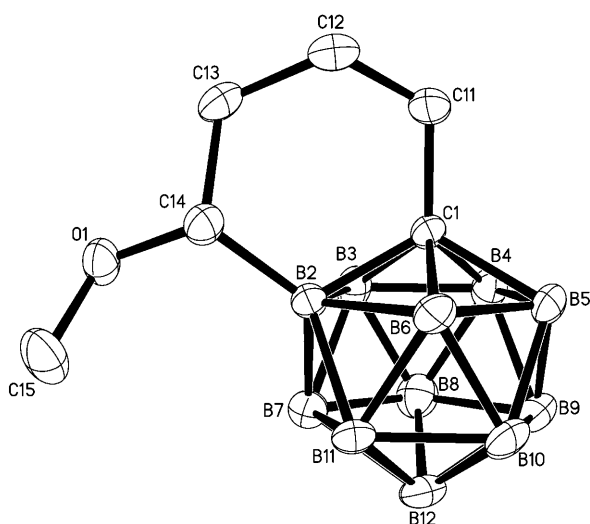


Figure 1. Molecular structure of $[1,2-(\text{CH}_2)_3\text{CH}(\text{OCH}_3)-1\text{-CB}_{11}\text{H}_{10}]^-$ in **2**. Selected bond lengths [Å]: C1–B2 1.721(4), C1–B3 1.714(4), C1–B4 1.719(5), C1–B5 1.709(4), C1–B6 1.705(4), C1–C11 1.527(4), C11–C12 1.519(5), C12–C13 1.520(5), C13–C14 1.527(4), C14–B2 1.603(4), C14–O1 1.459(4), av B–B 1.771(5).

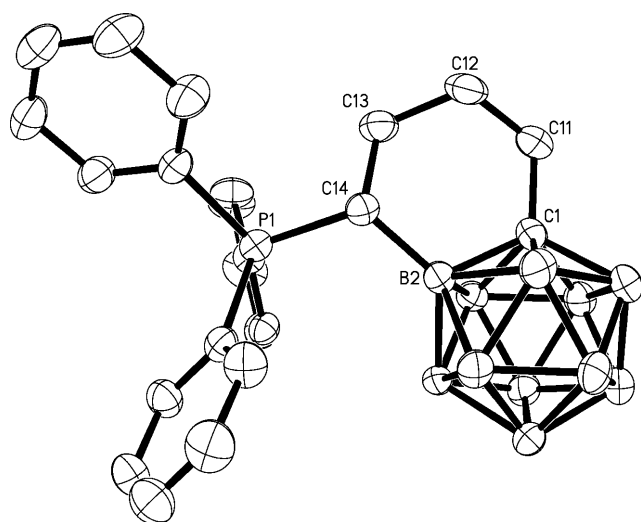


Figure 2. Molecular structure of $[1,2-(\text{CH}_2)_3\text{CH}(\text{PPh}_3)-1\text{-CB}_{11}\text{H}_{10}]$ (**3**). Selected bond lengths [Å]: C1–B2 1.724(4), C1–B3 1.719(4), C1–B4 1.713(4), C1–B5 1.727(5), C1–B6 1.700(5), C1–C11 1.517(4), C11–C12 1.532(5), C12–C13 1.523(5), C13–C14 1.560(4), C14–B2 1.625(4), C14–P1 1.815(3), av B–B 1.773(5).

that of 84 ppm in the corresponding 12-vertex carborane 1,2- $(\text{CH}_2)_3$ -1,2- $\text{C}_2\text{B}_{10}\text{H}_{10}$ offers some insight into the charge density of the cage carbon atoms. Clearly, the cage carbons in 13-vertex carboranes are much more electron-deficient than those in 12-vertex carboranes.

In conclusion, compared with 12-vertex carboranes, 13-vertex carboranes exhibit significantly different reactivity toward nucleophiles. A new cage-carbon extrusion reaction is observed that leads to formation of monocarba-*closo*-dodecaborate anions.

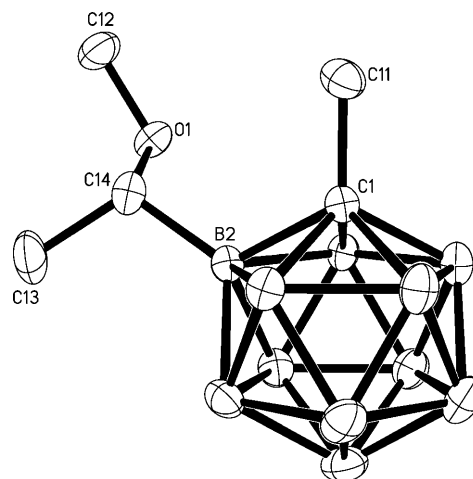
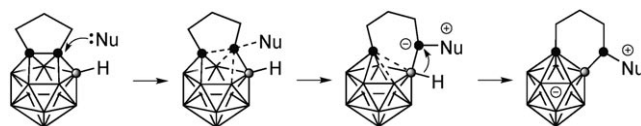


Figure 3. Molecular structure of $[1\text{-CH}_3\text{-}2\text{-CH}_3\text{CH}(\text{OCH}_3)\text{-}1\text{-CB}_{11}\text{H}_{10}]^-$ in **5**. Selected bond lengths [Å]: C1–B2 1.718(4), C1–B3 1.715(4), C1–B4 1.702(5), C1–B5 1.705(5), C1–B6 1.706(5), C1–C11 1.516(4), B2–C14 1.592(5), C14–C13 1.527(5), C14–O1 1.457(4), av B–B 1.767(6).



Scheme 2. Possible reaction pathway.

Experimental Section

2: Compound **1** (196 mg, 1.00 mmol) was dissolved in MeOH (10 mL), and the solution was stirred at room temperature for 1 d. After addition of $[\text{Me}_3\text{NH}]\text{Cl}$ (191 mg, 2.00 mmol), the mixture was further stirred for 1 h. MeOH was then pumped off, and the residue was thoroughly washed with water to give a white solid. Recrystallization from acetone gave **2** as colorless crystals (215 mg, 75 %). ^1H NMR (400 MHz, $[\text{D}_6]\text{acetone}$): δ = 3.87 (brs, 1H; NH), 3.34 (s, 3H; OCH_3), 3.20 (s, 9H; NCH_3), 3.11 (t, J = 6.6 Hz, 1H; BCH), 1.81 (m, 2H; $\delta\text{-CH}_2$), 1.68 (m, 1H; $\beta\text{-CH}_2$), 1.46 (m, 1H; $\gamma\text{-CH}_2$), 1.39 (m, 1H; $\beta\text{-CH}_2$), 1.21 ppm (m, 1H; $\gamma\text{-CH}_2$); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, $[\text{D}_6]\text{acetone}$): δ = 74.2 (br; BCH), 69.2 (cage C), 57.7 (OCH_3), 46.2 (NCH_3), 36.7 ($\delta\text{-CH}_2$), 29.6 ($\beta\text{-CH}_2$), 23.2 ppm ($\gamma\text{-CH}_2$); ^{11}B NMR (96 MHz, $[\text{D}_6]\text{acetone}$): δ = −7.7 (s, 1B), −9.3 (d, $J_{\text{B,H}}$ = 145 Hz, 1B), −12.3 (d, $J_{\text{B,H}}$ = 113 Hz, 6B), −13.5 (overlapping, 1B), −13.9 ppm (overlapping, 2B); IR (KBr): $\tilde{\nu}$ = 2539 cm^{-1} (B–H); elemental analysis (%) calcd for $\text{C}_9\text{H}_{30}\text{B}_{11}\text{NO}$: C 37.63, H 10.53, N 4.88; found: C 37.98, H 11.05, N 4.79.

3: PPh_3 (276 mg, 1.05 mmol) was added to a solution of **1** (196 mg, 1.00 mmol) in toluene (20 mL), and the reaction vessel was closed. The mixture was heated at 110 °C for 12 h to give a white suspension. After removal of toluene, the white solid was recrystallized from CH_2Cl_2 to give **3** as colorless crystals (435 mg, 80 %). ^1H NMR (400 MHz, $[\text{D}_6]\text{acetone}$): δ = 8.08 (m, 6H; C_6H_5), 7.80 (m, 3H; C_6H_5), 7.70 (m, 6H; C_6H_5), 5.62 (s, 2H; CH_2Cl_2), 3.73 (m, 1H; BCH), 2.14 (m, 1H; $\beta\text{-CH}_2$), 1.98 (m, 1H; $\delta\text{-CH}_2$), 1.64 (m, 2H; $\delta\text{-CH}_2$ and $\gamma\text{-CH}_2$), 1.56 (m, 1H; $\gamma\text{-CH}_2$), 1.47 ppm (m, 1H; $\beta\text{-CH}_2$); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, $[\text{D}_6]\text{acetone}$): δ = 135.2 (d, $^2J_{\text{PC}}$ = 9.3 Hz), 134.8 (d, $^4J_{\text{PC}}$ = 2.9 Hz), 130.4 (d, $^3J_{\text{PC}}$ = 12.2 Hz), 121.6 (d, $^1J_{\text{PC}}$ = 82.9 Hz) (C_6H_5), 67.7 (cage C), 55.0 (CH_2Cl_2), 36.2 ($\delta\text{-CH}_2$), 25.3 (d, $^3J_{\text{PC}}$ = 14.3 Hz; $\gamma\text{-CH}_2$), 24.9 (d, $^2J_{\text{PC}}$ = 3.6 Hz; $\beta\text{-CH}_2$), 17.2 ppm (br; BCH); ^{11}B NMR (128 MHz, $[\text{D}_6]\text{acetone}$): δ = −8.4 (d, $J_{\text{B,H}}$ = 151 Hz, 1B), −11.1 (d, $J_{\text{B,H}}$ = 144 Hz, 3B), −12.4 ppm (d, $J_{\text{B,H}}$ = 122 Hz, 7B); ^{31}P NMR (121 MHz, $[\text{D}_6]\text{acetone}$): δ = 32.7 ppm; IR (KBr): $\tilde{\nu}$ = 2539 cm^{-1}

(B–H); elemental analysis (%) calcd for $C_{23}H_{32}B_{11}P$ (**3**– CH_2Cl_2): C 60.26, H 7.04; found: C 60.38, H 6.81.

5: Compound **4** (184 mg, 1.00 mmol) was dissolved in MeOH (10 mL), and the solution was stirred at room temperature for 1 d. After addition of $[Me_3NH]Cl$ (191 mg, 2.00 mmol), the mixture was stirred for a further 1 h. MeOH was pumped off and the residue was thoroughly washed with water to give a white solid. Recrystallization from acetone gave **5** as colorless crystals (152 mg, 55%). 1H NMR (400 MHz, $[D_6]acetone$): δ = 3.30 (brs, 1H; NH), 3.23 (s, 3H; OCH_3), 3.13 (s, 9H; NCH_3), 3.03 (m, 1H; BCH), 1.51 (s, 3H; CH_3), 1.28 ppm (d, J = 6.7 Hz, 3H; β - CH_3); ^{13}C NMR (100 MHz, $[D_6]acetone$): δ = 72.2 (br; BCH), 65.2 (cage C), 57.1 (OCH_3), 46.1 (NCH_3), 25.0 (CH_3), 19.6 ppm (β - CH_3); ^{11}B NMR (96 MHz, $[D_6]acetone$): δ = –5.0 (s, 1B), –9.1 (d, J_{BH} = 123 Hz, 1B), –11.4 (d, J_{BH} = 180 Hz, 6B), –13.6 ppm (d, J_{BH} = 181 Hz, 3B); IR (KBr): $\tilde{\nu}$ = 2530 cm^{-1} (B–H); elemental analysis (%) calcd for $C_8H_{30}B_{11}NO$: C 34.91, H 10.99, N 5.09; found: C 34.63, H 10.52, N 4.65.

Received: August 28, 2008

Published online: October 31, 2008

Keywords: boron · cage compounds · carboranes · cluster compounds · nucleophilic addition

tal data for **3**: $C_{24}H_{34}B_{11}Cl_2P$, M_r = 543.3, orthorhombic, space group $P2_12_12_1$, a = 10.629(1), b = 12.942(1), c = 21.764(1) Å, V = 2994(1) Å³, T = 296 K, Z = 4, ρ_{calcd} = 1.205 g cm^{–3}, $2\theta_{max}$ = 50°, $\mu(Mo_{K\alpha})$ = 0.71073 Å, absorption corrections applied by using SADABS,^[18] relative transmission factors in the range 0.800–1.000. A total of 27791 reflections were collected and led to 5234 unique reflections, 5234 of which with $I > 2\sigma(I)$ were considered as observed, R_1 = 0.049, $wR_2(F^2)$ = 0.134. Crystal data for **5**: $C_8H_{30}B_{11}NO$, M_r = 275.2, monoclinic, space group $P2_1/n$, a = 7.966(3), b = 11.576(4), c = 19.451(7) Å, β = 94.58(1)°, V = 1788(1) Å³, T = 293 K, Z = 4, ρ_{calcd} = 1.022 g cm^{–3}, $2\theta_{max}$ = 50°, $\mu(Mo_{K\alpha})$ = 0.71073 Å, absorption corrections applied by using SADABS,^[18] relative transmission factors in the range 0.979–1.000. A total of 9443 reflections were collected and led to 3150 unique reflections, 3150 of which with $I > 2\sigma(I)$ were considered as observed, R_1 = 0.072, $wR_2(F^2)$ = 0.189. The structures were solved by direct methods and refined by full-matrix least-squares techniques on F^2 by using the SHELXTL/PC package of crystallographic software.^[19] For the noncentrosymmetric structure of **3**, the appropriate enantiomorph was chosen by refining Flack's parameter x toward zero.^[20] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were geometrically fixed using the riding model. CCDC 699713, 699714, 699715 contain 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.

- [1] For reviews, see: a) L. Deng, Z. Xie, *Organometallics* **2007**, *26*, 1832; b) L. Deng, Z. Xie, *Coord. Chem. Rev.* **2007**, *251*, 2452; c) R. N. Grimes, *Angew. Chem.* **2003**, *115*, 1232; *Angew. Chem. Int. Ed.* **2003**, *42*, 1198.
- [2] A. Burke, D. Ellis, B. T. Giles, B. E. Hodson, S. A. Macgregor, G. M. Rosair, A. J. Welch, *Angew. Chem.* **2003**, *115*, 235; *Angew. Chem. Int. Ed.* **2003**, *42*, 225.
- [3] L. Deng, H.-S. Chan, Z. Xie, *Angew. Chem.* **2005**, *117*, 2166; *Angew. Chem. Int. Ed.* **2005**, *44*, 2128.
- [4] L. Deng, H.-S. Chan, Z. Xie, *J. Am. Chem. Soc.* **2006**, *128*, 5219.
- [5] L. Deng, J. Zhang, H.-S. Chan, Z. Xie, *Angew. Chem.* **2006**, *118*, 4415; *Angew. Chem. Int. Ed.* **2006**, *45*, 4309.
- [6] R. D. McIntosh, D. Ellis, G. M. Rosair, A. J. Welch, *Angew. Chem.* **2006**, *118*, 4419; *Angew. Chem. Int. Ed.* **2006**, *45*, 4313.
- [7] J. Zhang, L. Deng, H.-S. Chan, Z. Xie, *J. Am. Chem. Soc.* **2007**, *129*, 18.
- [8] X. Fu, H.-S. Chan, Z. Xie, *J. Am. Chem. Soc.* **2007**, *129*, 8964.
- [9] T. E. Paxson, M. K. Kaloustian, G. M. Tom, R. J. Wiersema, M. F. Hawthorne, *J. Am. Chem. Soc.* **1972**, *94*, 4882.
- [10] D. G. Gorenstein, *Phosphorus-31 NMR, Principles and Applications*, Academic Press, New York, **1984**, p. 10.
- [11] Crystal data for **2**: $C_9H_{30}B_{11}NO$, M_r = 287.3, monoclinic, space group $P2_1/c$, a = 7.924(3), b = 23.339(9), c = 9.662(4) Å, β = 97.49(1)°, V = 1772(1) Å³, T = 293 K, Z = 4, ρ_{calcd} = 1.077 g cm^{–3}, $2\theta_{max}$ = 50°, $\mu(Mo_{K\alpha})$ = 0.71073 Å, absorption corrections applied by using SADABS,^[18] relative transmission factors in the range 0.411–1.000. A total of 9415 reflections were collected and led to 3118 unique reflections, 3118 of which with $I > 2\sigma(I)$ were considered as observed, R_1 = 0.079, $wR_2(F^2)$ = 0.199. Cry-
- [12] S. Körbe, P. J. Schreiber, J. Michl, *Chem. Rev.* **2006**, *106*, 5208.
- [13] M. Finze, *Angew. Chem.* **2007**, *119*, 9036; *Angew. Chem. Int. Ed.* **2007**, *46*, 8880.
- [14] A. Laromaine, F. Teixidor, C. Viñas, *Angew. Chem.* **2005**, *117*, 2260; *Angew. Chem. Int. Ed.* **2005**, *44*, 2220.
- [15] It has been reported that PPh_3 attacks the nonclassical carbon atom of the μ -(9,10-HR'C) unit in [7-R- μ -(9,10-HR'C)-7-nido-CB₁₀H₁₁][–]: J. Bould, A. Laromaine, C. Viñas, F. Teixidor, L. Barton, N. P. Rath, R. E. K. Winter, R. Kivekäs, R. Sillanpää, *Organometallics* **2004**, *23*, 3335.
- [16] R. A. Wiesboeck, M. F. Hawthorne, *J. Am. Chem. Soc.* **1964**, *86*, 1642.
- [17] For reviews, see: a) N. S. Hosmane, J. A. Maguire in *Comprehensive Organometallic Chemistry III*, Vol. 3 (Eds.: D. M. P. Mingos, R. H. Crabtree), Elsevier, Oxford, **2007**, p. 175; b) Z. Xie, *Acc. Chem. Res.* **2003**, *36*, 1; c) Z. Xie, *Coord. Chem. Rev.* **2002**, *231*, 23; d) R. N. Grimes in *Comprehensive Organometallic Chemistry II*, Vol. 1 (Eds.: E. W. Abel, F. G. A. Stone, G. Wilkinson), Pergamon, Oxford, **1995**, p. 373.
- [18] G. M. Sheldrick, SADABS: Program for Empirical Absorption Correction of Area Detector Data, University of Göttingen, Germany, **1996**.
- [19] G. M. Sheldrick, SHELXTL 5.10 for Windows NT: Structure Determination Software Programs, Bruker Analytical X-ray Systems, Inc., Madison, Wisconsin, USA, **1997**.
- [20] H. D. Flack, *Acta Crystallogr. Sect. A* **1983**, *39*, 876.