to eq IIIa, there is nothing known about ClClO in the gas phase yet.

Reaction II should be taken into consideration as a source of stratospheric $ClClO_2$ if this reaction is very fast; but it is more likely that Cl atoms will be consumed in the reaction with the much more abundant O_3, CH_4, etc. Nevertheless, this reaction should be considered in kinetic and spectroscopic investigations involving ClO_2 and Cl atoms.

If the photolytic decomposition of $ClClO_2$ to a Cl atom and ClO_2 in the electronic ground state were the most important reaction of this species under stratospheric conditions, its influence on ozone depletion would be small, although $ClClO_2$ might have a significant concentration in the stratosphere. Photolytic decomposition of ClO_2 into ClO + O would neutralize the Cl atom generated before. If on the other hand photolysis of $ClClO_2$ proceeded via electronic excited ClO_2 and a Cl atom, isomerization of ClO_2 to ClOO with subsequent decomposition into Cl + O_2 could contribute to ozone destruction.[58]

Conclusion

We have synthesized chloryl chloride for the first time according to four different routes. This novel chlorine oxide is of sufficient stability at room temperature and low pressure to allow its characterization by IR and UV spectroscopy not only in cryogenetic matrices but also in the gas phase.

Comparison of its IR spectrum with those of related compounds showed this spectrum to fit a general trend and allowed us to estimate geometric parameters for $ClClO_2$. Our spectroscopic findings allow the identification of $ClClO_2$ in mixtures of chlorine oxides. Results of ab initio calculations were useful for analyzing and interpreting our experimental results, although significant deviations were observed even for higher level calculations.

$ClClO_2$ is thermally quite stable but is easily decomposed by irradiation with visible light. These properties are necessary conditions that $ClClO_2$ might play a role in the chemistry of the polar stratosphere. Nevertheless, further investigations are necessary to evaluate its importance there.

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Supplementary Material Available: Tables of vibrational frequencies for $ClCl^{16}O_2$ and $ClCl^{18}O_2$ isolated in an Ar matrix and of $ClCl^{16}O^{18}O$ and IR spectra of $ClClO_2$ in the regions of $\nu_1/2\nu_2$ and $\nu_2/2\nu_4$ (4 pages). Ordering information is given on any current masthead page.

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Synthesis of ω-(Aminoalkyl)-1,2-*closo*-dicarbadodecaboranes(12)

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Hydrogen chlorides of four 1,2-dicarba-*closo*-dodecaborane(12) derivatives containing ω-(aminoalkyl) substituents, namely 1-(aminomethyl)-, 1-(3-aminopropyl)-, 1-(3-aminopropyl)-2-methyl-, and 1,2-bis(3-aminopropyl)-1,2-dicarba-*closo*-dodecaborane(12) (**1**–**4**, respectively), were synthesized via deprotection of the corresponding *N,N*-di-*tert*-butyloxycarbonyl derivatives (**8**, **9**, **16**, and **19**, respectively) using hydrogen chloride in anhydrous ether. The salt **1** was also obtained from its mono *N*-*tert*-butyloxycarbonyl derivative **7**. The diprotected compounds **9**, **16**, and **19** were synthesized from the corresponding bromides by ion-pair alkylation of the Gabriel reagent di-*tert*-butyl iminodicarboxylate (**6**) using a stoichiometric amount of tetrabutylammonium hydroxide in the two-phase system water/methylene chloride. No degradation of the carborane cage to the nido compounds was observed. Alkylation of **6** with propargyl bromide gave *N,N*-di-*tert*-butyloxycarbonylpropargylamine (**5**), which upon reaction with the bisacetonitrile complex of decaborane gave a mixture of **7** and **8**.

Introduction

It has recently been shown[1] by members of our research group that epidermal growth factor (EGF) when conjugated to dextran binds to cultured human malignant glioma, U343MGaC12:6, cells. The binding is receptor specific, most of the conjugate is located intracellularly, and the conjugate remains cell-associated for more than 24 h. Thus, it seems promising to use dextran, conjugated with EGF, as a carrier for toxic agents. We are presently examining the possibility of combining EGF–dextran targeting with boron neutron capture therapy (BNCT),[2] and for that purpose we are preparing boron cluster compounds, amino acids, and amines, for coupling to the dextran in the EGF–dextran conjugates.

Here we report the synthesis of the hydrogen chlorides of four ω-(aminoalkyl)-substituted 1,2-dicarba-*closo*-dodecaboranes(12) (*o*-carboranes): 1-(aminomethyl)-, 1-(3-aminopropyl)-, 2-(3-aminopropyl)-1-methyl-, and 1,2-bis-(3-aminopropyl)-*o*-carborane (**1**–**4**, respectively).

Experimental Section

General Details. The ^1H, ^{13}C, and ^{11}B NMR spectra were recorded on a Varian XL-300 spectrometer operating at 300, 75.4, and 96.2 MHz, respectively. Boron fluoride etherate was used as external standard for the boron spectra. The IR spectra were obtained with a Perkin-Elmer 1600 FT-IR spectrometer. Mass spectra were recorded on a Finnigan Mat INCOS 50 instrument in the electron-impact mode or on a Jeol DX-303 instrument connected to a Jeol DA-5000 computer system for FAB spectrum. The fast atom bombardment spectra were recorded at a resolution set to 3000. The samples were prepared of a methanol solution of the compound with PEG 400 on the stainless steel target. The fast atom bombardment gun was operated at 6 kV producing a beam of xenon neutrals. Elemental analyses were performed by Analytische Laboratorien, Engelskirchen, FRG, and Mikrokemi AB, Uppsala, Sweden.

Merck Silica Gel 60 (230–400 mesh) and Merck Silica Gel 60 F_{254} were used for flash chromatography and TLC, respectively. Melting points are uncorrected and were obtained using a Buchi capillary melting point apparatus or a Leitz hot-stage microscope. "Q^+" is used for the tetrabutylammonium ion.

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***N,N*-Di-*tert*-butyloxycarbonylpropargylamine (5).** To a stirred mixture of tetrabutylammonium hydrogen sulfate, $QHSO_4$ (4.29 g, 12.6 mmol), and 2.00 M aqueous sodium hydroxide (13.3 mL) was added, at ambient temperature, methylene chloride (10 mL) and solid di-*tert*-butyl iminodicarboxylate (**6**) (2.48 g, 11.4 mmol). To this mixture propargyl bromide (3.67 g, 24.7 mmol) in methylene chloride (5 mL) was added dropwise, and the mixture was refluxed for 1.5 h. After the mixture was cooled to room temperature, the layers were separated, the water phase was extracted with methylene chloride (5 mL), and the combined organic phases were evaporated to dryness. QBr was precipitated by adding ether (25 mL) to the residue. The precipitate was extracted with ether (3 × 20 mL), and the combined extracts were dried over sodium sulfate. Concentration gave the crude product, which was purified by flash chromatography on silica gel using ether/petroleum ether (1:3) as eluent, R_f = 0.47, giving 3.06 g (95%) of **5**. The analytical sample was obtained by bulb to bulb distillation (80–85 °C, 4 mmHg). Mp: 31–32 °C. Anal. Calcd for $C_{13}H_{21}NO_4$: C, 61.2; H, 8.3; N, 5.5. Found: C, 61.1; H, 8.3; N, 5.0. ^{1}H NMR (CD_3OD): δ 4.37 (d, J = 2.4 Hz, 2 H, CH_2), 2.65 (t, J = 2.4 Hz, acetylenic H), 1.56 (s, 18 H, CH_3). ^{13}C NMR (CD_3OD): δ 153.1 (C=O), 84.4 (C–O), 80.5 (C), 72.1 (HC), 36.8 (CH_2), 28.2 (CH_3). IR (Nujol): 3314 (m), 2977 (s), 2877 (s), 2841 (s), 1797 (m), 1757 (s), 1724 (s), 1703 (s), 1368 (s), 1148 (s) cm^{-1}.

***N*-*tert*-Butyloxycarbonyl-1-(aminomethyl)-*o*-carborane (7) and *N,N*-Di-*tert*-butyloxycarbonyl-1-(aminomethyl)-*o*-carborane (8).** To a refluxing mixture of the bisacetonitrile complex of decaborane[3] (0.870 g, 4.31 mmol) in dry benzene (40 mL) was added the acetylene **5** (1.00 g, 3.92 mmol). After 3 h of reflux under nitrogen atmosphere the reaction mixture was cooled to ambient temperature and filtered. The filtrate was concentrated. To remove undesired boron compounds, a crude purification was done using flash chromatography on silica with chloroform as the mobile phase. The fractions, containing mainly **7** and **8**, respectively, were rechromatographed to give **7** (0.134 g, 13%) and **8** (0.223 g, 17%) using hexane/ethyl acetate (4:1) for **7** (R_f = 0.60) and hexane/ethyl acetate (19:1) for **8** (R_f = 0.17). The analytical samples were obtained by crystallization from heptane. Data for compound **7** are as follows. Mp: 155.5–157.5 °C. Anal. Calcd for $C_8H_{23}B_{10}NO_2$: C, 35.2; H, 8.5; N, 5.1. Found: C, 35.6; H, 8.6; N, 4.8. ^{1}H NMR ($CDCl_3$): δ 5.11 (broad s, 1 H, NH), 3.95 (broad s, 1 H, HC), 3.78 (d, 2 H, CH_2); 1.44 (s, 9 H, CH_3). ^{13}C NMR ($CDCl_3$): δ 155.8 (C=O), 81.1 (O–CMe$_3$), 75.6 (C cage), 60.1 (HC cage), 46.1 (CH_2), 28.2 (–CH_3). ^{11}B NMR ($CDCl_3$): δ –2.0, –5.4, –10.0, –12.1, –13.1. IR (KBr disk): 3350 (s), 3062 (m), 2983 (m), 2928 (m), 2638 (m), 2594 (s), 1688 (s), 1526 (s), 1308 (s), 1280 (s), 1257 (s) 1164 (s) cm^{-1}. Data for compound **8** are as follows. Mp: 152–153 °C. Anal. Calcd for $C_{13}H_{31}B_{10}NO_4$: C, 41.8; H, 8.4; N, 3.8. Found: C, 42.0; H, 8.8; N, 3.8. ^{1}H NMR ($CDCl_3$): δ 4.34 (s, 2 H, CH_2), 4.06 (broad s, 1 H, HC); 1.52 (s, 18 H, CH_3). ^{13}C NMR ($CDCl_3$): δ 152.2 (C=O), 84.2 (O–CMe$_3$), 74.6 (C cage), 60.7 (HC cage), 50.1 (CH_2), 27.9 (–CH_3). ^{11}B NMR ($CDCl_3$): δ –2.3, –5.4, –10.6, –11.8, –13.4. IR (KBr disk): 3031 (s), 2981 (m), 2624 (s), 2605 (s), 2592 (s), 2558 (m), 2361 (m), 2343 (m), 1785 (s), 1458 (m), 1369 (s), 1358 (s), 1155 (s), 1131 (s), 849 (m), 782 (m) cm^{-1}.

Preparation of 1-(Aminomethyl)-*o*-carborane Hydrogen Chloride (1) from 7 and 8. A solution of the monoprotected amine **7** (49.5 mg, 0.181 mmol) in dry ether (5 mL) was kept saturated with dry hydrogen chloride gas at ambient temperature for 1 h and then concentrated to ca. half of its original volume by bubbling nitrogen through the solution. The precipitate of fluffy white crystals was filtered off and washed with dry ether (3 × 1 mL) to give 34.3 mg (90%) of **1**. This compound easily looses HCl under reduced pressure. The analytical sample was precipitated from a methanol solution by adding dry ether. Mp: 230–233 °C dec (starts subliming at ca. 175 °C). Anal. Calcd for $C_3H_{16}B_{10}NCl$: C, 17.2; H, 7.7; N, 6.7. Found: C, 17.6; H, 7.7; N, 6.4. ^{1}H NMR (CD_3OD): δ 4.77 (broad s, 1 H, CH), 3.90 (s, 2 H, CH_2). ^{13}C NMR (CD_3OD): δ 71.1 (C cage), 63.6 (HC cage), 44.9 (CH_2). ^{11}B NMR (D_2O): δ –0.1, –2.3, –7.0, –10.4. IR (KBr disk): 3447 (m), 3030 (m), 2855 (s), 2594 (s), 2362 (s), 2343 (s), 1584 (m), 1508 (m), 1126 (m), 1064 (m), 727 (m), 668 (s) cm^{-1}. FAB-MS: calcd for (M – Cl)$^+$, m/z 174.2287; obsd, m/z 174.2289.

In a similar fashion **1** was obtained in 98% yield from the diprotected amine **8**.

***N,N*-Di-*tert*-butyloxycarbonyl-1-(3-aminopropyl)-*o*-carborane (9).** To a stirred mixture of $QHSO_4$ (1.46 g, 4.31 mmol) and NaOH (4.31 mL of 2.00 M, 8.62 mmol) were added methylene chloride (10 mL) and **6** (0.937 g, 4.31 mmol) followed by dropwise addition of 1-[3-bromopropyl]-*o*-carborane[4] (**10**) (1.00 g, 4.13 mmol) (prepared in 92% yield from the corresponding alcohol **11** as described below for **14**) in methylene chloride (5 mL). The resulting mixture was refluxed for 2 h and cooled to room temperature, and water (5 mL) was added. The water phase was extracted with methylene chloride (10 mL). The combined organic phases were washed with water (5 mL), dried over $MgSO_4$, and concentrated. The residue was stirred with dry ether (20 mL) in order to precipitate QBr, the precipitate was extracted with dry ether (2 × 20 mL), and the combined extracts were concentrated. The crude product (1.59 g) was purified by flash chromatography on silica (30 g) with hexane/ethyl acetate (4:1) as the solvent to give **9** (R_f = 0.46). Yield: 1.38 g (79%). The analytical sample was recrystallized from heptane. Mp: 107.5–109.0 °C. Anal. Calcd for $C_{15}H_{35}B_{10}NO_4$: C, 44.9; H, 8.8; N, 3.5; B, 26.9. Found: C, 44.8; H, 8.6; N, 3.6; B, 26.7. ^{1}H NMR ($CDCl_3$): δ 3.61 (s, 1 H, H–C), 3.53 (t, J = 6.9 Hz, 2 H, CH_2–N), 2.21 (m, 2 H, C–CH_2–), 1.74 (m, 2 H, CH_2–CH_2–CH_2), 1.50 (s, 18 H, CH_3). ^{13}C NMR ($CDCl_3$): δ 152.5 (C=O), 82.8 (O–CMe$_3$), 74.7 (C cage), 61.0 (HC cage), 45.0 (CH_2–N), 35.2 (C–CH_2–CH_2–), 28.5 (CH_2–C–H_2–CH_2), 28.0 (–CH_3). ^{11}B NMR ($CDCl_3$): δ –2.7, –6.1, –9.7, –11.8 (with shoulders at –12.5 and –13.1). IR (KBr disk): 3446 (w), 3047 (s), 2978 (m), 2931 (m), 2605 (s), 2563 (s), 2365 (w), 2343 (w), 1788 (s), 1733 (s), 1717 (s), 1369 (s), 1156 (s), 1110 (s) cm^{-1}.

Alternatively, **9** was prepared in 15% yield from *N,N*-di-*tert*-butyloxycarbonyl-5-amino-1-pentyne (**12**) and the acetonitrile complex of decaborane[3] by a method analogous to that described for the reaction of **5**. In this case, no mono-*N*-BOC compound was isolated.

***N,N*-Di-*tert*-butyloxycarbonyl-5-amino-1-pentyne (12)** was obtained from 1-iodo-pent-4-yne[5] (**13**) (0.491 g, 2.53 mmol) according to the procedure described for **9**. The reaction time was 1 h. The crude **12** was purified by flash chromatography on silica (30 g) with hexane/ethyl acetate (5:1) as eluent (R_f = 0.46). Yield: 0.585 g, 91%. The analytical sample was obtained by bulb to bulb distillation (100–110 °C, 4 mmHg). Mp: 46–47 °C. Anal. Calcd for $C_{15}H_{25}NO_4$: C, 63.6; H, 8.9; N, 4.9. Found: C, 63.4; H, 8.8; N, 4.8. ^{1}H NMR ($CDCl_3$): δ 3.66 (t, J = 7.3 Hz, 2 H, CH_2–N), 2.18 (dt, J = 7 and 2.6 Hz, 2 H, C–CH_2–CH_2), 1.94 (t, J = 2.5 Hz, 1 H, H–C), 1.79 (m, 2 H, CH_2–CH_2–CH_2), 1.49 (18 H, s, CH_3). ^{13}C NMR ($CDCl_3$): δ 152.7 (C=O), 83.5 (acetylenic C), 82.3 (O–CMe$_3$), 68.6 (HC), 45.5 (CH_2–N), 27.9 (–CH_3), 27.6 (C–CH_2–C–H_2), 16.0 (CH_2–CH_2–CH_2). IR (NaCl): 3279 (w), 2980 (s), 2934 (m), 1791 (m), 1747 (s), 1718 (s), 1698 (s), 1368 (s), 1141 (s), 1113 (s), 857 (m) cm^{-1}.

1-(3-Aminopropyl)-*o*-carborane hydrogen chloride (2) was obtained in a yield of 94% by deprotection of **9** using the method of synthesis described for **1**. The analytical sample was precipitated from a methanol solution by adding dry ether. Mp: 303–306 °C dec (starts subliming at ca. 220 °C). Anal. Calcd for $C_5H_{20}B_{10}NCl$: C, 25.3; H, 8.5; N, 5.9. Found: C, 25.2; H, 8.7; N, 6.0. ^{1}H NMR (CD_3OD): δ 4.66 (s, 1 H, H–C), 2.94 (t, 2 H, J = 7.5 Hz, CH_2–N), 2.44 (m, 2 H, C–CH_2–), 1.89 (m, 2 H, CH_2–CH_2–CH_2). ^{13}C NMR (CD_3OD): δ 75.9 (C cage), 64.0 (HC cage), 39.7 (CH_2–N), 35.4 (C–CH_2–CH_2), 28.1 (CH_2–CH_2–CH_2). ^{11}B NMR (D_2O): δ –1.0, –4.1, –7.6, –9.7, –10.8. IR (KBr disk): 3446 (w), 3030 (s), 2855 (s), 2598 (s), 2577 (s), 2359 (w), 2342 (w), 1498 (m), 1069 (m), 1019 (w), 723 (m), 668 (w) cm^{-1}. FAB-MS: calcd for (M – Cl)$^+$, m/z 202.2601; obsd, m/z 202.2606.

1-Methyl-2-(3-bromopropyl)-*o*-carborane (14). To an ice-cold solution of 1-methyl-2-(3-hydroxypropyl)-*o*-carborane[6] (**15**) (650 mg, 3.01 mmol) and carbon tetrabromide (1.25 g, 3.76 mmol) in dry methylene chloride (3 mL) was added dropwise a solution of triphenylphosphine (1.18 g, 4.51 mmol) in methylene chloride (1.5 mL). The resulting solution was stirred for 5 min and concentrated. The residue was stirred with dry ether (15 mL). After filtration and concentration of the filtrate the crude product was flash chromatographed on silica with hexane/ethyl acetate (4:1) as the mobile phase to give **14** (R_f = 0.47). Yield: 720 mg (86%). The analytical sample was obtained by crystallization from heptane. Mp: 46–48 °C. Anal. Calcd for $C_6H_{19}B_{10}Br$: C, 25.8; H, 6.9. Found: C, 25.8; H, 7.0. ^{1}H NMR ($CDCl_3$): δ 3.42 (t, J = 6.0 Hz, 2 H, CH_2–Br), 2.38 (m, 2 H, C–CH_2–CH_2), 2.13 (m, 2 H, CH_2–CH_2–CH_2), 2.04 (s, 3 H, CH_3). ^{13}C NMR ($CDCl_3$): δ 76.7 (C in cage), 74.9 (C in cage), 33.7 (C–CH_2–), 32.0 (CH_2–CH_2–CH_2–Br), 23.2 (CH_3). ^{11}B NMR ($CDCl_3$): δ –4.5, –5.8, –10.3 (sh), –10.5. IR (KBr disk): 2578 (s), 1448 (m), 1265 (m), 732 (m) cm^{-1}. MS (EI): m/z 278, 280 (0.03% each).

***N,N*-Di-*tert*-butyloxycarbonyl-1-methyl-2-(3-aminopropyl)-*o*-carborane (16)** was obtained from the bromide **14** (0.690 g, 2.46 mmol) according to the procedure described for **9**. The crude **16** was purified by flash chromatography on silica (30 g) with hexane/ethyl acetate (5:1) as the eluent (R_f = 0.36). Yield: 0.930 g (84%). The analytical sample was recrystallized from heptane. Mp: 105–106 °C. Anal. Calcd for

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$C_{16}H_{37}B_{10}NO_4$: C, 46.2; H, 9.0; B, 26.0; N, 3.4. Found: C, 46.2; H, 8.8; B, 25.8; N, 3.6. ^{1}H NMR ($CDCl_3$): δ 3.57 (t, J = 7.0 Hz, 2 H, CH_2–N), 2.17 (m, 2 H, C–CH_2–CH_2), 1.98 (s, 3 H, CH_3–), 1.81 (m, 2 H, CH_2–CH_2–CH_2), 1.50 (s, 18 H, CH_3). ^{13}C NMR ($CDCl_3$): δ 152.5 (*C*=O), 96.0 (Me*C* cage), 82.7 (O–*C*Me$_3$), 74.6 (C cage), 45.2 (*C*-H_2–N), 32.5 (C–CH_2–CH_2), 29.0 (CH_2–CH_2–CH_2), 28.0 (CH_3 in ^{t}Bu), 23.0 (CH_3 cage). ^{11}B NMR ($CDCl_3$): δ –4.4, –5.7, –9.9 (sh), –10.6. IR (KBr disk): 3405 (w), 2980 (m), 2589 (s), 1735 (s), 1692 (s), 1366 (s), 1344 (s), 1177 (s), 1147 (s), 1128 (s), 850 (m) cm^{-1}.

2-(3-Aminopropyl)-1-methyl-*o*-carborane hydrogen chloride (3) was obtained in 93% yield by deprotection of **16** using the method of synthesis described for **1**. The analytical sample was precipitated from a methanol solution by adding dry ether. Mp: 265–272 °C dec (starts subliming at 190 °C). Anal. Calcd: C, 28.6; H, 8.8; B, 42.9; N, 5.6. Found: C, 28.4; H, 8.6; N, 5.6; B, 42.7. ^{1}H NMR (CD_3OD): δ 3.01 (t, 2 H, J = 7.4 Hz, CH_2–N), 2.48 (m, 2 H, cage CH_2–), 2.14 (s, 3 H, CH_3 cage), 1.96 (m, 2 H, CH_2–CH_2–CH_2). ^{13}C NMR (CD_3OD): δ 78.7 (CH_3–*C* cage), 77.0 (C cage), 39.8 (CH_2–N), 32.8 (C–CH_2–CH_2), 28.7 (CH_2–CH_2–CH_2), 23.5 (CH_3 cage). ^{11}B NMR (CD_3OD): δ –4.2, –5.7, –4.8 (2 B, d), –9.0 (sh), –9.4, –10.6 (4 B, d). IR (KBr disk): 3447 (m), 3001 (s), 2933 (s), 2767 (m), 2585 (s), 2361 (w), 1030 (w), 743 (w), 730 (w) cm^{-1}. FAB-MS: calcd for (M – Cl)$^+$, m/z 216.2758; obsd, m/z 216.2778.

1,2-Bis(3-bromopropyl)-*o*-carborane (17)[7] was prepared in 90% yield from the corresponding diol **18** using the method of synthesis described for **14**.

***N*,*N*-Di-*tert*-butyloxycarbonyl-1,2-bis(3-aminopropyl)-*o*-carborane (19)**[7] was prepared from the corresponding dibromide (**17**) (0.462 g, 1.20 mmol) according to the procedure described for **9**. The reaction time was 2.5 h. The crude **19** was purified by flash chromatography on silica (30 g) with hexane/ethyl acetate (4:1) as the eluent (R_f = 0.45). Yield: 0.605 g (77%). The analytical sample was obtained by crystallization from heptane. Mp: 91–93 °C. ^{1}H NMR and ^{13}C NMR spectra (both samples in $CDCl_3$) were in accord with published data.[7] ^{11}B NMR (CD_3OD): δ –5.2, –11.0. IR (KBr disk): 3007 (w), 2984 (m), 2935 (w), 2622 (m), 2574 (m), 2560 (m), 2361 (w), 2343 (w), 1735 (s), 1691 (s), 1438 (m), 1398 (s), 1351 (s), 1277 (m), 1258 (m), 1213 (m), 1177 (s), 1148 (s), 1126 (s) cm^{-1}.

1,2-Bis(3-aminopropyl)-*o*-carborane hydrogen chloride (4) was obtained in 98% yield by deprotection of **19** using a method similar to that described for **1**. The analytical sample was precipitated from a methanol solution by adding dry ether. Mp: 315–325 °C dec (starts subliming at 220 °C). Anal. Calcd for $C_8H_{28}N_2Cl_2$: C, 29.0; H, 8.5; N, 8.5. Found: C, 28.8; H, 8.8; N, 8.1. ^{1}H NMR (CD_3OD): δ 3.05 (t, 2 H, J = 7.4 Hz, CH_2–N), 2.51 (m, 2 H, C–CH_2–CH_2), 1.99 (m, 2 H, CH_2CH_2–CH_2). ^{13} NMR (CD_3OD): δ 80.7 (*C* cage), 39.8 (CH_2–N), 32.8 (C–CH_2–CH_2), 28.7 (CH_2–CH_2–CH_2). ^{11}B NMR (CD_3OD): δ –4.6, –10.4. IR (KBr disk): 3480 (m), 3010 (s), 2918 (s), 2565 (s), 2362 (m), 2341 (m), 1602 (m), 1028 (m), 840 (m), 792 (m) cm^{-1}. FAB-MS: calcd for (M – HCl_2)$^+$, m/e 259.3182; obsd, m/e 259.3170.

Results and Discussion

Deprotection of *N*-alkyl-substituted phthalimides according to the classical method developed by Gabriel is a well-established method for the synthesis of primary amines. The basic conditions commonly used for deprotection are not recommended for compounds containing a 1,2-dicarba-*closo*-decaboranyl(12) group, as the cage is easily degraded by base.[8]

Several methods using alternative deprotection conditions and other Gabriel reagents are now available, and the present state of the art has been reviewed recently.[9] In the synthesis of (aminoalkyl)carboranes we have focused our attention on the use of the Gabriel reagent di-*tert*-butyl iminodicarboxylate (**6**) introduced by Carpino[10] and made commercially available via a recently developed method of synthesis.[9] Alkylation of the sodium, potassium, and lithium salts of **6** under anhydrous conditions has been described.[9]

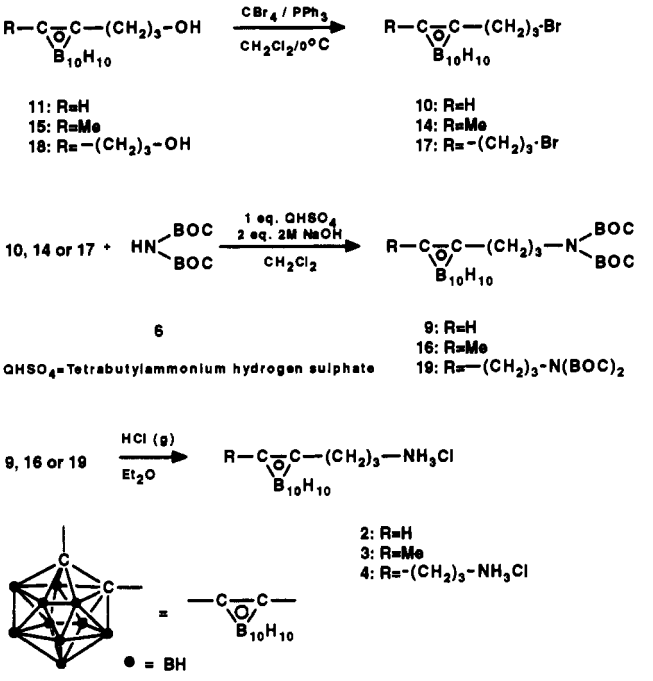
The amine hydrogen chlorides **2–4** were obtained in two steps from the corresponding bromides in 74%, 78%, and 75% yield, respectively, using the general phase transfer alkylation described by Brändström[12] and subsequent deprotection using hydrogen chloride in ether (Scheme I). The reaction times for the alkylation and deprotecting steps are 2–2.5 and 1 h, respectively. The bromides used were all prepared in high yields and short reaction times (5–10 min) from the corresponding alcohols using the reagents[13] carbon tetrabromide and triphenylphosphine in methylene chloride as described in the Experimental Section for the synthesis of **14** (85% yield).

Compound **19** has previously been synthesized by reacting the sodium salt of **6** and the dibromide **17** in dry dimethylformamide for 56 h at 95 °C.[7]

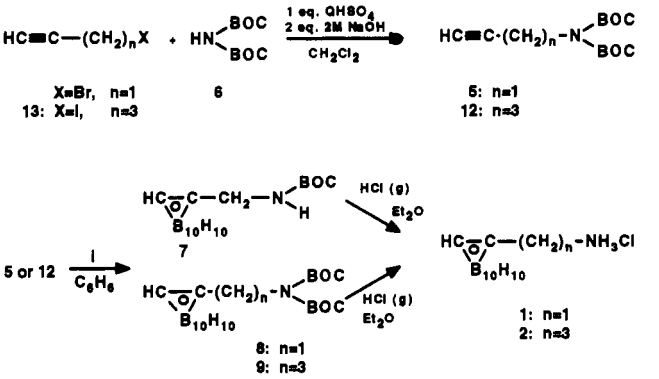
1-(Halomethyl)-1,2-dicarba closo derivatives react extremely slowly with nucleophiles, e.g. (chloromethyl)-*o*-carborane gives a 70% yield of the iodide only after heating for 20 h at 160–170 °C.[14] This observation prompted the use of an alternative route to **1** other than that used for the synthesis of **2–4** (Scheme II).

The doubly protected propargylamine **5** gave a mixture of **7** and **8** on reaction with the bisacetonitrile complex of decaborane, the relative amounts of **7** and **8** varying with the reaction conditions

Scheme I



Scheme II



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used. Prolonged heating seems to favor the formation of 7. However, both compounds are easily deprotected by hydrogen chloride in ether. The overall yield of 1 calculated from 6 was 27%.

The amine salt 2 was also prepared by this route starting with 1-iodopent-4-yne (13). In this case the yield was 13%.

The phase transfer alkylation route to *N,N-tert*-butyloxycarbonyl(aminoalkyl)carboranes should be quite general and useful not only for the synthesis of primary *o-closo*-carboranyl(12)amines but also for the synthesis of corresponding protected nido amines. The stability of the protected amines, such as 9, toward base allows the degradation to the nido analogues without deprotection of the amino group.[15]

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Registry No. 1, 140662-84-6; 2, 140662-87-9; 3, 141120-02-7; 4, 141120-03-8; 5, 141120-04-9; 6, 51779-32-9; 7, 141120-05-0; 8, 141120-06-1; 9, 141120-07-2; 10, 12072-30-9; 11, 23835-93-0; 12, 141120-08-3; 13, 2468-55-5; 14, 51276-07-4; 15, 17815-32-6; 16, 141120-09-4; 17, 141120-10-7; 18, 75611-01-7; 19, 141120-11-8; propargyl bromide, 106-96-7; bis(acetonitrile) complex of decaborane, 28377-97-1.

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Trifluoromethylation and Pentafluorophenylation of Sulfur and Carbon Centers Using (Trifluoromethyl)- and (Pentafluorophenyl)trimethylsilane

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Trifluoromethyl and pentafluorophenyl moieites are easily transferred to a variety of fluorinated inorganic and organic sulfur and carbon centers by using (trifluoromethyl)trimethylsilane and (pentafluorophenyl)trimethylsilane in the presence of catalytic amounts of fluoride ion. This methodology is readily applied to the simple, efficient preparation of known, previously difficult to obtain molecules, as well as a number of new perfluoroalkyl and perfluoroaryl sulfuranes, sulfoxides, ketones, esters, and alcohols. In addition, the first stable oxysulfurane containing more than two sulfur–carbon bonds has been prepared.

Introduction

The importance of methods for the introduction of perfluorinated moieties into molecules is well-known, but such perfluoroalkylations have historically been extremely difficult to achieve, primarily because of the dearth of transfer reagents with general applicability. Methods to place per- or polyfluoroalkyl groups on sulfur are often fraught with problems, such as multistep syntheses, extreme conditions of temperature and pressure, and low-yield reactions.

While there are a variety of easily accessible and quite stable MR_f alkylating reagents where M = Hg, Ag, Cd, Cu, or Zn,[2-5] the formation of sulfonium salts from the reaction of S(IV) sulfuranes with most of these reagents rather than covalent products is observed.[6,7] Some investigators have examined the potential of selected sulfonium salts for use as perfluoroalkylating reagents.[8] However, the usefulness of these reagents for fluoroalkylation of carbon centers is limited to nonfluorinated or polyfluorinated compounds containing labile halogen atoms, e.g., CH_3I, $R_fCH_2CH_2I$, or C_6H_5(Br, I).

While lithium poly- and perfluoroalkoxides, e.g., CF_3CH_2O and $(CF_3)_2CHO$,[9] and (pentafluorophenyl)lithium[10] have been used extensively to alkylate sulfur, lithium salts of perfluoroalkyls are subject to decomposition by elimination of lithium fluoride at ambient temperatures. Thus, the utility of this method for the general introduction of perfluoroalkyl moieties is limited to low-temperature conditions.

The focus of the work described in this paper is the application of (trifluoromethyl)- and (pentafluorophenyl)trimethylsilane to the trifluoromethylation and pentafluorophenylation of a variety of sulfur and carbon centers. Since the reactions of (trifluoromethyl)trimethylsilane with per- or polyfluorinated inorganic substrates (e.g., COF_2, $SOCl_2$, SOF_2, SO_2F_2, and $C_2O_2F_2$) or other classes of perfluoroalkyl compounds such as perfluoroalkyl sulfoxides, perfluoroalkyl sulfones, or perfluoroalkyl aldehydes have not been reported, we have examined the reactions of these substrates in detail. Much of the arylation chemistry achieved with (pentafluorophenyl)trimethylsilane in reactions with per- and polyfluorinated substrates has been reviewed.[11] Recently, trifluoromethylation reactions of (trifluoromethyl)trimethylsilane with nonfluorinated aldehydes, ketones, alkyl nitroso compounds, esters, sulfonyl fluorides, acid halides, and aryl halides have been studied in some detail.[12-20] Perfluoroalkyl ketones and acid halides

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