purfication with freshly prepared Ag_2O (1.42 g) in CH_2Cl_2 to afford an orange precipitate (0.21 g, 0.84 mmol, 40%). Recrystallization from Et_2O gave **1** as orange prisms. M.p. 200–202 °C, ^1H NMR (270 MHz, $CDCl_3$): $\delta = 7.40$ (*s*, 4H), 1.68 (*s*, 18H); FAB-MS (*m*-nitrobenzyl alcohol matrix): *m*/*z* 252 $[M^+ + 2]$; elemental analysis calcd for $C_{14}H_{22}N_2O_2$: C 67.17, H 8.86, N 11.19; found: C 67.22, H 8.85, N, 11.17. Crystal data: $C_{14}H_{22}N_2O_2$, $M_r = 250.34$, monoclinic, space group $P2_1/c$ (no. 14) $a = 10.572(1)$, $b = 11.829(2)$, $c = 11.658(2)$ Å, $\beta = 96.720(8)^\circ$, $V = 1447.9(3)$ Å^3, $T = 296$ K, $Z = 4$, $\rho_{calcd} = 1.148\ g\,cm^{-3}$, $\mu(Cu_{K\alpha}) = 6.16\ cm^{-1}$; of 2417 total reflections, 2281 were independent; $R = 0.081$ and $R_w = 0.100$ for 1754 reflections with $I > 3\sigma(I)$.[15]

2: 1,2,4,5-Tetramethoxybenzene (1.0 g, 5.3 mmol) in Et_2O (60 mL) was lithiated with a 1.6 M solution of *n*-butyllithium (19.3 mL, 32.0 mmol) in the presence of TMEDA (7.7 g, 66 mmol) at −78 °C and then treated with 2-methyl-2-nitrosopropane (5.5 g, 63.2 mmol). The reaction mixture was stirred for 1 h at −78 °C and then left overnight at room temperature. The crude hydroxyamine, containing a small amount of the corresponding diradical, was obtained as a brown solid (0.44 g, ca. 23% yield) and oxidized as for **1**. Recrystallization from Et_2O gave **2** as red bricklike crystals. M.p. 252 °C; FAB-MS (*m*-nitrobenzyl alcohol matrix): *m*/*z* 372 $[M^+ + 2]$; elemental analysis calcd for $C_{18}H_{30}N_2O_6$: C 58.36, H 8.16, N 7.56; found: C 58.61, H 8.13, N 7.50. Crystal data: $C_{18}H_{30}N_2O_6$, $M_r = 370.44$, triclinic, space group $P\bar{1}$ (no. 2) $a = 19.087(2)$, $b = 19.288(2)$, $c = 6.261(2)$ Å, $\alpha = 92.89(2)$, $\beta = 106.48(2)$, $\gamma = 86.48(2)^\circ$, $V = 504.4(2)$ Å^3, $T = 296$ K, $Z = 1$, $\rho_{calcd} = 1.217\ g\,cm^{-}$, $\mu(Cu_{K\alpha}) = 7.55\ cm^{-1}$; of 1604 total reflections, 1493 were independent; $R = 0.071$ and $R_w = 0.084$ for 1240 reflections with $I > 3\sigma(I)$. The structure was solved by direct methods, and the refinement converged with the full-matrix least-squares method of the TEXSAN program (version 1.6, Molecular Structure Corporation).[15]

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Adaptation of the Barton Reaction to Carborane Chemistry: The Synthesis and Reactivity of 2-Hydroxyimino-1-hydroxymethylnona-*B*-methyl-1,12-dicarba-*closo*-dodecaborane(12)**

Axel Herzog, Carolyn B. Knobler, and
M. Frederick Hawthorne*

In memory of Sir Derek H. R. Barton

Recently, we reported the synthesis of deca-*B*-methyl-1,12-dicarba-*closo*-dodecaborane(12) (**1**) by electrophilic methylation of 1,12-dicarba-*closo*-dodecaborane(12) with methyl trifluoromethanesulfonate (methyltriflate). Permethylated 1,12-dicarba-*closo*-dodecaborane(12) (**2**) was obtained by a similar method from 1,12-dimethyl-1,12-dicarba-*closo*-dodecaborane(12).[1] Since this initial report, preparations of other permethylated polyhedral boranes have appeared.[2,3] These results, and those to follow, establish "camouflaged" carboranes (and similarly constituted polyhedral boranes) as a new branch of polyhedral borane chemistry with compounds that show novel structure–reactivity relationships and new applications in chemistry. Species **1** and **2** provide a unique hydrocarbon surface due to their methyl substituents. This lipophilic surface offers excellent solubility and improved stability and, most importantly, it allows chemical transformations at the boron cluster surface which are independent

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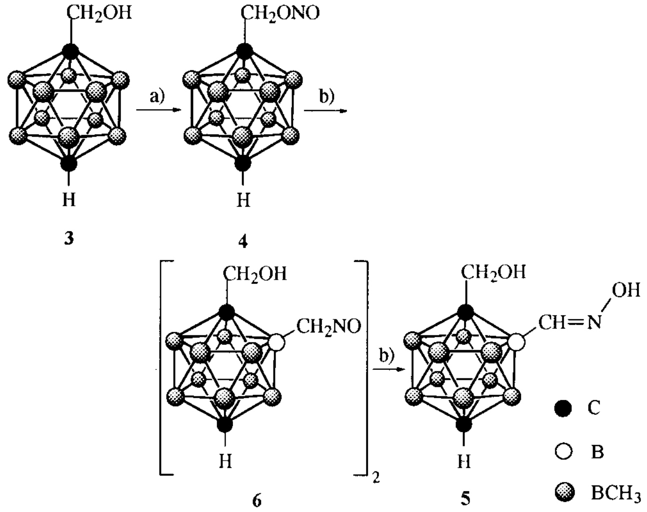
of the delocalized polyhedral cage bonding. The utility of **1** as a synthetic intermediate has already been demonstrated by its facile photochlorination to produce decakis(dichloromethyl)-1,12-dicarba-*closo*-dodecarborane.[4] Since reactions of this type are characteristic of aliphatic hydrocarbons, both **1** and **2** should be viewed as such.

Here we focus on the exclusive functionalization of **1** at one of its ten available methyl groups, which leads to an isomerically pure product.[5] Normal radical-mediated reactions of hydrocarbons are generally nonselective, and under stoichiometric control alone mono- or disubstituted products derived from **1** or **2** cannot be obtained. However, an intramolecular regiospecific radical reaction capable of activating the C–H bonds of pendant methyl groups was viewed as an attractive approach. Such a reaction is the well-known Barton reaction,[6] the photochemical decomposition of a nitrite to produce both NO and an alkoxy radical, both in close proximity to a C–H bond. The latter is most often present in a methyl group with a rigid and favorable orientation with respect to the nitrite functionality. Mechanistic studies of the Barton reaction have demonstrated that a cyclic six-membered transition state, containing the alkoxyl radical and the targeted C–H bond, results in a formal 1,5-hydrogen shift[7] followed by collapse of the NO-alkyl radical pair to form the corresponding nitroso derivative. Isomerization of the latter leads to the observed oxime.

This reaction can be applied to the case at hand if a suitable nitrite functionality is attached to a carbon vertex of **1** since the NO and $CH_2O^{\bullet}$ photointermediates would then be surrounded by a forest of methyl groups. Consequently, the nitrite **4**, derived from deca-*B*-methyl-1-hydroxymethyl-1,12-dicarba-*closo*-dodecaborane(12) (**3**) was prepared. The synthesis of **3** was achieved by lithiation of **1** with methyllithium and subsequent addition of paraformaldehyde. The nitrite **4** was obtained by reaction of **3** with nitrosyl chloride in pyridine.[8] In comparison to organic nitrites,[9] **4** is more sensitive to moisture, especially in the presence of acids and bases. The purity of **4** may be determined from the ^{1}H NMR spectrum since the signal due to the methylene protons shifts from $\delta = 3.28$ in **3** to $\delta = 4.39$ in **4** in [D$_6$]benzene.

The time required for the photolysis of **4** can be monitored by ^{1}H NMR spectroscopy, by observing the disappearance of the characteristic nitrite methylene resonance at $\delta = 4.39$. The reaction time for the photolysis of **4** is dependent upon its concentration in benzene and ranges from 24 h ($2.6 \times 10^{-2}\,\mathrm{mol\,L^{-1}}$) to 60 h ($8.3 \times 10^{-3}\,\mathrm{mol\,L^{-1}}$). Furthermore, the composition of the resulting product mixture varied. In the first case, the predicted product, the hydroximinoalcohol **5**, was isolated by preparative thin-layer chromatography in 42 % yield, while the alcohol **3** was recovered in 25 % yield. With a less concentrated solution, the yields of **5** and **3** were 25 and 20 %, respectively, and the nitroso dimer reaction intermediate **6** could be isolated in 30 % yield (Scheme 1). The ^{1}H NMR spectrum of **6** in [D$_8$]toluene at 97 °C indicates, in contrast to previous reports,[10] neither thermal rearrangement to **5** nor dissociation into its monomeric components. Hence, the rearrangement from **6** to **5** is apparently initiated by UV light, and the reaction rate is dependent upon the pathlength through benzene.



Scheme 1. Barton reaction adapted for carborane chemistry. a) NOCl, C_6H_5N/C_6H_6; b) UV light, C_6H_6, 24–60 h.

Recrystallization of **5** from benzene afforded single crystals suitable for an X-ray crystallographic analysis.[11a] The unit cell contains two crystallographically unrelated molecules of **5**, herein labeled as A and B (Figure 1). Two molecules of A form a dimer with twofold rotation symmetry by hydrogen bonding between the oxime hydrogen and the alcohol oxygen atoms (O–H 0.93(4), H···O 1.76(4), O···O 2.672(3) Å, O-H···O 165(3)°). Two molecules of B also form a dimer with a center of inversion by means of the same type of hydrogen bonding (O–H 0.89(4), H···O 1.87(4), O···O 2.723(5) Å, O-H-O 158(4)°). Each molecule also contains an intramolecular hydrogen bond between the alcohol hydrogen atom and the nitrogen atom of the oxime (O–H 0.99(4) and 0.90(5) Å, H···N 1.75(4) and 1.81(5) Å, O···N 2.715(3) and 2.698(5) Å, O-H···N 164(4) and 171(5)°). The structural properties of the ten-membered HNO ring system forces the oxime into an exclusively *trans* solid-state configuration. The ^{1}H NMR data obtained for **5** show no indication of the presence of the *cis* isomer in solution. The length of the C–N double bond in **5** (mean 1.255 Å) is not significantly shorter

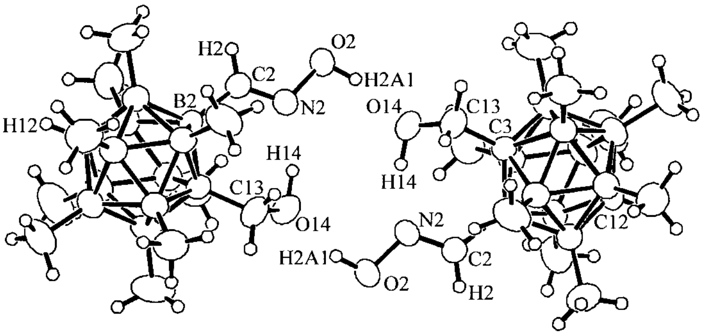


Figure 1. ORTEP representation of the crystal structure of **5**. Of the two crystallographically nonrelated molecules A (C_2 symmetry) and B (C_i symmetry), molecule A is shown. Selected bond lengths [Å] and angles [°]: O2–H2A1 0.78(6), H···O 1.92(6), O2···O14 2.678(4), C2–N2 1.266(5), B2–C2 1.572(6), C1–C13 1.528(6); O-H···O 162(6), C1-C13-O14 114.7(4), B2-C2-N2 122.1(4), C2-N2-O2 113.6(3).

than those of typical oximes, including bulky substituted ketoximes.[12] The carborane cage, therefore, has no apparent electron-withdrawing effect on the oxime functionality.

X-ray analysis of a single crystal of **6**[11b] revealed that it is a centrosymmetric dimer linked by an N–N bond of 1.272(6) Å. This distance is in total agreement with the N–N bond of organic nitroso dimers.[13] An O–H ⋯ O hydrogen bond links the CH_2OH ligand to the oxygen atom of CH_2NO of the same carborane cage (O–H 1.2, O ⋯ H 1.6, O ⋯ O 2.746(5) Å). The six atoms of the ligand that link the two carborane moieties together (C1B, N2B, O3B) are coplanar within 0.008 Å.

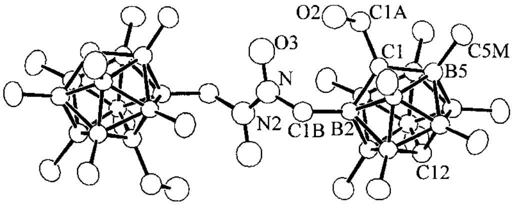
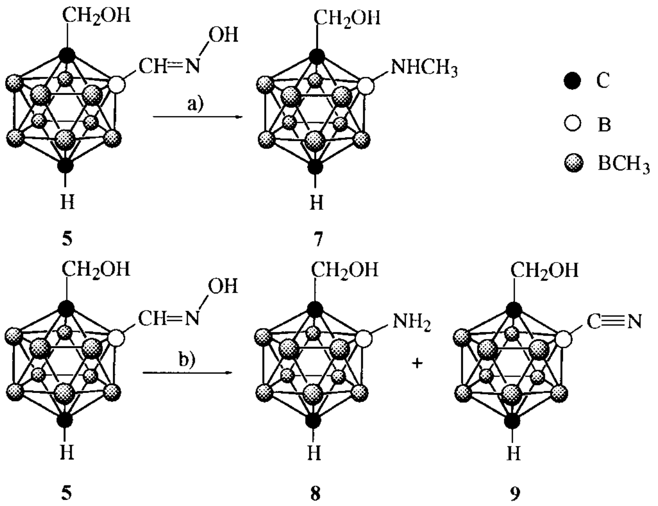


Figure 2. ORTEP representation of the crystal structure of **6**. Hydrogen atoms of the methyl groups are omitted for clarity. Selected bond lengths [Å] and angles [°]: N–N2 1.272(6), N–O3 1.293(6), O2 ⋯ H 1.2, O3 ⋯ H 1.6, O2O3 2.746(5); O3-N-N2 119.2(4)°.

A preliminary study investigated the possible reduction of **5** to the corresponding aminomethyl derivative. However, the methyl amino compound **7** was isolated in 75% yield when **5** was treated with $LiAlH_4$. The formation of the $B{-}NHCH_3$ moiety can be explained as a Beckmann rearrangement under reductive conditions. To the best of our knowledge, this is the first observation of a Beckmann rearrangement of a boron-substituted oxime.[14] The yield of **7** is 45% if **5** is refluxed with diisobutylaluminum hydride (DIBAH, 10 equiv) in toluene for 12 h, but no reduction of the alcohol function was observed.[15] The reduction of **5** with H_2/Pd on C[16] in absolute ethanol in the presence of dry hydrogen chloride is exothermic and leads unexpectedly to the amine **8**. Nitrile **9** can be isolated as a by-product, as a result of a dehydration reaction (Scheme 2).



Scheme 2. Reduction of **5**. a) $LiAlH_4$, THF, reflux; b) H_2/Pd on C, EtOH/HCl, 60 °C.

The photochemical conversion of **4** into **5** is the first example of the application of the Barton reaction to organometallic syntheses and opens new dimensions in carborane chemistry. The deprotonation of the CH vertices of **1** provides valuable information on the stability and reactivity of deca-*B*-methyl-1,12-dicarba-*closo*-dodecaborane(12). We are currently exploring the use of **5** as a synthetic intermediate while further developing hydrocarbon functionalization chemistry as well as the application of the Barton reaction to other methylated carborane derivatives.

Experimental Section

Standard Schlenk-line techniques were used for the preparation of **3** and **4** and for the photolysis of **4**. The THF solvent was purified before use by distillation from sodium/benzophenone. The benzene solvent was distilled from potassium, and pyridine was distilled from calcium hydride. Additionally, benzene was degassed by two freeze-pump-thaw cycles. All reactions were carried out under argon. Compound **1**[1] and nitrosyl chloride[9] were prepared according to methods described in the literature. Paraformaldehyde (Fisher) was stored in a desiccator over concentrated sulfuric acid; methyllithium, $LiAlH_4$, DIBAH, H_2, and 5% Pd on carbon were purchased from Aldrich and used without further purification. The photolysis reaction was carried out with a 450W Hanovia high-pressure quartz mercury-vapor lamp (Ace Glass Inc.).

3: A 1.4 M solution of MeLi (2.6 mL, 3.7 mmol) in Et_2O was added dropwise to a solution of **1** (1.00 g, 3.51 mmol) in THF at room temperature, and the mixture was stirred for 5 h. Solid paraformaldehyde (0.11 g, 3.7 mmol) was added, and the mixture was allowed to react for 30 min at room temperature and then for an additional 15 min at 50 °C. After hydrolysis of the mixture with dilute aqueous hydrochloric acid, the organic layer was separated from the water phase, the latter was extracted twice with Et_2O, and the combined organic phases were dried over $MgSO_4$. The solvent was removed under reduced pressure and the remaining off-white solid was purified by chromatography on silica gel (Et_2O/pentane 1/3) to yield **3** ($R_f = 0.55$) as a colorless solid (0.94 g, 85%); m.p. > 350 °C. ^1H NMR (400.13 MHz, $CDCl_3$): $\delta = 3.50$ (s, 2H, CH_2OH), 2.05 (s, 1H, CH), 1.20 (br s, 1H, OH), 0.06, 0.03 (2 × s, 15H, BCH_3); $\{^1H\}^{13}C$ NMR (100.62 MHz, $CDCl_3$): $\delta = 78.43$, 75.21 (2 × s, carboranyl C), 61.35 (CH_2OH), −4.04 (br, BCH_3); $\{^1H\text{-coupled}\}^{11}B$ NMR (160.46 MHz, Et_2O): $\delta = -7.3$, −8.6 (2 × s, 5B, BCH_3); IR (KBr): $\tilde{\nu} = 3444$, 2963, 2908, 1434, 1322, 1261, 1099, 1044, 1018, 800 cm^{-1}; HR-MS (EI): *m*/*z* calcd 314.3613, found 314.3615 [M^+].

4: Nitrosylchloride (0.66 g, 10.0 mmol) was condensed into a frozen solution of **3** (0.90 g, 2.86 mmol) in benzene (20 mL) and pyridine (20 mL) at −78 °C. The mixture was allowed to warm to room temperature and stirred for an additional 30 min. All volatile components were removed in vacuo, and **4** was isolated (0.93 g, 95%) by extraction with pentane (three times) followed by removal of the solvent. An analytically pure sample was obtained by repeated recrystallization from pentane; m.p. > 350 °C. ^1H NMR (400.13 MHz, C_6D_6): $\delta = 4.39$ (s, 2H, CH_2ONO), 1.39 (s, 1H, CH), 0.06, 0.03 (2 × s, 15H, BCH_3); $\{^1H\}^{13}C$ NMR (100.62 MHz, C_6D_6): $\delta = 75.91$ (br, CH), 66.21 (br, CH and CCH_2ONO),[17] −3.91 (br, BCH_3); $\{^1H\text{-coupled}\}^{11}B$ NMR (160.46 MHz, pentane): $\delta = -7.7$, −8.6 (2 × s, 5B, BCH_3); IR (KBr): $\tilde{\nu} = 2956$, 2909, 2833, 1673, 1434, 1322, 1261, 1190, 1150, 1117, 1046, 1014, 923, 800 cm^{-1}; HR-MS (EI): *m*/*z* calcd 343.3514, found 343.3506 [M^+].

5: A solution of the nitrite **4** (0.90 g, 2.62 mmol) in benzene (100 mL) was placed in a 150-mL pyrex Schlenk tube and irradiated with a high-pressure quartz mercury-vapor lamp for 20 h. During irradiation, the reaction mixture was air-cooled with a ventilation device. The solvent was removed in vacuo, and the remaining off-white solid was purified by chromatography on silica gel (Et_2O/pentane 1/4) to yield **5** (0.38 g, 42%, $R_f = 0.45$) as a colorless solid; m.p. > 350 °C. ^1H NMR (400.13 MHz, C_6D_6): $\delta = 9.95$ (br s, 1H, N=OH), 7.79 (s, 1H, CH=N), 6.06 (br s, 1H, OH), 3.52 (s, 2H, CH_2OH), 1.37 (s, 1H, CH), 0.29 (s, 6H, BCH_3), 0.01 (s, 6H, BCH_3), −0.03 (s, 15H, BCH_3); ^1H NMR (400.13 MHz, $CDCl_3$): $\delta = 10.10$ (br s, 1H, N=OH), 7.58 (s, 1H, CH=N), 3.52 (s, 2H, CH_2OH), 2.13 (s, 1H, CH), 0.17

(s, 6H, BCH_3), 0.15 (s, 6H, BCH_3), 0.08 (s, 9H, BCH_3), 0.01 (br s, 6H, BCH_3); {^{1}H}^{13}C NMR (100.62 MHz, $CDCl_3$): $\delta = 152.50$ (br, BCH=NOH), 79.70, 75.63 (2 × s, carboranyl C), −3.71 (br, BCH_3); {^{1}H-coupled}^{11}B NMR (160.46 MHz, Et_2O): $\delta = -6.2$ (s, 4B, BCH_3), −7.0 (s, 3B, BCH_3), −8.1 (s, 5B, BCH_3), −11.2 (s, 1B, BCH=NOH); HR-MS (EI): *m*/*z* calcd 344.3593, found 344.3593 [M^++H].

6: Nitrite **4** (1.00 g, 2.91 mmol) dissolved in benzene (350 mL) was allowed to react in a 500-mL pyrex Schlenk tube for 48 h, and worked up as described for **5**. Chromatography on silica gel (Et_2O/pentane 1/4) provided **6** (0.38 g, 30 %, $R_f = 0.35$) as a colorless solid and **5** (25 %); m.p. > 350 °C. ^{1}H NMR (400.13 MHz, $CDCl_3$): $\delta = 5.05$ (brs, 2H, OH), 4.39 (s, 4H, CH_2NO), 3.60 (s, 4H, CH_2OH), 2.12 (s, 2H, CH), 0.23 (s, 12H, BCH_3), 0.13 (s, 12H, BCH_3), 0.06 (s, 18H, BCH_3), 0.062 (s, 12H, BCH_3); {^{1}H}^{13}C NMR (100.62 MHz, $CDCl_3$): $\delta = 80.00$, 76.10 (2 × s, carboranyl C), 61.18 (s, CH_2OH), 49.40 (br, CH_2NO), −3.70, −5.70 (br, BCH_3); {^{1}H-coupled}^{11}B NMR (160.41 MHz, Et_2O): $\delta = -6.9$ (s, 5B, BCH_3), −8.3 (s, 4B, BCH_3), −12.2 (s, 1B, BCH_2NO); HR-MS (EI): *m*/*z* calcd 344.3593, found 344.3603 [M^++H].

7: Variation a: A solution of **3** (0.20 g, 0.58 mmol) in THF (30 mL) was added to a suspension of $LiAlH_4$ (0.13 g, 3.48 mmol) at 0 °C. The mixture was allowed to warm to room temperature, and then refluxed for 2 h and finally poured onto ice. Dilute NaOH solution was added, and the product mixture was extracted with Et_2O. Variation b: A 1 M solution of DIBAH in toluene (5.8 mL, 5.8 mmol) was added to a solution of **3** (0.20 g, 0.58 mmol) in toluene (20 mL). The reaction mixture was refluxed for 8 h and worked up as described for variation a. In both cases, the solvent was removed in vacuo and the remaining off-white solid was purified by chromatography on silica gel (Et_2O/pentane/NEt_3 1/3/0.1) to provide **7** as a colorless solid (variation a: 0.14 g, 75 %, $R_f = 0.4$; variation b: 86 mg, 45 %); m.p. > 350 °C; ^{1}H NMR (400.13 MHz, $CDCl_3$): $\delta = 4.30-3.70$ (brs, 1H, $NHCH_3$), 3.67 (s, 2H, CH_2OH), 2.62 (s, 3H, $NHCH_3$), 2.06 (s, 1H, CH), 0.24, 0.22 (2 × s, 12H, BCH_3), 0.02 (s, 6H, BCH_3), 0.00 (s, 3H, BCH_3), −0.07 (s, 6H, BCH_3); {^{1}H}^{13}C NMR (100.62 MHz, $CDCl_3$): $\delta = 74.2$ (brs, both carboranyl C), 62.5 (s, CH_2OH), 31.2 (s, $NHCH_3$), −3.71 (brs, BCH_3); {^{1}H-coupled}^{11}B NMR (160.46 MHz, Et_2O): $\delta = -2.9$ (s, 1B, $BNHCH_3$), −8.2 (s, 4B, BCH_3), −9.7 (s, 2B, BCH_3), −10.2 (s, 2B, BCH_3), −11.2 (s, 1B, BCH_3); HR-MS (EI): *m*/*z* calcd 329.3722, found 329.3721 [M^+].

8 and **9**: A solution of oxime **5** (0.25 g, 0.72 mmol) in absolute ethanol (30 mL) was hydrogenated at room temperature with palladium (0.1 g, 5 % Pd on carbon) for 3 h. During the reaction, dry hydrogen chloride was slowly passed through the solution. After 5 min an exothermic reaction occurred. The reaction mixture was stirred for a further 2.5 h, and filtered through celite. The ethanol was removed in vacuo, and the remaining off-white solid was purified by chromatography on silica gel (Et_2O/pentane/NEt_3 1/4/0.1) to yield **8** (0.10 g, 45 %, $R_f = 0.45$) and **9** (71 mg, 30 %, $R_f = 0.65$) as colorless solids.

8: M.p. > 350 °C; ^{1}H NMR (400.13 MHz, $CDCl_3$): $\delta = 3.68$ (s, 2H, CH_2OH), 2.10 (s, 1H, CH), 0.19 (s, 6H, BCH_3), 0.11 (s, 6H, BCH_3), 0.05 (s, 9H, BCH_3) −0.05 (s, 6H, BCH_3); {^{1}H}^{13}C NMR (100.62 MHz, $CDCl_3$): $\delta = 77.5$, 75.2 (2 × s, carboranyl C), 62.6 (s, CH_2OH), −4.9 (br, BCH_3); {^{1}H-coupled}^{11}B NMR (160.46 MHz, Et_2O): $\delta = -3.7$ (s, 1B, BNH_2), −9.0 (s, 4B, BCH_3), −10.1 (s, 2B, BCH_3), −10.9 (s, 2B, BCH_3), −11.8 (s, 1B, BCH_3); HR-MS (EI): *m*/*z* calcd 315.3565, found 315.3559 [M^+].

9: M.p. > 350 °C; ^{1}H NMR (400.13 MHz, $CDCl_3$): $\delta = 3.61$ (s, 2H, CH_2OH), 2.21 (s, 1H, CH), 0.31 (s, 6H, BCH_3), 0.27 (s, 6H, BCH_3), 0.10 (s, 6H, BCH_3), 0.08 (s, 3H, BCH_3), 0.06 (s, 6H, BCH_3); ^{13}C{^{1}H} NMR (100.62 MHz, $CDCl_3$): $\delta = 122.5$ (brs, BCN), 80.5, 75.2 (2 × s, carboranyl C), 60.4 (s, CH_2OH), −4.5 (br, BCH_3); ^{1}B{^{1}H coupled} NMR (160.46 MHz, Et_2O): $\delta = -6.4$ (s, 1B, BCH_3), −7.4 (s, 4B, BCH_3), −8.2 (s, 2B, BCH_3), −8.9 (s, 2B, BCH_3), −18.1 (s, 1B, BCN); HR-MS (EI) (m/z): calcd 325.3409, found 325.3415 [M^+].

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calculations, but parameters were not refined. Methyl and methylene hydrogen atoms were placed in calculated positions. Hydrogen atoms were assigned isotropic displacement values based approximately on the value for the attached atom. The largest peak maximum and minimum on a final difference electron density map were 0.21 and -0.25 e Å^{-3}. Scattering factors for hydrogen atoms for both **5** and **6** were obtained from Stewart et al.[19] and those for other atoms were taken from ref. [19]. Programs used in this work include locally modified versions of the following programs: CARESS (Broach, Coppens, Becker, and Blessing), peak-profile analysis, Lorentzian and polarization corrections; ORFLS (Busing, Martin, and Levy), structure-factor calculation and full-matrix least-squares refinement; SHELXL (Sheldrick), crystal structure refinement; SHELX86 (Sheldrick), crystal structure solution; ORTEP (Johnson). Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101178. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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A Photoluminescent Copper(I) Complex with an Exceptionally High Cu^{II}/Cu^{I} Redox Potential: $[Cu(bfp)_2]^+$ (bfp = 2,9-bis-(trifluoromethyl)-1,10-phenanthroline)**

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The continued exploration of copper(I) bis(1,10-phenanthroline) complexes primarily results from their interesting photophysical properties.[1] In these systems it has been established that emission originates from low-lying metal-to-ligand charge transfer (MLCT) excited states.[2] Since these states are best described as copper in the +2 oxidation state, it is believed that these pseudotetrahedral copper(I) complexes reorganize towards square-planar geometry in the excited state.[3] Substituents at the 2 and 9 positions reduce the degree of excited-state distortion,[3, 4] leading to room-temperature emission for most copper(I) complexes of 2,9-disubstituted-1,10-phenanthrolines.[5] Photochemical studies of $[Cu(N-N)_2]^+$ complexes (N–N = 1,10-phenanthroline ligand) with 2,9-dialkyl and 2,9-diaryl substituents have demonstrated that the steric bulk of the substituents has a profound effect on the ground-state electrochemistry and the emission properties of the complexes in solution.[3, 4, 5b,g, 6] Bulkier substituents increase the Cu^{II}/Cu^{I} redox potential by stabilization of the copper(I) species, and increase both the lifetimes and energies of the MLCT excited states.

Metal complexes of electron-deficient ligands are often studied as catalysts due to their high chemical stability and, in certain cases, enhanced reactivity.[7] Since copper(I) complexes have been widely studied in photocatalytic processes,[1b,c, 8] the effects of electron-withdrawing groups on the photochemistry of these complexes are of interest. Here we report the first investigation of the copper(I) complex cation $[Cu(bfp)_2]^+$ (bfp = 2,9-bis(trifluoromethyl)-1,10-phenanthroline). In comparison to previously studied luminescent $[Cu(N-N)_2]^+$ complexes, the trifluoromethyl groups dramatically perturb the electronic structure of the complex, and consequently enhance the ability of the copper(I) complex to act as a photooxidant.

The air-stable complex $[Cu(bfp)_2](PF_6)$ was characterized by ^1H NMR spectroscopy, mass spectrometry, and X-ray crystallography.[9] An ORTEP view of the cation is shown in Figure 1. The structure of $[Cu(bfp)_2]^+$ resembles the known structures of the $[Cu(dmp)_2]^+$ complex (dmp = 2,9-dimethyl-1,10-phenanthroline).[10] However, there are notable differences. In the solid state, the $[Cu(dmp)_2]^+$ cation tends to show variable degrees of distortion from D_{2d} symmetry, which has

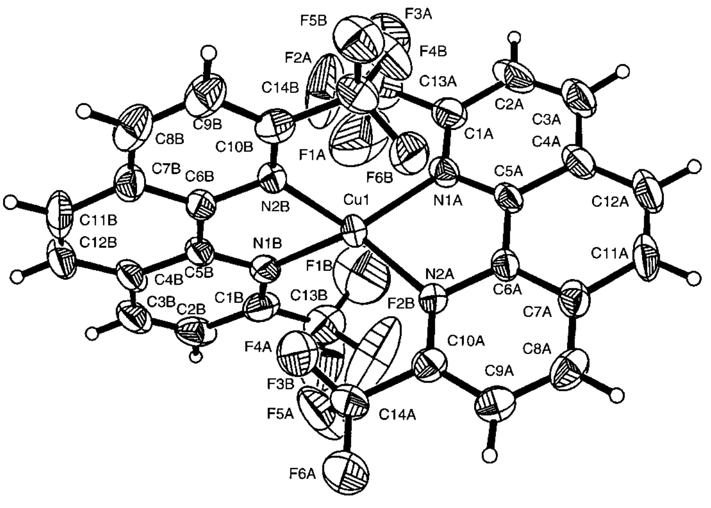

Figure 1. ORTEP diagram of the complex cation $[Cu(bfp)_2]^+$. Selected bond distances [Å] and angles [°]: Cu1–N1A 2.037(6), Cu1–N2A 2.052(6), Cu1–N1B 2.025(6), Cu1–N2B 2.063(7); N1A-Cu1-N2A 83.3(3), N1B-Cu1-N1A 134.6(3), N1A-Cu1-N2B 118.4(3), N1B-Cu1-N2A 124.2(3), N2A-Cu1-N2B 117.0(3), N1B-Cu1-N2B 83.2(3).

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