Proton sponge as a carbon nucleophile, addition to a putative carbocation linked to a dicarbacobaltaborane cage

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Abstract

The proton sponge tetra-N-methyl-1,8-diaminonaphthalene reacts as a carbon nucleophile towards the carbocation centre in [{Co($C_2B_9H_{10}$S)$_2$}CH] to produce [4-{Co($C_2B_9H_{10}$S)$_2$CH}-$C_{10}H_5$-1,8-{(NMe$_2$)$_2$H}] mixed with the related compound [4-{Co($C_2B_9H_{10}$S)$_2$C(OH)}-$C_{10}H_5$-1,8-{(NMe$_2$)$_2$H}], both being found in the X-ray crystal structure of the reaction product. [4-{Co($C_2B_9H_{10}$S)$_2$CH}-$C_{10}H_5$-1,8-{(NMe$_2$)$_2$H}]-[4-{Co($C_2B_9H_{10}$S)$_2$C(OH)}-$C_{10}H_5$-1,8-{(NMe$_2$)$_2$H}] · 2MeCN. In [4-{Co($C_2B_9H_{10}$S)$_2$C(OH)}-$C_{10}H_5$-1,8-{(NMe$_2$)$_2$H}], the oxygen forms a hydrogen bond with a {BH} group from one carbaborane cage and is bound to carbon with an unusually long C–O bond distance of 1.691(11) Å. © 1997 Elsevier Science S.A.

Keywords: Metallocarbaborane; Crystal structure; Carbon nucleophile; Hydrogen bond; Proton sponge

1. Introduction

The unusually high Brønsted basicity and low nucleophilicity of tetra-N-methyl-1,8-diaminonaphthalene [1a,1b,1c,1d,1e,1f,1g,1h], widely known as 'proton sponge' (Aldrich trade name), has led to the use of this, and related compounds [2a,2b], as proton abstractors in synthetic applications. In an attempt to produce new metallocarbaborane derivatives containing the {S$_2$C = CS$_2$} core, found in tetrathiofulvalene, we sought to deprotonate the carbocation centre in [{Co($C_2B_9H_{10}$S)$_2$}CH] in the hope that this might result in dimerisation and the formation of [{Co($C_2B_9H_{10}$S)$_2$}C = C{SC$_2B_9H_{10}$)$_2$Co}]$^{2-}$. However, the product actually obtained resulted from the reaction of the proton sponge as a carbon nucleophile rather than as a proton abstractor. Although the steric disposition of the {NMe}$_2$ groups in the proton sponge restricts its ability to act as a nucleophile through the nitrogen atoms [3a,3b,3c], previous examples have emerged in which it can act as a carbon nucleophile through the 4-position of one aromatic ring. These reactions involve addition to strongly electrophilic elec-

tron deficient aromatic compounds [4a,4b] or to coordinated alkenes [5]. Here we report further evidence of the ability of this reagent to act as a carbon nucleophile in its reaction with the {S$_2$CH} carbocation centre in [{Co($C_2B_9H_{10}$S)$_2$}CH].

2. Results and discussion

2.1. Synthetic studies

The reaction of the 'proton sponge' tetra-N-methyl-1,8-diaminonaphthalene with [{Co($C_2B_9H_{10}$S)$_2$}CH], prepared according to the previously reported procedure [6a,6b], proceeds rapidly in tetrahydrofuran or dichloromethane solution to afford a red crystalline product, 1. The IR spectrum of 1 contained bands attributable to ν_{max}(BH) at 2545 cm^{-1} and the 128 MHz ^{11}B{^{1}H} NMR spectrum contained signals at 8.88 (2B), −2.42 (2B), −7.28 (4B), −9.06 (4B), −20.3 (4B) and −26.2 ppm (2B) consistent with the presence of the {SC$_2B_9H_{10}$}$_2$Co} moiety. However, the negative ion fast atom bombardment (FAB) mass spectrum contained no ions attributable to the presence of the target compound [$C_{10}H_6$(NMe$_2$)$_2$H]$_2$[{Co($C_2B_9H_{10}$S)$_2$}C = C{SC$_2B_9H_{10}$)$_2$Co}]. Instead an ion based at $m/z = 613$

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was present. This value is consistent with the formulation [4-{Co($C_2B_9H_{10}$S)$_2$}CH][$C_{10}H_5$-1,8-{(NMe$_2$)$_2$H}] and, after drying in vacuo, elemental analyses of a sample of 1 were also consistent with this formulation. However, the solution conductivity of 1 indicated that a neutral species had been formed, rather than a salt. In order to definitively characterise 1 an X-ray crystal structure analysis was carried out. This showed that crystals of 1 contain two slightly different molecules, [4-{Co($C_2B_9H_{10}$S)$_2$}C(X)-$C_{10}H_5$-1,8-{(NMe$_2$)$_2$H}] (A) and [4-{Co($C_2B_9H_{10}$S)$_2$}CH-$C_{10}H_5$-1,8-{(NMe$_2$)$_2$H}] (B). The species X in A could not be uniquely identified from the X-ray data, the light elements B, C, N or O, fitting the data almost equally well. However, in addition to a strong ion cluster based at $m/z = 613$, corresponding with the formulation [{Co($C_2B_9H_{10}$S)$_2$}C(H)C$_{10}H_5${(NMe$_2$)$_2$H}], the positive ion FAB mass spectrum of 1 also contains an ion cluster at $m/z = 629$ corresponding with the formulation [{Co($C_2B_9H_{10}$S)$_2$}C(OH)C$_{10}H_5${(NMe$_2$)$_2$H}]. High resolution accurate mass measurements give m/z values of 613.3683 and 629.3654 for these ions compared to the respective calculated values of 613.3671 (difference 2 ppm) and 629.3620 (difference 5 ppm) for $C_{10}H_{39}^{10}B_3^{11}B_{15}N_2S_2Co$ and $C_{19}H_{39}^{10}B_3^{11}B_{15}N_2OS_2Co$; thus identifying X as oxygen. A comparison of the ^{11}B and ^{11}B{^{1}H} NMR spectra of the compound revealed that the signal at ca. 8.88 ppm comprised two partly overlapping singlets attributable to two different environments for the boron atoms bonded to sulphur. This observation is in accord with the presence of molecules A and B in 1 although differing environments for the boron atoms associated with the remaining signals could not be resolved.

The two molecules A and B in 1 differ both chemically and with respect to the orientation of the tetra-N-methyl-1,8-diaminonaphthalene residue relative to the
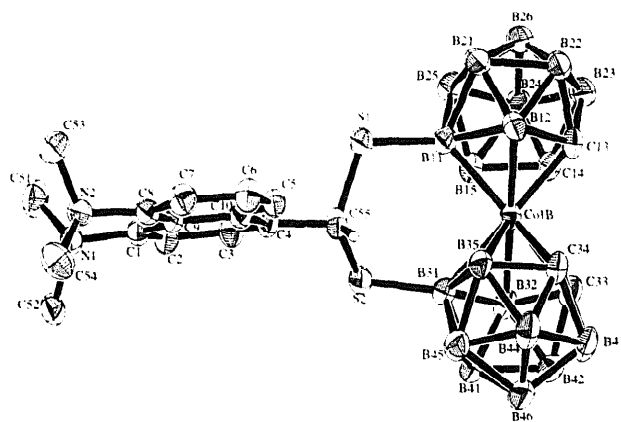
Fig. 2. A view of molecule B oriented similarly to the view of molecule A in Fig. 1. Only the hydrogen atom bonded to C55 has been included in its calculated position for comparison with molecule A.

carborane moieties as shown in Figs. 1 and 2. In molecule A (Fig. 1), the carbon atom of the S-C-S group [C55] is bonded to a hydroxyl group [O56-H] whereas, in molecule B, (Fig. 2), this position is occupied by a hydrogen atom. In both molecules the geometry at C55 is essentially tetrahedral but, in A, the C-OH bond is exceptionally long [1.691(11) Å] (Table 1) and contrasts with other examples of C-O bond distances within {S$_2$C(C)-O} fragments which fall in the range 1.393 [7a] to 1.435 Å [7b]. The distance between the oxygen atom and the calculated position of the hydrogen atom bonded to B35 is only 1.61 Å, with the O...B35 separation 2.084(15) Å, and the angle O...H-B35 is 98.3°. We consider the hydroxyl moiety to form a weak covalent bond to C55 and possibly a hydrogen bond to B35. The presence of the hydrogen atom bonded to B35, which is involved in the postulated hydrogen bond, was confirmed from a difference map, but the hydroxylic hydrogen atom could not be located. It may be noted that the O-C-S angles are distorted from normal tetrahedral values in such a way as to bring O56 closer to S2 and B35 [angles O56-C55-S1,S2 112.5(6), 89.4(5)°, distances O...S1,S2 2.908(8), 2.433(10) Å]. A comparison of the C55 bonding environments in molecules A and B indicates that the presence of the hydroxyl group has no significant effect on the geometry of the {C55-S1-S2-C4} fragment. In view of the unexpected results concerning the C55-O56 moiety, the structure determination was repeated using a different type of diffractometer (see Section 3). This gave essentially the same result, the C55-O56 length being measured as 1.64(3) Å.

Boron-boron and boron-carbon bonds have mean lengths of 1.766(7) and 1.685(7) Å, with reasonably good agreement between the mean values of the two molecules (see Table 1). They are, however, slightly shorter than the values given by Allen et al. [8], 1.775 Å
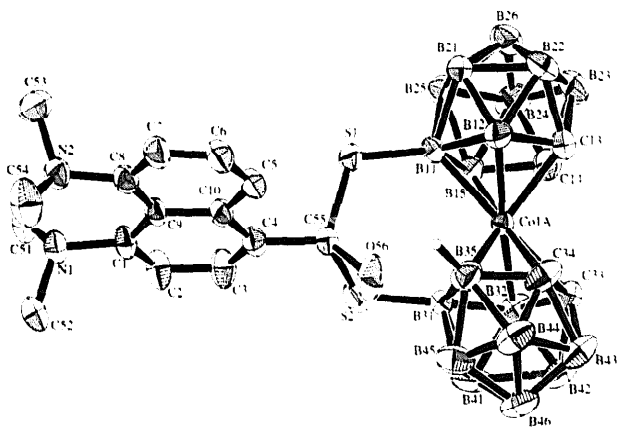

Fig. 1. A view of molecule A in a direction perpendicular to the plane of atoms Co1, B11 and B31, showing the atom labelling. Hydrogen atoms, except for H35, involved in the O56···B35 hydrogen bond, have been omitted for the sake of clarity.

Table 1
Selected bond distances and angles and torsion angles

|	Molecule A	Molecule B
Distances (Å)		
C55–C4	1.524(11)	1.517(10)
C55–S1	1.806(8)	1.821(9)
C55–S2	1.766(9)	1.783(8)
C55–O56	1.691(11)	–
S1–B11	1.830(9)	1.872(9)
S2–B31	1.883(11)	1.861(10)
C13–C14	1.544(15)	1.590(11)
C33–C34	1.581(13)	1.577(12)
Angles (°)		
S1–C55–C4	107.0(6)	107.8(6)
S2–C55–C4	112.9(6)	111.8(5)
S1–C55–S2	112.7(5)	115.4(4)
S1–C55–O56	112.5(6)	–
S2–C55–O56	89.4(5)	–
C4–C55–O56	121.6(7)	–
Torsion angles (°)		
S1–C55–C4–C3	109.1(9)	90.3(8)
S1–C55–C4–C10	–69.7(9)	–90.5(8)
S2–C55–C4–C3	–15.5(11)	–37.5(10)
S2–C55–C4–C10	165.8(10)	141.6(10)
C51–N1–C1–C2	–55.5(13)	–54.8(11)
C51–N1–C1–C9	126.7(10)	127.7(9)
C52–N1–C1–C2	70.0(12)	71.8(12)
C52–N1–C1–C9	–107.8(10)	–105.7(10)
C53–N2–C8–C7	71.8(12)	67.2(11)
C53–N2–C8–C9	–106.2(10)	–110.0(9)
C54–N2–C8–C7	–59.0(12)	–59.9(11)
C54–N2–C8–C9	123.0(10)	122.9(10)
Mean distances (Å)		
Co–B	2.093(11)[a]	2.114(4)[a]
Co–C	2.045(13)[b]	2.042(8)[b]
B–B	1.761(10)[c]	1.771(5)[c]
B–C	1.671(11)[d]	1.700(6)[d]

[a] Mean of 6 values.
[b] Mean of 4 values.
[c] Mean of 36 values.
[d] Mean of 12 values.

for B–B and 1.716 Å for B–C in comparable cage structures. The cobalt atom is 10-coordinated, sandwiched between two C_2B_3 rings; Co–B and Co–C bonds, with mean lengths of 2.104(6) and 2.044(7) Å, compare with mean values of 2.115 and 2.027 Å for

four comparable bis(1,2-dicarbaundecaborane)cobalt structures [9a,9b,9c,9d]. In an earlier study of [(C$_2$B$_9$H$_{10}$)$_2$CoS$_2$CH], Co–B and Co–C bonds were found [6a,6b] to average 2.079(35) and 2.047(8) Å. The C_2B_3 rings bonded to cobalt are tilted very slightly with respect to one another, by 0.9(7)° in molecule A and by 2.3(7)° in molecule B, so that the carbaborane ligands are essentially parallel. As is commonly observed [6a,6b,9a,9b,9c,9d] in sandwich compounds of this type, the ligands are mutually staggered, rotation from the eclipsed conformation, 32° in A, 29° in B, compared with 36° for an ideal staggered conformation.

The orientation of the naphthalene residue, defined as the angle its plane makes with the plane formed by the cobalt atom and the two boron atoms, B11 and B31, bonded to the sulphur atoms of the S–C–S bridge is 62.0(5)° in molecule A and 84.4(3)° in molecule B. Consideration of torsion angles about the C55–C4 bond (Table 1) also indicates a conformational difference of some 22° between molecules A and B. There does not appear to be any obvious reason for this difference in orientation and it may be due to packing forces. The geometry at the nitrogen atoms of the tetra-*N*-methyl-1,8-diaminonaphthalene residue is consistent with mono-protonation in both molecules. The orientation of the NMe$_2$ groups is such that the methyl substituents on each nitrogen atom are positioned above and below the plane of the aromatic ring system, and the nitrogen lone pair electrons are brought face to face (see torsion angles in Table 1). This orientation is not found in neutral species. The cationic hydrogen atom has been located between the nitrogens [molecule A: N2–H 1.29 Å, N1...H 1.31 Å; molecule B: N1–H 1.23 Å, N2...H 1.46 Å]. Also, characteristic [3a,3b,3c,10] of protonation is the N...N non-bonded distance. A search of the Cambridge Structural Database [11] shows that for six neutral species of this type, the N...N distances are in the range 2.75 to 3.03 Å and for 22 protonated species this distance is significantly smaller, ranging from 2.56 to 2.65 Å. In molecules A and B, N...N distances are 2.589(11) and 2.586(11) Å, respectively, in good agreement with the distances found for the protonated molecules. The finding that solutions of 1 in MeCN are non-conducting is also consistent with this formulation

X = H. OH

● CH
○ BH
◯ B
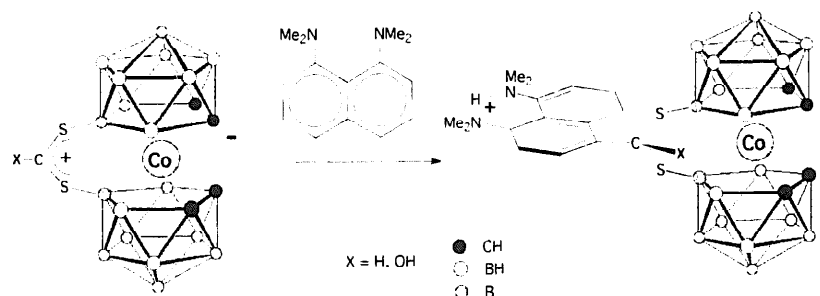
Scheme 1.

of A and B as neutral components, each containing a cationic protonated diamine moiety, {−$C_{10}H_6(NMe_2)_2H$}$^+$, linked to the anionic [{$Co(C_2B_9H_{10}S)_2$}C(X)−]$^-$ moiety. There are no abnormally short intermolecular contact distances. Excluding hydrogen atoms, the shortest contacts occur between NMe carbon atoms C51 of each of molecules A and B, and the nitrogen atoms of two independent molecules of acetonitrile of crystallisation of 3.27 and 3.32 Å.

The formation of molecule B in the structure, [4-{$Co(C_2B_9H_{10}S)_2$}CH-$C_{10}H_5$-1,8-{(NMe_2)_2H}], may be readily accounted for if the proton sponge acts as a carbon nucleophile towards the carbocation centre (Scheme 1). However, the formation of [4-{$Co(C_2B_9H_{10}S)_2$}C(OH)-$C_{10}H_5$-1,8-{(NMe_2)_2H}] was quite unexpected and prompted us to reexamine the reaction conditions and starting material used. The positive ion LSIMS mass spectrum of the precursor [{$Co(C_2B_9H_{10}S)_2$}CH] [6a,6b], was found to contain ion clusters based at m/z 415 (19%), 399 (100%) and 385 (26%) attributable respectively to [{$Co(C_2B_9H_{10}S)_2$}C(OH)]$^+$, [{$Co(C_2B_9H_{10}S)_2$}CH]$^+$ and {[{$Co(C_2B_9H_{10}S)_2$}]−H}$^+$ indicating the presence of a significant proportion of the hydroxyl derivative [{$Co(C_2B_9H_{10}S)_2$}C(OH)}] in the starting material, possibly formed during the work up of the reaction mixture which involves hydrolysis and column chromatography. This byproduct could then undergo nucleophilic attack by the proton sponge in a similar manner to [{$Co(C_2B_9H_{10}S)_2$}CH}] to give [4-{$Co(C_2B_9H_{10}S)_2$}C(OH)}·$C_{10}H_5$-1,8-{(NMe_2)_2H}]. The proximity of the carbaborane cage to the carbon bonded hydroxyl group in this molecule leads to the observed highly distorted coordination environment around carbon in which the oxygen is displaced towards the BH group. The similarities in the geometries of the {C55-S1-S2-C4} fragment in molecules A and B (Fig. 1) indicate that the effects of this interaction are confined to the C55-O56 bond. Formation of a hydrogen bond might normally be expected to provide an energy benefit of some 30–40 kJ mol^{-1}. Taking a standard C–O single bond to be 1.43 Å and the force constant for stretching to be 450 N m^{-1}, the energy required to elongate such a bond to 1.60 Å is estimated as 39 kJ mol^{-1} and to the measured length of 1.69 Å, 92 kJ mol^{-1}. Thus, a hydrogen bonding interaction with a B–H group could account for a large part, though not all, of the elongation of the C55-O56 bond.

3. Experimental details

3.1. Synthetic studies

Solvents were purified by distillation from standard drying agents under dinitrogen. All commercial reagents were pre-dried and recrystallised before use but otherwise were used as received unless otherwise stated. The complex [{$Co(C_2B_9H_{10}S)_2$}CH}] was prepared using the previously reported procedure [6a,6b] and further purified using column chromatography on silica gel using CH_2Cl_2 as the eluent.

3.2. Physical measurements

IR spectra were recorded from KBr discs using a Perkin Elmer 1600 series FT-IR spectrophotometer, ^{1}H NMR spectra using a Bruker WHM400 spectrometer, ^{11}B{^{1}H} NMR spectra using a Jeol GX270 spectrometer and positive or negative ion LSIMS from a 3-nitrobenzyl alcohol matrix using a Zabspec instrument. Solution conductivity measurements were recorded from 10^{-4} mol dm^{-3} solutions in MeCN using a PTI 58 digital conductivity meter. Elemental analyses were performed by the Microanalytical Service, School of Chemistry, University of Sheffield.

3.3. Synthetic studies

A sample of [{$Co(C_2B_9H_{10}S)_2$}CH] (150 mg, 0.376 mmol) was dissolved in THF (3 cm^3) and a solution of proton sponge [1,8-$(Me_2N)_2C_{10}H_6$] (81 mg, 0.376 mmol) in THF (1 cm^3) added dropwise. The red solution which formed was stirred at room temperature for 2 h and evaporated to dryness to afford a red solid. This product was purified by column chromatography on silica gel using MeCN/THF (1:9 v/v) as the eluent. The major dark orange band was collected, evaporated to dryness in vacuo and the crude product so obtained recrystallised from MeCN (206 mg, 89%). (Found: C, 36.7; H, 6.32; N, 4.58. $C_{19}H_{39}B_{18}N_2OS_2Co$ · $C_{19}H_{39}B_{18}N_2S_2Co$ requires: C, 36.7; H, 6.33; N, 4.51%); ν_{max}(BH) 2545s cm^{-1}; ^{1}H (CD_3CN) δ (ppm), 2.11, 2.19 (12H s, 12H s, NCH_3), 3.81, 4.03 (4H s, 4H s, B_9C_2H_2), 5.89, 7.70, 7.84, 8.12, 8.53 (2H s, 2H dd, JHH 7.8, 4H d, JHH 7.6 Hz, 2H br, 2H br, C_{10}H_5), 5.89/11.17 {2H s, (Me_2N)_2H}; ^{11}B{^{1}H} (CH_3CN) δ_B (ppm); 9.70, 8.88 (2B), −2.42 (2B), −7.28 (4B), −9.06 (4B), −20.3 (4B), −26.2 (2B); Mass Spectrum m/z (1%); +ve FAB, 629 (15) [M$^+$ (A)], 613 (100) [M$^+$ (B)]; Λ_m, 14 Ω cm^2 mol^{-1}.

3.4. Structural studies

Crystals from MeCN · $C_{19}H_{39}B_{18}N_2OS_2Co$. $C_{19}H_{39}B_{18}N_2S_2Co$ · 2CH_3CN, M_r = 1324.4, monoclinic, space group $P2_1/c$, a = 18.440(6), b = 25.358(13), c = 15.527(5) Å, β = 109.25(3)°, U = 6855(5) Å^3, Z = 4, D_c = 1.283 g cm^{-3}, $F(000)$ = 2736, μ(Mo K$^\alpha$) = 0.646 mm^{-1}. Cell dimensions and intensity data were measured on the Stoe Imaging Plate Diffraction System at Darmstadt using graphite-mono-

chromated Mo K^α radiation, $\lambda = 0.71073$; crystal size $0.16 \times 0.32 \times 0.46$ mm. The cell dimensions were obtained from three exposures at 45° intervals, each with oscillation angle of 0.1°. Data collection was performed with crystal to plate distance 70 mm, taking 137 exposures at increment 1.1°. A total of 36,946 reflections were measured in the range θ 4.5–26.0°, of which 12,312 were independent (R_{int} 0.089). Conventional absorption corrections were not applied since, on average, each unique reflection intensity is the mean of three intensities measured at different orientations of the crystal, thus minimising absorption effects. The structure was determined by Patterson and Fourier methods and refined on F^2 by least squares, using all independent reflection with anisotropic thermal parameters for the non-hydrogen atoms. The cage carbon atoms were identified in the first instance by these atoms having slightly lower apparent thermal parameters when all cage atoms were assigned scattering factors appropriate to boron. Confirmation of the assignment was provided by a consideration of mean B–B, B–C and C–C bond lengths, respectively, 1.761(10), 1.671(11) and 1.56(2) Å in molecule A and 1.771(5), 1.700(6) and 1.58(1) Å in molecule B, in accord with literature values [8]. Hydrogen atoms were placed in calculated positions [d(Csp^2–H) 0.93 Å, d(Csp^3–H 0.96 Å, d(B–H) 1.10 Å] riding on their respective bonded atoms. Weights of the form $w = 1/[\sigma^2(F_0^2) + aP^2 + bP]$, where $P = (F_0^2 + 2F_c^2)/3$, and $a = 0.109$, $b = 15.906$ were used in the final cycles of refinement. Convergence was achieved (maximum shift $< 0.05\sigma$) with conventional $R = 0.0857$ for the 6555 reflections with $I > 3\sigma(I)$, and $wR2 = 0.2878$ for all data. The residual electron density in a final difference map was within the range -0.80 to $+0.81$ eÅ^{-3}.

Computations were performed on the University of Birmingham IBM3090 computer and on the Cray CS6400 at the Manchester Computing Centre using the packages SHELXS86 [12] and SHELX93 [13]. The molecular diagrams were prepared with ORTEP [14].

In view of the unexpected results of the X-ray crystallographic study an independent analysis on another crystal was carried out using data collected on a CAD-4 four circle diffractometer. The structure refined to $R = 0.0988$ for 3325 observed [$F > 5\delta(F)$] reflections and yielded essentially the same results.

Acknowledgements

tional atomic coordinates, thermal parameters and complete bond lengths and angles.

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