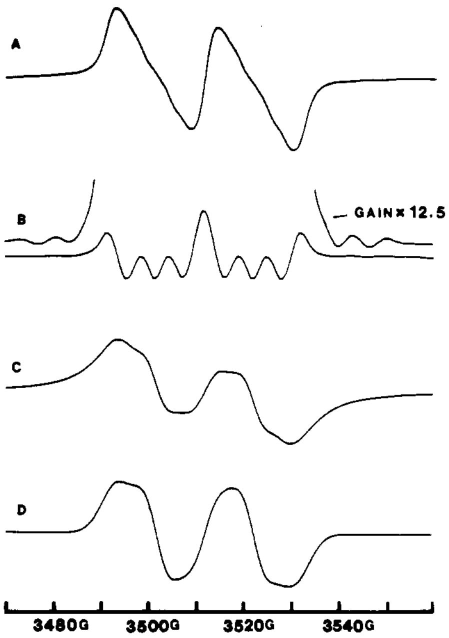

Figure 1. ESR spectra of $Cp_2Zr(CH_2C_6H_4\text{-}o\text{-}PPh_2)$: (a) experimental first-derivative spectrum; (b) experimental second-derivative spectrum showing ^{91}Zr satellites; (c) simulated first-derivative spectrum with Lorentzian line shapes and equal line widths; (d) simulated first-derivative spectrum with Gaussian line shapes and equal line widths.[19] An upper limit of about 10 G can be placed on the ^{91}Zr coupling constant. The ESR spectrum of this solution was also examined at 120 K. The frozen-solution spectrum showed the **g**-tensor anisotropy (1.938, 1.988, 2.001) expected for a $4d^1$ system, but no trace of hyperfine coupling was detectable.

In order to just lose resolution of a 1:2:1 triplet in a first-derivative spectrum, the Lorentzian component line width must be about 1.5 times the triplet splitting.[19] However, a simulated spectrum with 9-G line widths (Figure 1C) is a very poor match to the experimental spectrum. In particular, the wings of the simulated spectrum are much too broad. Indeed, the wings of the experimental spectrum closely approximate a Gaussian line shape, suggesting that the shape of the component lines is due largely to unresolved hyperfine coupling, probably to the protons of the benzene rings. Although a simulation with Gaussian line shapes (Figure 1D) substantially improves the fit of the wings of the spectrum, the central portions of the 1:2:1 multiplets are poorly reproduced. It appears that the central features of the triplets have substantially greater width (and hence smaller amplitudes) than the outer features. Simulations with a variety of arbitrary unresolved hyperfine patterns and Lorentzian line shapes have convinced us of the general validity of this conclusion.

It is well-known that the coupling constant of a methylene proton adjacent to a radical center depends on the dihedral angle. Thus in general, the two coupling constants are modulated out of phase by a rotation about the bond. When essentially free rotation is permitted, as in the propyl radical, the couplings are rapidly averaged and a 1:2:1 hyperfine pattern is obtained. When rotation is very slow or is stopped, a doublet of doublets is expected and often only the larger coupling is resolved. In intermediate cases, a triplet pattern may be observed, but with the central feature broadened.[19] Examples of all three cases are found in the ESR spectra reported here. Thus in **8** and $Cp_2Zr(CH_2Ph)_2$,[18] the ligands are freely rotating with apparently equivalent methylene protons. In **9** and $Cp_2Ti(CH_2C_6H_4\text{-}o\text{-}NMe_2)$,[9] rotation is slow and only one coupling is observed. In **10**, the chelate ring is sufficiently fluxional that the methylene proton couplings are nearly averaged but with broadening of the central feature of the triplet.

Conclusions. Compounds of the type $Cp_2Zr(Cl)(CH_2C_6H_4\text{-}o\text{-}ER_2)$ have been obtained with $ER_2 = NMe_2$ and PPh_2. Despite their size and potential chelating ability through the P of the PPh_2 moiety, the PPh_2-containing species do not bind significantly to Zr through the P atom. In the case of the smaller ($CH_2C_6H_4\text{-}o\text{-}NMe_2$) ligand, two ligands can be attached to yield $Cp_2M(A)_2$ (M = Zr, Hf) compounds, but the larger ($CH_2C_6H_4\text{-}o\text{-}PPh_2$) does not form analogous $Cp_2M(B)_2$ compounds by our methods. Although the $Cp_2M(A)_2$ species are accessible, the kinetic properties of $Cp_2M(Cl)(A)$ (kinetic stability of the M–C bond) do not lead to scrambling to form mixtures of Cp_2MCl_2, $Cp_2M(Cl)(A)$, and $Cp_2M(A)_2$. Upon reduction with Na(Hg) or the naphthalenide ion, M(III) compounds are formed. In the case of Zr-containing compounds, $Cp_2Zr(A)_2^-$ forms with freely rotating ligands and equivalent methylene protons, while $Cp_2Zr(A)$ and $Cp_2Zr(B)$ form with slower chelate ring fluctionality.

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Registry No. **1**, 96454-39-6; **2**, 96454-40-9; **3**, 96454-41-0; **4**, 96454-42-1; **5**, 96454-43-2; **6**, 96454-44-3; **7**, 96454-45-4; **8**, 96454-46-5; **9**, 96454-47-6; **10**, 96454-48-7; Cp_2ZrCl_2, 1291-32-3; Cp_2HfCl_2, 12116-66-4; $LiCH_2C_6H_4\text{-}o\text{-}NMe_2$, 96454-49-8; $LiCH_2C_6H_4\text{-}o\text{-}PPh_2$, 52891-06-2.

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Synthesis and Crystal Structure of a Simple Mononuclear Lithium Complex. Tetraethylammonium Bis(1,2-bis(2-hydroxyphenyl)-1,3-propanedionato)lithate

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As a part of a program to investigate synthesis-directing ligands such as 1,3-bis(2-hydroxyphenyl)-1,3-propanedione ($bhppH_3$),[1,2] we found that reaction of the zinc complex $Zn(bhppH_2)_2\cdot 2CH_3OH$ with LiMeO surprisingly yielded a mononuclear lithium complex. Several lithium complexes have been reported in the literature. Most of them exhibit a dimeric or cluster structure.[3,4] A few are monomeric, but to our knowledge no one is as simple and symmetric as the one reported in this paper. We report here details of the isolation, characterization, and X-ray crystal structure of $NEt_4[Li(bhppH_2)_2]$. The need for bulky terminal groups in the β-diketone is believed to be necessary in order to get lithium complexation and isolation.

Experimental Section

Unless specifically mentioned, all operations were performed under nitrogen. Absolute ethanol and ethyl acetate were reagent grade and were used as received. Lithium methoxide/sodium methoxide had been prepared from lithium/sodium metal and methanol dried with magnesium. $Zn(bhppH_2)\cdot 2CH_3OH$[2] and $Zn(acac)_2\cdot H_2O$[5] were prepared by literature methods. Microanalyses (C, H, N) were performed in our analytical laboratory on a Perkin-Elmer 240-B, and lithium was determined by atomic absorption on a Perkin-Elmer 370-A. ^1H NMR spectra were run on a Bruker WP.80SY.

Synthesis of $NEt_4[Li(bhppH_2)_2]$. A solution containing 1.98 mmol of LiMeO in ethanol (10 mL) was slowly added to a suspension of $Zn(bhppH_2)_2\cdot 2CH_3OH$ (0.2 g, 0.33 mmol) in ethanol (20 mL) at 0 °C.

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Table I. Atomic Coordinates ($\times 10^4$) in Crystalline $NEt_4[Li(bhppH_2)_2]$

atom	*x*	*y*	*z*
Li	2046 (14)	−1185 (12)	9773 (20)
O(1)	1940 (6)	−1130 (5)	11436 (8)
C(1)	1562 (8)	−1558 (7)	12129 (13)
C(2)	1106 (8)	−2121 (7)	11706 (11)
C(3)	1001 (7)	−2302 (7)	10477 (14)
O(3)	1336 (5)	−1960 (5)	9597 (8)
C(11)	1663 (6)	−1424 (5)	13475 (6)
C(12)	2231 (6)	−941 (5)	13884 (6)
C(13)	2347 (6)	−820 (5)	15126 (6)
C(14)	1894 (6)	−1182 (5)	15959 (6)
C(15)	1326 (6)	−1665 (5)	15550 (6)
C(16)	1211 (6)	−1786 (5)	14309 (6)
O(12)	2688 (6)	−566 (5)	13125 (8)
O(4)	3106 (5)	−1211 (5)	9395 (9)
C(4)	3491 (8)	−706 (8)	8921 (11)
C(5)	3178 (8)	−70 (7)	8440 (12)
C(6)	2375 (9)	85 (8)	8413 (11)
O(6)	1856 (5)	−355 (5)	8787 (8)
C(31)	488 (4)	−2915 (4)	10055 (9)
C(32)	375 (4)	−3061 (4)	8820 (9)
C(33)	−124 (4)	−3613 (4)	8444 (9)
C(34)	−510 (4)	−4019 (4)	9303 (9)
C(35)	−397 (4)	−3874 (4)	10538 (9)
C(36)	102 (4)	−3322 (4)	10914 (9)
O(32)	716 (5)	−2678 (5)	7954 (7)
C(41)	4366 (5)	−793 (6)	8987 (9)
C(42)	4676 (5)	−1336 (6)	9729 (9)
C(43)	5476 (5)	−1414 (6)	9864 (9)
C(44)	5968 (5)	−948 (6)	9258 (9)
C(45)	5659 (5)	−405 (6)	8517 (9)
C(46)	4858 (5)	−327 (6)	8381 (9)
O(42)	4227 (6)	−1811 (5)	10340 (9)
C(61)	2071 (7)	806 (4)	7964 (8)
C(62)	1275 (7)	885 (4)	7757 (8)
C(63)	972 (7)	1548 (4)	7385 (8)
C(64)	1465 (7)	2132 (4)	7220 (8)
C(65)	2261 (7)	2054 (4)	7427 (8)
C(66)	2563 (7)	1391 (4)	7799 (8)
O(62)	758 (5)	343 (6)	7879 (11)
N	1341 (4)	1330 (4)	2525 (7)
C(101)	757 (6)	1334 (6)	3493 (10)
C(102)	640 (6)	624 (6)	4153 (10)
C(103)	2138 (7)	1124 (6)	3129 (11)
C(104)	2430 (7)	1540 (9)	4227 (14)
C(105)	1364 (6)	2081 (5)	2034 (9)
C(106)	1905 (6)	2186 (5)	992 (10)
C(107)	1137 (7)	782 (5)	1541 (11)
C(108)	371 (7)	972 (7)	885 (12)

After complete solubilization, NEt_4Cl (0.4 g, 0.62 mmol) was added and the resulting clear solution was stirred for an additional 1-h period. All subsequent operations were carried out in an open vessel. Water was added until complete precipitation of a yellowish solid, which was filtered and washed with water and ether. The crude solid was extracted into boiling ethyl acetate (70 mL) containing a few drops of THF, and the resulting yellow solution was filtered. The volume was reduced to 20 mL with heating. Single crystals were obtained from the slow evaporation of the solution at room temperature. These were collected, washed with cold ethyl acetate and ether, and stored in a desiccator: yield 0.184 g, 86.2% based on $Zn(bhppH_2)_2 \cdot 2CH_3OH$; IR (KBr plates) selected absorptions ν(OH) 3300–3600, ν(CO) 1510–1515 cm^{-1}; ^1H NMR[6] 1.1 (t, 12, NCH_2CH_3), 3.15 (q, 8, NCH_2CH_3), 6.5–8 (m, 18, Ph and =CH), 14.8 ppm (s, 4, PhO*H*) in $Me_2SO\text{-}d_6$ at ambient temperature referenced to internal Me_4Si (δ 0.0). Anal. Calcd for $C_{38}H_{42}NO_8Li$: C, 70.49; H, 6.49; N, 2.16; Li, 1.07. Found: C, 70.56; H, 6.61; N, 2.22; Li, 1.11.

Table II. Principal Intramolecular Distances (Å) and Angles (deg) for $NEt_4[Li(bhppH_2)_2]$

(a) Distances

Li–O(1)	1.85 (2)	C(4)–C(5)	1.40 (2)
Li–O(3)	1.90 (2)	C(6)–C(5)	1.42 (2)
Li–O(4)	1.89 (3)	C(1)–C(11)	1.51 (2)
Li–O(6)	1.91 (2)	C(3)–C(31)	1.51 (1)
C(1)–O(1)	1.29 (2)	C(4)–C(41)	1.52 (1)
C(3)–O(3)	1.31 (2)	C(6)–C(61)	1.52 (2)
C(4)–O(4)	1.27 (2)	C(12)–O(12)	1.36 (1)
C(6)–O(6)	1.29 (2)	C(32)–O(32)	1.34 (1)
C(1)–C(2)	1.38 (2)	C(42)–O(42)	1.36 (1)
C(3)–C(2)	1.40 (2)	C(62)–O(62)	1.35 (1)

(b) Angles

O(1)–Li–O(3)	93 (1)	O(1)–C(1)–C(11)	116 (1)
O(1)–Li–O(4)	110 (1)	O(3)–C(3)–C(31)	114 (1)
O(3)–Li–O(4)	126 (1)	O(4)–C(4)–C(41)	116 (1)
O(1)–Li–O(6)	120 (1)	O(6)–C(6)–C(61)	115 (1)
O(4)–Li–O(6)	93 (1)	C(2)–C(1)–C(11)	120 (1)
O(3)–Li–O(6)	117 (1)	C(2)–C(3)–C(31)	122 (1)
C(1)–O(1)–Li	128 (1)	C(5)–C(4)–C(41)	119 (1)
C(3)–O(3)–Li	126 (1)	C(5)–C(6)–C(61)	121 (1)
C(4)–O(4)–Li	126 (1)	O(12)–C(12)–C(11)	123.2 (7)
C(6)–O(6)–Li	126 (1)	O(12)–C(12)–C(13)	116.8 (9)
O(1)–C(1)–C(2)	124 (1)	O(32)–C(32)–C(31)	122.7 (7)
O(3)–C(3)–C(2)	123 (1)	O(32)–C(32)–C(33)	117.3 (9)
O(4)–C(4)–C(5)	125 (1)	O(42)–C(42)–C(41)	122.9 (8)
O(6)–C(6)–C(5)	124 (1)	O(42)–C(42)–C(43)	117.1 (9)
C(1)–C(2)–C(3)	124 (1)	O(62)–C(62)–C(61)	123.8 (8)
C(4)–C(5)–C(6)	123 (1)	O(62)–C(62)–C(63)	116.2 (10)

Synthesis of $Na(bhppH_2) \cdot H_2O$. This compound was obtained by reacting $bhppH_3$ with NaMeO according to the synthesis procedure for making $NEt_4[Li(bhppH_2)_2]$. Anal. Calcd for $C_{15}H_{13}NaO_5$: C, 60.81; H, 4.39. Found: C, 60.45; H, 4.25.

Attempted Reaction of $Zn(acac)_2 \cdot H_2O$ with LiMeO. The reaction and workup conditions were the same as for the synthesis $NEt_4[Li(bhppH_2)_2]$. An examination of the proton NMR spectrum of the crude solid showed no resonances due to the NEt_4^+ cation.

X-ray Crystallography

A yellow prismatic crystal (0.1 × 0.1 × 0.2 mm) was selected and mounted on a Philips PW-1100 four-circle diffractometer. Unit-cell parameters were determined from automatic centering of 25 independent reflections and refining the orientation matrix by least-squares. Intensities were collected at room temperature with graphite-monochromatized Mo Kα radiation, by using the ω-scan technique, scan width 0.8°, and scan speed 0.03° s^{-1}; no significant intensity variation was observed in three standard reflections measured every 2 h as a control. A total of 2258 independent reflections were measured in the range $2 \leqslant \theta \leqslant 24.5°$; the ($hkl$) range was (±16,18,12); 2200 intensities were considered as observed by applying the condition $I \geqslant 2.5\sigma(I)$. Lorentz and polarization corrections were made, but none for absorption (μ(Mo Kα) = 0.9 cm^{-1}). Crystal data: formula $C_{30}H_{22}O_8Li \cdot C_8H_{20}N$, fw = 647.7, monoclinic, space group $P2_1/n$, a = 17.278 (4) Å, b = 18.571 (4) Å, c = 11.015 (3) Å, β = 91.62 (2)°, cell volume 3533 (2) $Å^3$, Z = 4, calculated density 1.22 g cm^{-3}.

The structure was solved by direct methods using the MULTAN system of computer programs.[7] An E map gave the localization of all non-hydrogen atoms. Refinements by full-matrix least-squares methods were carried out, by using the SHELX76 computer program.[8] The scattering factors and anomalous corrections were from ref 9. Benzene atoms were refined, assuming the benzene constraints in their localization. The function minimized was $w||F_o| - |F_c||^2$, where $w = (\sigma^2(F_o) + 0.00073|F_o|^2)^{-1}$. A difference synthesis revealed the positions of 39 hydrogen atoms (of 42), which were refined with an overall isotropic temperature factor; and the remaining atoms were refined anisotropically. The final R was 0.073 (R_w = 0.078). A final difference synthesis revealed peaks less than 0.2 e $Å^{-3}$.

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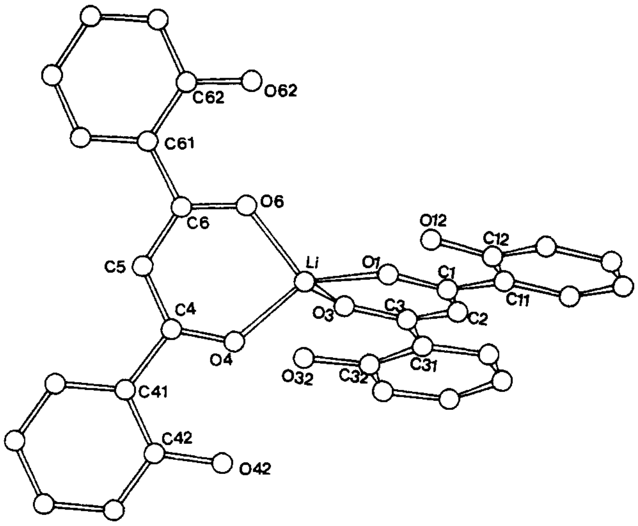

Figure 1. Perspective drawing of $[Li(bhppH_2)]^-$ showing the molecular structure and labeling scheme.

Positional parameters for the non-hydrogen atoms are given in Table I; selected bond distances and angles, in Table II; structure factors, positional parameters for hydrogen atoms, and anisotropic thermal parameters are available as supplementary material. The molecular geometry and labeling diagram are shown in Figure 1.

Results and Discussion

The interaction of $Zn(bhppH_2)_2 \cdot 2CH_3OH$ with 6 equiv of LiMeO in ethanol at 0 °C produces a yellowish homogeneous solution that, upon the addition of NEt_4Cl and a large excess of water, yields an amorphous solid. Purification of the solid was achieved by treatment with warm ethyl acetate. The insoluble residue was discarded. Cooling the warm solution to room temperature afforded yellow crystals that were suitable for X-ray diffraction studies. The compound is air stable.

Until recently, few well-characterized mononuclear lithium complexes where the only metal present is Li were known. Some of these complexes have at least one C–Li bond, examples are 2-lithio-2-phenyl-1,3-dithiane–tetrahydrofuran–tetramethylethylenediamine[10] and $Li[CH(SiMe_3)_2](pmdeta)$.[11] Others are not organometallic, but in them, lithium reaches tetrahedral coordination by means of different kind of ligands in a tridimensional arrangement. In most of them hydrogen bonds are involved. One example is lithium hydrogen acetylenedicarboxylate hydrate.[12] In this case the lithium is surrounded by four oxygen atoms from three anions and one water molecule. Another example is $(B15C5)Li(picrate) \cdot 2H_2O$[13] (B15C5 = benzo-15-crown-5). In it the cation is coordinated by two oxygen atoms from the chelating picrate anion and two water molecules. Surprisingly, the crown ether molecule is not bound to the Li ion but to water molecules through weak hydrogen bonds. To our knowledge there is no structural information about a discrete molecular complex as simple as the one presented in this paper, where the tetrahedral coordination around the Li ion is achieved by donor atoms from two identical bidentate $(bhppH_2)$ molecules. There was more information about these kind of compounds in solution where a few complexes of the type 1:2 Li:L (e.g., L = dipivaloylethane, diisobutyrylmethane)[14] had been described.

The structure of $NEt_4[Li(bhppH_2)_2]$ as revealed by X-ray crystallography shows a Li atom surrounded by four oxygen atoms in a distorted tetrahedral geometry where the 1,3-bis(2-hydroxyphenyl)-1,3-propanedionate ligand acts in a bidentate fashion. The Li–propanedionate rings adopt a half-chair form with Li deviating 0.10 (2) and 0.31 (2) Å from the mean plane defined by the propanedionate moiety. The most planar ring shows the shorter Li–O bond distances while the dihedral angle between the two ring planes is equal to 99 (1)°. The phenyl rings linked to C(1), C(3), C(4), and C(6) atoms are twisted by 10, 11, 12, and 13°, respectively with regard to the plane defined by the β-diketone moiety. These twistings and the $C(sp^2)$–C(phenyl) bond distances (e.g., C(1)–C(11)) indicate that the electron delocalization of the propanedionate ring does not extend to the phenyl rings. The hydroxy groups are hydrogen bonded to the adjacent metal-coordinated O atoms $O(1) \cdots O(12)$, $O(3) \cdots O(32)$, $O(4) \cdots O(42)$, and $O(6) \cdots O(62)$ with distances equal to 2.47 (1), 2.47 (1), 2.44 (1), and 2.48 (1) Å, respectively). The Li–O bond distances are all different with values 1.85 (2), 1.90 (2), 1.89 (2), and 1.91 (2) Å (average value 1.885 (5) Å). This large Li–O bond distance is very similar to the value 1.99 (9) Å (average) found in LiSiONα[12] or 1.97 (5) Å found in 2-lithio-2-phenyl-1,3-dithiane–tetrahydrofuran–tetramethylethylene, precluding, consequently, the possibility of aromatic character in the six-membered β-diketonate chelate ring. On the other hand, the $C\overset{\cdots}{-}O$ distances of 1.29 (4) Å (average) found in this $NEt_4[Li(bhppH_2)_2]$ complex are similar to these observed in $Zn(bhppH_2) \cdot 2EtOH$ ($C\overset{\cdots}{-}O$ = 1.303 (13) Å). This close similarity is a clear indication of the lack of aromatic character in the Zn–β-diketone ring of $Zn(bhppH_2)_2 \cdot 2EtOH$.

The interaction of $Zn(bhppH_2)_2 \cdot 2EtOH$ with 6 equiv of NaMeO, in conditions similar to these described to get $NEt_4[Li(bhppH_2)_2]$ yielded $Na(bhppH_2) \cdot H_2O$, as evidenced by analysis and ^1H NMR.

Following a similar procedure, reaction of $Zn(acac)_2 \cdot H_2O$ with 6 equiv of LiMeO did not yield $NEt_4[Li(acac)_2]$. No further attempts were made to identify the nature of the resulting compounds.

These results in the solid state and others previously reported in solution for dipivaloylethane and diisobutyrylmethane[14] as complexing β-diketones show the great affinity of chelating agents of the type R″COCH(R′)COR″, where R′, R″ are bulky terminal groups, for the lithium ion. The affinity for Na^+ had been proven to decrease in solution for large β-diketones; e.g., the chelating tendency of dipivaloylethane for lithium was 1000 times greater than that for sodium.[15] As indicated earlier these results are in agreement with ours where $[Li(bhppH_2)_2]^-$ has been obtained but not $[Na(bhppH_2)_2]^-$.

Registry No. $NEt_4[Li(bhppH_2)_2]$, 96212-06-5; $Zn(bhppH_2)_2$, 93401-40-2; $Na(bhppH_2)$, 96212-07-6; $Zn(acac)_2$, 14024-63-6; LiMeO, 865-34-9.

Supplementary Material Available: Tables of structure factors, positional parameters for hydrogen atoms, and anisotropic thermal parameters (12 pages). Ordering information is given on any current masthead page.

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Symmetry Lowering in B_3H_9 and B_4H_{12}

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The usual symmetry assignments are D_{3h} for B_3H_9 and D_{4h} for B_4H_{12}, both of which are ring structures in which BH_2 groups are

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