If there are no strong ion-pairing interactions between the uncomplexed cation and its counterion, we may assume that the formation constant (and presumably the enthalpy of formation) for the crown ether complex is determined entirely by the competition between the solvent and the ligand for the cation. It is well known[12] that there are very large differences between the single ion enthalpies of transfer for different solvents. These differences are greatest between the small ions of highest charge density, Li^+ and Na^+, compared to the larger ions of the Ia series. It is therefore not surprising that the greatest apparent selectivity of crown ether toward large cations is found in H_2O and DMSO, the solvents in Table I, in which the smaller cations are most strongly (*i.e.*, selectively) solvated. In less polar media, such as THF or acetone, the specific fit of the cation in the crown ether cavity must play a greater role, since all cations are less strongly held to the solvent, and the selectivity factor between them is accordingly reduced.[13]

These results suggest, since ion selectivity depends on the solvent as well as the ligand, that the ability of macrocyclic ligands to specifically affect ion transport through membranes will vary considerably depending on their molecular environment within the membrane.

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(12) See, for example, G. Choux and R. L. Benoit, *J. Amer. Chem. Soc.*, **91**, 6221 (1969).

(13) K. H. Wong, G. Konizer, and J. Smid (*ibid.*, **92**, 666 (1970)) have also observed solvent effects on ion selectivity and interpreted them in a similar manner.

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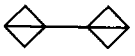
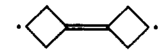
The Synthesis of 2,2,3,2′,2′,3′-Hexamethylbis(1-bicyclo[1.1.0]butyl). Conjugation in a Formally Saturated System[1]

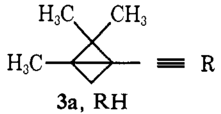
Sir:

The carbon–carbon bonds of bicyclobutane, particularly the central bond, have unusually high p character.[2] As a consequence, electronic interaction should be possible between the bicyclobutane orbitals and those of certain bridgehead substituents.[3,4] Thus, it appeared to us that bis(1-bicyclo[1.1.0]butyl) (**1**), a compound which has two bicyclobutane rings joined at bridgehead positions, although formally saturated, might show properties which could be considered to indicate conjugation. Increased stability relative to "isolated" bicyclobutanes need not be one such property since joining the rings in this manner offers enhanced possibilities for ring opening. For example, we estimate that while breaking the central bond of bicyclobutane to form a diradical is endothermic by *ca.* 41 kcal/mol, opening both central bonds of **1** to form **2** is endothermic by only *ca.* 25 kcal/mol.[5]


1


2

One approach to the synthesis of **1** is through the thermal or oxidative coupling of appropriate organometallic derivatives of bicyclobutane. However, the great sensitivity of the bicyclobutane ring[7] to numerous metal cations[8] makes the possibility of rearrangement a constant hazard. We elected to study derivatives of 1,2,2-trimethylbicyclobutane (**3a**), a readily available compound.[9]



3a, RH
3b, RD
3c, RLi
3d, RAg
3e, RCu
3f, R_2CuLi
3g, RCH_3

The lithium derivative **3c**[9a] reacted rapidly with 1 equiv of silver iodide in ether–pentane at −80° to give the insoluble silver derivative **3d**. This compound proved to be remarkably stable; it resisted all attempts to induce thermal coupling. No decomposition was noted over a period of several days at room temperature or several hours in refluxing benzene. Quenching with water resulted in the essentially quantitative recovery of **3a**; when deuterium oxide was used, the expected d_1 species, **3b**, was obtained. Employing tetrakis[iodo(tri-*n*-butylphosphine)silver(I)] to form **3d** (and apparently partially solubilize it) did not noticeably affect its stability. Thus **3d** does not behave like alkyl or alkenylsilver(I) compounds, which are thermally labile;[10] rather the striking stability of **3d** is reminiscent

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(1) Acknowledgment is made to the National Science Foundation for support of this research (GP 25216).

(2) (a) G. L. Closs and L. E. Closs, *J. Amer. Chem. Soc.*, **83**, 1003 (1961); **85**, 2022 (1963); (b) M. Pomerantz and E. W. Abrahamson, *ibid.*, **88**, 3970 (1966); (c) K. B. Wiberg, *Tetrahedron*, **24**, 1083 (1968).

(3) Bridgehead carbomethoxy, phenyl, and cyano groups lead to ultraviolet absorption at longer wavelengths than would be expected if the chromophore did not interact with the bicyclobutane ring: (a) K. B. Wiberg, G. M. Lampman, R. P. Ciula, D. S. Connor, P. Scherter, and J. Lavanish, *Tetrahedron*, **21**, 2749 (1965); (b) H. K. Hall, Jr., E. P. Blanchard, Jr., S. C. Cherkofsky, J. B. Sieja, and W. A. Sheppard, *J. Amer. Chem. Soc.*, **93**, 110 (1971); (c) H. K. Hall, Jr., C. D. Smith, E. P. Blanchard, Jr., S. C. Cherkofsky, and J. B. Sieja, *ibid.*, **93**, 121 (1971); (d) W. R. Moore and G. Astrologes, unpublished observations.

(4) Based on combustion data, a claim of stabilization for 1-cyanobicyclobutane has been made: H. K. Hall, Jr., and J. H. Baldt, *J. Amer. Chem. Soc.*, **93**, 140 (1971).

(5) These estimates are based on the heats of formation of bicyclobutane,[6a] cyclobutane,[6b] and methylenecyclobutane (estimated),[6c,d] the bond dissociation energy of a cyclobutyl–H bond,[6e] and the group parameters for calculating heats of formation of either Cox and Pilcher[6b] or Benson[6c,f] (which give slightly different absolute values, but essentially the same differences). These calculations do not include the possibility of stabilization of either the trimethylene[6g] obtained on opening bicyclobutane or **2**.

(6) (a) K. B. Wiberg and R. A. Fenoglio, *J. Amer. Chem. Soc.*, **90**, 3395 (1968); (b) J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds," Academic Press, London, 1970; (c) S. W. Benson, *et al.*, *Chem. Rev.*, **69**, 279 (1969); (d) R. B. Turner and R. H. Garner, *J. Amer. Chem. Soc.*, 80, 1424 (1958); (e) J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966); (f) S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968; (g) R. Hoffmann, *J. Amer. Chem. Soc.*, **90**, 1475 (1968).

(7) For a review of bicyclobutanes, see K. B. Wiberg, *Advan. Alicyclic Chem.*, **2**, 185 (1968).

(8) (a) L. A. Paquette, R. P. Henzel, and S. E. Wilson, *J. Amer. Chem. Soc.*, **93**, 2335 (1971), and preceding papers by L. A. P. cited therein; (b) P. G. Gassman, T. J. Atkins, and F. G. Williams, *ibid.*, **93**, 1812 (1971), and preceding papers by P. G. G. cited therein; (c) M. Sakai, H. Yamaguchi, H. H. Westberg, and S. Masamune, *ibid.*, **93**, 1043 (1971); (d) W. R. Moore and B. J. King, *J. Org. Chem.*, **36**, 1882 (1971).

(9) (a) W. R. Moore, K. G. Taylor, P. Müller, S. S. Hall, and Z. L. F. Gaibel, *Tetrahedron Lett.*, 2365 (1970); (b) L. Skattebøl, *ibid.*, 2361 (1970).

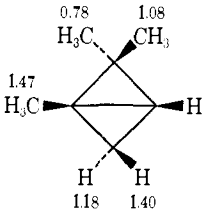
(10) (a) C. D. M. Beverwijk, G. J. M. van der Kerk, A. J. Leusink, and J. G. Noltes, *Organometal. Chem. Rev. A*, **5**, 215 (1970); (b) G. M. Whitesides, C. P. Casey, and J. K. Krieger, *J. Amer. Chem. Soc.*, **93**, 1379 (1971); (c) M. Tamura and J. Kochi, *ibid.*, **93**, 1483 (1971), and references cited in these three articles.

of the behavior of silver acetylides.[11] Also, note that the carbon–metal bonding has totally cancelled the pronounced catalytic effect of ionic silver[8a,d] in inducing rearrangement of the bicyclobutane system.

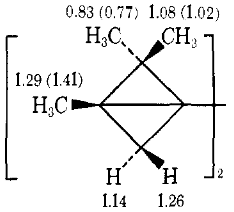
An attempt to couple **3a** by a modified version[12] of the Glaser method resulted in recovery of the starting material, probably because **3a** is not sufficiently acidic to undergo metalation under these conditions. Success was realized, however, with preformed copper reagents.

Oxidation of **3f** (as the tri-*n*-butylphosphine complex) with nitrobenzene at −78° gave a 62% yield of coupled product **4** along with a 33% recovery of **3a**.[13] Compound **4** was isolated as a colorless liquid by preparative glc and characterized as a $C_{14}H_{22}$ compound on the basis of its elemental analysis and mass spectrum.[14a] Stored under nitrogen, pure **4** appears to be quite stable; however, exposure to air does lead to decomposition.

As is indicated by the summary of assignments given with the accompanying formulas, the pmr spectrum of **4** is closely similar to that of **3a**[9a] but with each of the methyl singlets of the latter replaced by two singlets of unequal intensity;[14b] the methylene protons appear as narrow multiplets. This spectrum indicates that **4**

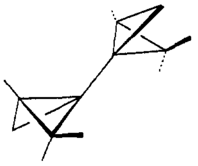


3a

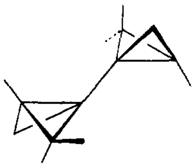


4

is a mixture of two stereoisomers, one exhibiting the more intense (δ 0.83, 1.08, 1.29) and the other the less intense (δ 0.77, 1.02, 1.41) methyl singlets. Molecular models suggest that these stereoisomers should exist mainly in the rotational conformations **4a** and **4b**.[14b]



4a



4b

In the *dl* isomer **4a** each bridgehead methyl group lies in the shielding region of an adjacent cyclopropane ring causing the signal (δ 1.29) to fall upfield from that (δ 1.41) in the meso isomer **4b**.

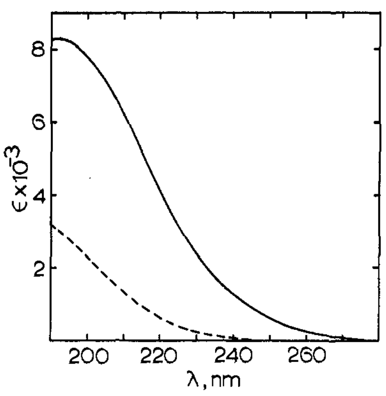
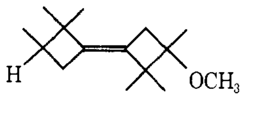


Figure 1. Ultraviolet absorption spectra of **3g** (– – –) and **4** (**4a**:**4b**, 10:1) (——) in pentane.

A lower yield of **4** and a correspondingly higher recovery of **3a** are obtained when the copper derivative **3e** is employed (as the phosphine complex). Utilizing oxygen as the oxidant with either **3e** or **3f** gives essentially the same yields of **4** as are found with nitrobenzene, but no **3a** is recovered. Heterogeneous coupling of **3e** and **3f** (both are insoluble in the absence of the phosphine) succeeds with either nitrobenzene or oxygen as the oxidant, but again lower yields of **4** are found. However, these conditions lead to an increase in the amount of the meso isomer formed. Although **3e** and **3f** decompose slowly at 25° (judged by the decreasing recovery of **3a** in quenching) we have not detected any dimer **4** as a product.[15]

Bicyclobutanes devoid of the usual chromophores show only end absorption in the ultraviolet. However, comparison of the spectrum of the model monobicyclobutane **3g** with that of **4** (Figure 1) clearly shows that the absorption of the latter is shifted to significantly longer wavelengths—apparently peaking at *ca.* 190 nm.[16] We believe that this red shift provides spectroscopic evidence supporting the idea of bicyclobutane conjugation.[17]

As expected, **4** is highly reactive toward electrophilic reagents which, on the basis of preliminary results, appear to add in the conjugate sense. For example, methanol containing a trace of *p*-toluenesulfonic acid gives **5** (stereochemistry not determined).



5

Finally, it is noteworthy that interconversion of **4a** and **4b** does not occur at room temperature, nor have we detected interconversion when **4a**–**4b** is heated for a few hours at 115°.[18] This lack of interconversion indicates that the substituted diradical corresponding to **2** does not intervene, implying that there is a substantial

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[11] Heavy metal acetylides, *e.g.*, silver(I), copper(I), and mercury(II), are readily isolable although derivatives of acetylene itself are explosive. Unlike **3d**, such acetylides are not hydrolyzed by water; *cf.* R. F. Garwood, "Rodd's Chemistry of Carbon Compounds," 2nd ed, S. Coffey, Ed., Elsevier, Amsterdam, 1964, p 453.

[12] A. S. Hay, *J. Org. Chem.*, 27, 3320 (1962).

[13] A solution of 3c (1.00 mmol) in ether was added to a solution of tetrakis[iodo(tri-*n*-butylphosphine)copper(I)] (0.50 mequiv, 0.125 mmol) in tetrahydrofuran at −78° (transient yellow color) giving a colorless solution of **3f**. After 30 min (−78°), nitrobenzene (1.0 mmol) was added giving a red-brown solution. After 30 min (−78°) aqueous K_2CO_3 was added and 4 was extracted with pentane which was washed (7 times) with 10:1 methanol–water to remove polar materials. Glc analysis (75 × 0.2 cm, 5% Carbowax 600–5% KOH on Chromosorb P, 55°) showed **4**, t_r 0.77 (dodecane, internal standard 1.00). Short-path distillation (<1 mm, bath 50°) afforded pure **4**.

[14] (a) *Anal.* Found: C, 88.14; H, 11.79. Mass spectrum *m/e* 190 (M^+, 6% of base peak at *m/e* 41). (b) The **4a**:**4b** ratio has varied from about 10:1 to 2.5:1.

[15] Dimer **4** may not be stable under these conditions.

[16] (a) Cary Model 14 spectrophotometer (1-mm cells); (b) this conclusion is not changed even if ε is halved for **4** (giving a comparison of absorption for equal numbers of bicyclobutane rings).

[17] Samples of **4** having different ratios of the meso and *dl* isomers give similar curves, suggesting that absorption is not highly dependent upon the conformation (cisoid or transoid).

[18] At 115°, neat **4** has undergone some decomposition (∼25% in 2 days) to unidentified materials, but the **4a**:**4b** ratio has remained essentially constant. A more detailed thermal study is in progress.

"excess"[6f] of activation energy for opening.[19] An appreciable activation energy providing a barrier to opening will be of crucial importance when one attempts to put "stabilizing" substituents (other than alkyl groups) at the bridgehead positions of **1**. In any event, the coupling method described here should be applicable to other derivatives of **1**.[20]

[19] Thermochemical considerations[6b,c,e,f] make it clear that the bridgehead methyl groups of **4** should facilitate opening, *i.e.*, $\Delta H < 25$ kcal/mol.

[20] The potential of employing "cross-coupling" for placing substituents on a bicyclobutane ring will be discussed elsewhere.

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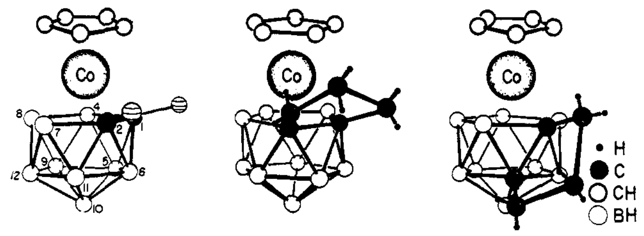
Received June 19, 1971

Novel Isomers of π-Cyclopentadienyl-π-(3)-1,2-dicarbollylcobalt(III)

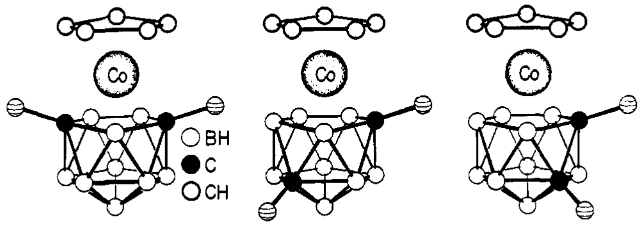
Sir:

Rearrangement of π-cyclopentadienyl-π-(3)-1,2-dicarbollylcobalt(III),[1] 1a (Figure 1), in the vapor phase at elevated temperatures (400–700°) led to excellent yields (87–93%) of six new isomers, **1b**–**1g**.[2] The complexes, isolated by preparative thin-layer chromatography,[3] result from the migration of the carbon atoms of the dicarbollyl ligand over the polyhedral surface.[4] **1b**–**1d** are formed at 400–500°, **1e**–**1g** at 600–700°.



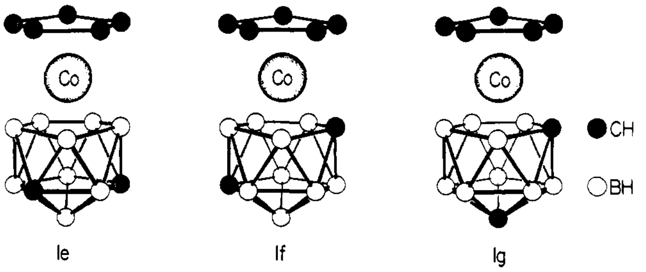
1a : ⊜ = H
2a : ⊜ = CH_3
3a
3d

Figure 1. Proposed structures of π-cyclopentadienyl-π-(3)-1,2-dicarbollylcobalt(III) (**1a**), π-cyclopentadienyl-π-(3)-1,2-dimethyl-1,2-dicarbollylcobalt(III) (**2a**), π-cyclopentadienyl-π-(3)-μ-1,2-trimethylene-1,2-dicarbollylcobalt(III) (**3a**), and π-cyclopentadienyl-π-(3)-μ-1,6-trimethylene-1,6-dicarbollylcobalt(III) (**3d**).



⊜ = H : **1b** **1c** **1d**
⊜ = CH_3 : **2b** **2c** **2d**

Figure 2. Proposed structures of isomers **1b**, **1c**, **1d**, **2b**, **2c**, and **2d** resulting from the rearrangement of $(\pi\text{-}C_5H_5)Co(\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_9R_2)$ (R = H, CH_3) at 400–500°.



1e **1f** **1g**

Figure 3. Proposed structures of isomers **1e**, **1f**, and **1g**, resulting from the rearrangement of $(\pi\text{-}C_5H_5)Co(\pi\text{-}1,11\text{-}B_9C_2H_{11})$ at 600–700°.

When $(\pi\text{-}C_5H_5)Co(\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_9(CH_3)_2)$ (**2a**) was sublimed through a hot tube (400–500°) packed with quartz wool, **2b**–**2d** were obtained. Rearrangement of $(\pi\text{-}C_5H_5)Co(\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_9(CH_2)_3)$[5] (**3a**) at 500°, on the other hand, gave only **3d**, mp 197–198°. *Anal.* Calcd for $B_9C_{10}H_{20}Co$: B, 32.80; C, 40.54; H, 6.79; Co, 19.85. Found: B, 32.55; C, 40.69; H, 6.61; Co, 19.85. The mass spectrum showed a cutoff at *m/e* 298 ($^{11}B_9{}^{12}C_{10}{}^{1}H_{20}{}^{59}Co^+$). Owing to the presence of the trimethylene linkage in **3a**, the ligand carbon atoms are forced to remain in adjacent or ortho positions,[5,6] thereby prohibiting any 1,7 or 1,11 rearrangements. There are at least four distinct resonances of area 1 in the 80.5-MHz ^{11}B spectrum of **3d** (six doublets in the ratio 1:3:1:1:1:2, acetone-d_6); consequently, the complex is of C_1 symmetry[7] and the most plausible

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[1] M. F. Hawthorne, D. C. Young, T. D. Andrews, D. V. Howe, R. L. Pilling, A. D. Pitts, M. Reintjes, L. F. Warren, and P. A. Wegner, *J. Amer. Chem. Soc.*, **90**, 879 (1968).

[2] **1b**, **1c**, **1e**, and **1f** gave satisfactory elemental analyses; **1d** was analyzed as a 1:1 mixture with **1b**; no analysis was carried out on the small amount of **1g** obtained. All seven isomers manifested a mass spectral cutoff at *m/e* 258 ($^{11}B_9{}^{12}C_7{}^{1}H_{16}{}^{59}Co^+$), and the cyclic voltammograms exhibited reversible one-electron waves (*vide infra*). Each ^1H nmr spectrum (acetone-d_6) showed a sharp singlet in the δ 5.3–5.9 region (5 H, cyclopentadienide C–H), and either one broad singlet (2 H, dicarbollyl C–H) or two singlets (each 1 H, dicarbollyl C–H) in the δ 2.3–3.9 region.

[3] The order of chromatographic elution on silica gel using hexane–benzene mixtures is **1a** < **1b** ≤ **1d** < **1c** < **1g** ≤ **1f** < **1e**, with R_f increasing left to right.

[4] In principle, the possible interconversions of the isomeric $(\pi\text{-}C_5H_5)Co(\pi\text{-}(3)\text{-}B_9C_2H_{11})$ complexes by Lipscomb's dsd (diamond–square–diamond) mechanism (W. N. Lipscomb, *Science*, **153**, 373 (1966), and references cited therein) are as follows

$$\begin{tikzcd}
1,2 \arrow[r, shift left] \arrow[r, leftarrow, shift right] \arrow[d, shift left] \arrow[d, leftarrow, shift right] & 1,6 \arrow[r, shift left] \arrow[r, leftarrow, shift right] & 5,6 \arrow[d, shift left] \arrow[d, leftarrow, shift right] \\
1,7 \arrow[r, shift left] \arrow[r, leftarrow, shift right] & 1,11 \arrow[r, shift left] \arrow[r, leftarrow, shift right] & 5,11 \\
1,10 \arrow[r, shift left] \arrow[r, leftarrow, shift right] & 5,10 &
\end{tikzcd}$$

Interestingly, the 1,10, 5,10, and 1,12 complexes cannot be generated by this mechanism from the 1,2 isomer. On the other hand, all isomers can interconvert by rotation of B_2C triangular faces of the icosahedron (E. L. Muetterties and W. H. Knoth, "Polyhedral Boranes," Marcel Dekker, New York, N. Y., 1968, p 70) according to the following scheme

$$\begin{tikzcd}
 & 1,2 \arrow[rr, shift left] \arrow[rr, leftarrow, shift right] \arrow[dr, shift left] \arrow[dr, leftarrow, shift right] \arrow[ddl, shift left] \arrow[ddl, leftarrow, shift right] & & 1,7 \arrow[dl, shift left] \arrow[dl, leftarrow, shift right] \arrow[ddr, shift left] \arrow[ddr, leftarrow, shift right] & \\
 & & 1,11 \arrow[dll, shift left] \arrow[dll, leftarrow, shift right] \arrow[drr, shift left] \arrow[drr, leftarrow, shift right] \arrow[dd, shift left] \arrow[dd, leftarrow, shift right] \arrow[dddl, shift left] \arrow[dddl, leftarrow, shift right] \arrow[dddr, shift left] \arrow[dddr, leftarrow, shift right] & & \\
1,6 \arrow[drr, shift left] \arrow[drr, leftarrow, shift right] \arrow[ddr, shift left] \arrow[ddr, leftarrow, shift right] & & & & 1,12 \arrow[dll, shift left] \arrow[dll, leftarrow, shift right] \arrow[ddl, shift left] \arrow[ddl, leftarrow, shift right] \\
 & & 1,10 \arrow[dd, shift left] \arrow[dd, leftarrow, shift right] & & \\
 & 5,6 \arrow[rr, shift left] \arrow[rr, leftarrow, shift right] \arrow[dr, shift left] \arrow[dr, leftarrow, shift right] & & 5,11 \arrow[dl, shift left] \arrow[dl, leftarrow, shift right] & \\
 & & 5,10 & &
\end{tikzcd}$$

Actually, the observed kinetically controlled isomeric interconversions may employ both the dsd and the triangular-face-rotation processes either in the icosahedron or in the cuboctahedral intermediate: H. D. Kaesz, R. Bau, H. A. Beall, and W. N. Lipscomb, *J. Amer. Chem. Soc.*, **89**, 4218 (1967).

[5] T. E. Paxson, M. K. Kaloustian, G. M. Tom, R. J. Wiersema, and M. F. Hawthorne, manuscript in preparation.

[6] L. F. Warren and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **92**, 1157 (1970).

[7] Isomers of **1a**, **2a**, and **3a** are either of C_1 (B atoms in the ratio of 1:1:1:1:1:1:1:1:1) or C_s symmetry (B atoms in the ratio 2:2:2:1:1:1 or 2:2:2:2:1).