"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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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°.

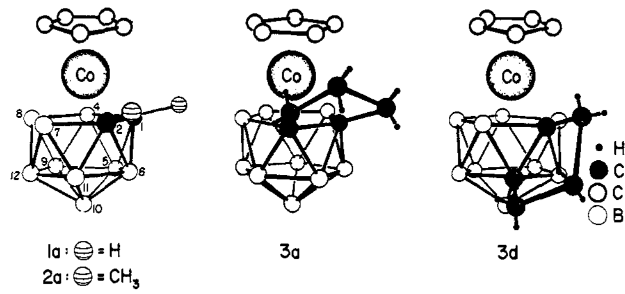

Figure 1. Proposed structures of π-cyclopentadienyl-π-(3)-1,2-dicarbollylcobalt(III) (**1a**), π-cyclopentadienyl-π-(3)-1,2-dimethyl-1,2-dicarbollylcobalt(III) (**2a**), π-cyclopentadienyl-π-(3)-μ-1,2-trimethylene-1,2-dicarbollylcobalt(III) (**3a**), and π-cyclopentadienyl-π-(3)-μ-1,6-trimethylene-1,6-dicarbollylcobalt(III)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

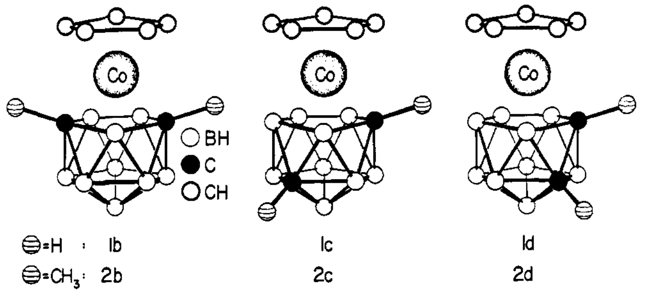

Figure 2. Proposed structures of isomers **1b**, **1c**, **1d**, **2b**, **2c**, and **2d** resulting from the rearrangement of $(\pi\text{-}C_5H_5)Co(\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_9R_2)$ (R = H, CH_3) at 400–500°.

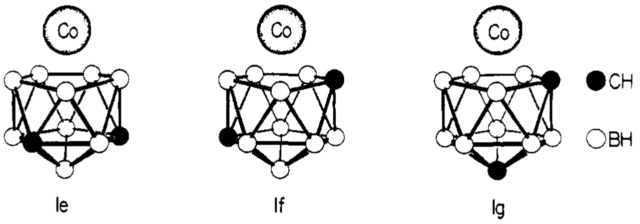

Figure 3. Proposed structures of isomers **1e**, **1f**, and **1g**, resulting from the rearrangement of $(\pi\text{-}C_5H_5)Co(\pi\text{-}1,11\text{-}B_9C_2H_{11})$ at 600–700°.

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).

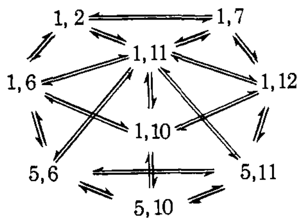
(2) **1b**, **1c**, **1e**, and **1f** gave satisfactory elemental analyses; **1d** was analyzed as a 1:1 mixture with **1b**; no analysis was carried out on the small amount of **1g** obtained. All seven isomers manifested a mass spectral cutoff at m/e 258 ($^{11}B_9{}^{12}C_7{}^{1}H_{16}{}^{59}Co^+$), 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 $\mathbf{1a} < \mathbf{1b} \leq \mathbf{1d} < \mathbf{1c} < \mathbf{1g} \leq \mathbf{1f} < \mathbf{1e}$, 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

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

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



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).

structure is that of the 1,6 isomer shown in Figure 1. **1d**, mp 146–148°, also belongs to point group C_1, since the high-resolution ^{11}B spectrum revealed nine unique B atoms. By correlation of R_f's of **1d** (R_f = 0.22), **2d** (R_f = 0.30), and **3d** (R_f = 0.32), the former two are assigned the structures in Figure 2.[8]

The 80.5-MHz ^{11}B spectrum of **1c**, mp 152–153°, also showed nine different B atoms. Models indicate that the only possible structure[7] is that of (π-C_5H_5)Co(π-(3)-1,11-$B_9C_2H_{11}$) (Figure 2).

The melting point, 239–239.5°, R_f (0.20), and ir and ^1H nmr spectra of **1b** were identical with those of authentic (π-C_5H_5)Co(π-(3)-1,7-$B_9C_2H_{11}$) synthesized from potassium (3)-1,7-dicarbadodecahydroundecaborate-(−1),[9] according to the method of Hawthorne, *et al.*[1] By correlation of R_f's, the structures of **2b** (R_f = 0.26) and **2c** (R_f = 0.53) follow.

^{11}B spectra of **1e**, mp 116–116.5°, showed six types of B atoms in the ratio 2:1:2:1:2:1, and in the 250-MHz ^1H nmr spectra one could discern only one type of dicarbollyl C–H. Of the two possible structures for **1e**, *viz.*, (π-C_5H_5)Co(π-(3)-5,6-$B_9C_2H_{11}$) and (π-C_5H_5)Co(π-(3)-5,11-$B_9C_2H_{11}$), we prefer the latter (Figure 3). **1e** is the first metallocarborane with *five B atoms in the π-bonding face.*

In the series **1a** → **1b** → **1c** → **1d** → **1e**, as the number of carbon atoms in the metal-bonding face decreases (two → zero), the complexes are reduced with greater difficulty and their λ_{max} values (d–d transitions) undergo a hypsochromic shift (Table I).

Table I. Reduction Potentials, R_f's, and Electronic Spectral Data for (π-C_5H_5)Co(π-(3)-$B_9C_2H_{11}$) Complexes

Compd	No. of C atoms in π-bonding face	R_f[a]	$E_{p/2}$ *vs.* sce[b] $M^{III} + e^- \rightarrow M^{II}$	λ_{max}, mμ (ϵ)[c]
1a	2	0.01	−1.22	426 (400)
1b	2	0.20	−1.03	414 (298)
1c	1	0.45	−1.33	402 (340)
1d	1	0.22	−1.39	404 (290)
1e	0	0.65	−1.75	386 (284)
1f	1	0.57	−1.42	408 (350)
1g	1	0.56	−1.44	414 (320)

[a] On E. Merck precoated silica gel F-254 (0.25 mm) on aluminum, eluting with hexane–benzene [1:1 (v/v)]. [b] In acetonitrile solution, 0.1 *M* $(C_2H_5)_4NClO_4$ as supporting electrolyte, Pt button electrode. [c] Acetonitrile solution.

On the basis of the above correlations, the ^{11}B spectra (each shows five doublets in the ratio 2:2:2:2:1), and the $E_{p/2}$ and λ_{max} values for **1f** and **1g** (Table I), we assign to **1f**, mp 159–159.5°, and **1g**, mp 128–130°, the structures having the 1,12 and 1,10 skeletal arrangements (Figure 3).[10] All the assignments will be discussed in detail in a forthcoming publication.

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[8] The R_f's of **1a**, **2a**, and **3a** vary in a parallel manner: R_f(**1a**) = 0.01, R_f(**2a**) = 0.14, R_f(**3a**) = 0.16.

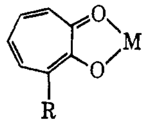
[9] M. F. Hawthorne, D. C. Young, P. M. Garrett, D. A. Owen, S. G. Schwerin, F. N. Tebbe, and P. A. Wegner, *J. Amer. Chem. Soc.*, **90**, 862 (1968).

[10] The alternative structure for **1g**, *viz.*, (π-C_5H_5)Co(π-(3)-5,10-$B_9C_2H_{11}$), cannot be rigorously excluded.

Stereochemically Nonrigid Cobalt(III) Complexes

Sir:

Rates of substitution and intramolecular rearrangement reactions of cobalt(III) complexes are slow compared to rates for complexes of other trivalent ions of the first transition series [excluding chromium(III)] and d^0 ions such as aluminum(III).[1] Neither tris(β-diketonato)cobalt(III) complexes[2–5] nor any other cobalt(III) chelates have been reported to exhibit exchange-broadened nmr spectra. The rearrangement rates of tris(β-diketonato)aluminum(III) complexes are faster and can be studied by nmr methods.[2,6–8] Noting that the rearrangement reactions of Al(α-C_3H_7T)$_3$[9,10] (**1**, R = C_3H_7) are considerably faster than those of aluminum β-diketonates[2,6–8] under comparable conditions, an investigation of rearrangements of complexes **1** with M = Al(III) and Co(III), R = C_3H_5 and *i*-C_3H_7, has been undertaken using variable-temperature pmr spectra.



1

α-Isopropenyl- and α-isopropyltropolone were synthesized by the method of Asao, *et al.*,[11] and their Al(III) and Co(III) complexes prepared and purified by standard procedures.[3,10,12] The spectrum of Al(α-C_3H_5T)$_3$ in 1,1,2,2-tetrachloroethane (*cf.* Figure 1) clearly reveals both cis (C) and trans (T) isomers below *ca.* 0°. Slow-exchange chemical shifts are 1.81–2.03 ppm downfield from TMS. From relative intensity measurements isomer distribution was found to be nonstatistical, with $\Delta F = -1.7 - 0.0027T$ and $K_{eq}(-24°) = 8.1$ for C $\rightleftharpoons$ T. The molecule undergoes intramolecular[13] C–T isomerization, resulting in simul-

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[1] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, Chapters 3 and 4.

[2] R. C. Fay and T. S. Piper, *Inorg. Chem.*, **3**, 348 (1964).

[3] J. G. Gordon, II, and R. H. Holm, *J. Amer. Chem. Soc.*, **92**, 5319 (1970).

[4] R. C. Fay, A. Y. Girgis, and U. Klabunde, *ibid.*, **92**, 7056 (1970).

[5] A. Y. Girgis and R. C. Fay, *ibid.*, **92**, 7061 (1970).

[6] J. J. Fortman and R. E. Sievers, *Inorg. Chem.*, **6**, 2022 (1967).

[7] B. Jurado and C. S. Springer, Jr., *Chem. Commun.*, 85 (1971).

[8] J. R. Hutchison, J. G. Gordon, II, and R. H. Holm, *Inorg. Chem.*, **10**, 1004 (1971).

[9] The following abbreviations of ligand anions are employed: α-C_3H_5T, α-isopropenyltropolonate; α-C_3H_7T, α-isopropyltropolonate.

[10] E. L. Muetterties and C. W. Alegranti, *J. Amer. Chem. Soc.*, **91**, 4420 (1969).

[11] T. Asao, T. Machiguchi, T. Kitamura, and Y. Kitahara, *Chem. Commun.*, 89 (1970); Y. Kitahara, private communication.

[12] All new compounds gave satisfactory elemental analyses.

[13] Rearrangement processes were shown to be intramolecular by examination of the pmr spectra of the following mixtures: M(α-C_3H_5T)$_3$ + M(α-C_3H_7T)$_3$, M(α-C_3H_5T)$_3$ + H(α-C_3H_5T), and M(α-C_3H_7T)$_3$ + H(α-C_3H_7T). In temperature intervals where signals of pure complexes were fully coalesced, separate resonances of mixed-ligand species or the free ligand were observed.