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 $(\pi\text{-}C_5H_5)Co(\pi\text{-}(3)\text{-}1,11\text{-}B_9C_2H_{11})$ (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 $(\pi\text{-}C_5H_5)Co(\pi\text{-}(3)\text{-}1,7\text{-}B_9C_2H_{11})$ 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.*, $(\pi\text{-}C_5H_5)Co(\pi\text{-}(3)\text{-}5,6\text{-}B_9C_2H_{11})$ and $(\pi\text{-}C_5H_5)Co(\pi\text{-}(3)\text{-}5,11\text{-}B_9C_2H_{11})$, 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 $\lambda_{max}$ values (d–d transitions) undergo a hypsochromic shift (Table I).

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

| Compd | No. of C atoms in π-bonding face | $R_f$[a] | $E_{p/2}$ *vs.* sce[b] $M^{III} + e^- \rightarrow M^{II}$ | $\lambda_{max}$, 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 $\lambda_{max}$ 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.

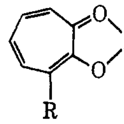
(9) M. F. Hawthorne, D. C. Young, P. M. Garrett, D. A. Owen, S. G. Schwerin, F. N. Tebbe, and P. A. Wegner, *J. Amer. Chem. Soc.*, **90**, 862 (1968).

(10) The alternative structure for **1g**, *viz.*, $(\pi\text{-}C_5H_5)Co(\pi\text{-}(3)\text{-}5,10\text{-}B_9C_2H_{11})$, 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 $Al(\alpha\text{-}C_3H_7T)$[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 $i\text{-}C_3H_7$, 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 $Al(\alpha\text{-}C_3H_5T)_3$ 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: $\alpha\text{-}C_3H_5T$, α-isopropenyltropolonate; $\alpha\text{-}C_3H_7T$, 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: $M(\alpha\text{-}C_3H_5T)_3 + M(\alpha\text{-}C_3H_7T)_3$, $M(\alpha\text{-}C_3H_5T)_3 + H(\alpha\text{-}C_3H_5T)$, and $M(\alpha\text{-}C_3H_7T)_3 + H(\alpha\text{-}C_3H_7T)$. In temperature intervals where signals of pure complexes were fully coalesced, separate resonances of mixed-ligand species or the free ligand were observed.

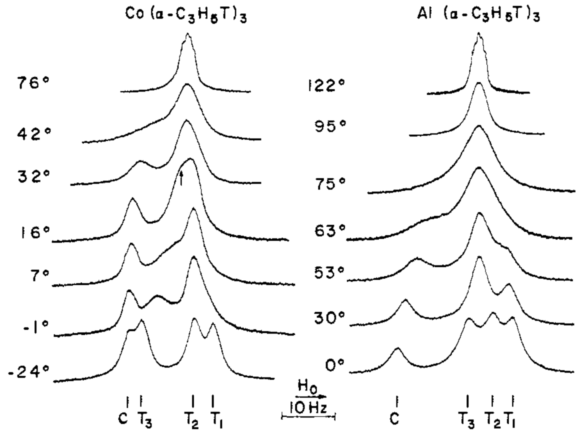

Figure 1. Methyl pmr spectra (100 MHz) of $Co(\alpha\text{-}C_3H_5T)_3$ in $CDCl_3$ and $Al(\alpha\text{-}C_3H_5T)_3$ in 1,1,2,2-tetrachloroethane. The arrow indicates the coalesced $T_1$ and $T_3$ signals.

taneous exchange broadening of all four resonances (C, $T_1$, $T_2$, $T_3$) and coalescence at higher temperatures to a single feature. Utilizing a total line-shape analysis,[8,14] methyl resonance averaging can be fit to a single kinetic process characterized by $\Delta H^{\ddagger} = 18.3 \pm 1.1$ kcal/mol, $\Delta S^{\ddagger} = 1.3 \pm 3.1$ eu, $E_a = 18.8 \pm 1.2$ kcal/mol, $\log A = 13.6 \pm 1.1$, and $k = 1/\tau = 0.4$ sec$^{-1}$ (25°). The simultaneous exchange of all four resonances is similar to the coalescence pattern of unsymmetrical Al(III) β-diketonates.[2,8]

The methyl spectrum of $Co(\alpha\text{-}C_3H_5T)_3$ in $CDCl_3$ below −20° shows the presence of C and T isomers, with $\Delta F = -0.8 \pm 3.0 \times 10^{-4}T$ and $K_{eq}$ (−24°) = 4.4. Slow-exchange chemical shifts are 1.79–1.93 ppm downfield from TMS. The pattern of line-shape changes at higher temperatures clearly proves that the molecule is stereochemically nonrigid on the pmr time scale.[15] Two essentially distinct kinetic processes are operative. In the low-temperature process (LTP, −20 to 20°), signals $T_1$ and $T_3$ exchange broaden and coalesce. At higher temperatures, all resonances broaden and average to a single resonance (HTP). By a total line-shape analysis the following kinetic parameters [LTP, HTP (T → C)] were obtained: $\Delta H^{\ddagger} = 16.2 \pm 1.1$, $16.5 \pm 1.1$ kcal/mol; $\Delta S^{\ddagger} = 5.4 \pm 3.9$, $-2.9 \pm 3.5$ eu; $E_a = 16.7 \pm 0.9$, $16.9 \pm 1.2$ kcal/mol, $\log A = 14.4 \pm 1.0$, $12.5 \pm 1.0$, $k(25°) = 100$, 1.5 sec$^{-1}$. Recent analyses of isomerization and inversion mechanisms for $M(A\text{-}B)_3$ complexes[3,8] show that the observed site interchange between two of the three inequivalent T sites without exchange with the C site (which has not been observed previously in $M(A\text{-}B)_3$ complexes) may be accommodated by a non-bond-rupture pathway traversed by a twist around the pseudo-threefold axis of the T isomer as illustrated in Figure 7 of ref 8. Inasmuch as this site interchange can be achieved[8] otherwise only by highly selective bond-rupture mechanisms in the T form with no simultaneous bond breaking in the C form, and cannot be accommodated by twists about imaginary $C_3$ axes of C and T, the p-$C_3$ or "trigonal" twist[16] is deduced to be the most probable mechanism for the LTP of *trans*-$Co(\alpha\text{-}C_3H_5T)_3$.

Both $Al(\alpha\text{-}C_3H_7T)_3$[10] and $Co(\alpha\text{-}C_3H_7T)_3$ have also been shown to be stereochemically nonrigid by similar experiments. The exchange-broadened methyl region of the latter occurs from −10 to 75° (100 MHz) in $CDCl_3$. A line-shape analysis[17] of the former complex in 1,1,2,2-tetrachloroethane indicates that below *ca.* 30° the C and T isomers invert by twists about the real and p-$C_3$ axes, respectively.

The above results reveal that Co(III) tropolonates invert *ca.* $10^{10}$ times faster than β-diketonates[2–5] at 25°. The physical basis for this remarkable rate enhancement and for the operation of a twist mechanism, presumably involving a trigonal-prismatic (TP) transition state, is not presently understood. Distortions from octahedral toward TP, found in $FeT_3$[18] and expected for $CoT_3$ and $AlT_3$, might facilitate rotations about the $C_3$ axes and enhance the probability of twist mechanisms. However, such distortion does not necessarily lead to stereochemical nonrigidity of Co(III) chelates on the pmr time scale.[19] An apparent correlation of distorted structures and inversion by a twist pathway has recently been found for $Fe(R_1R_2\text{-dtc})_2(S_2C_2R_2)$ complexes.[20]

**Acknowledgment.** This work was supported by NSF Grants No. GP-7576X and GP-18978X.

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[14] Chemical shifts were observed over a *ca.* 40° range in the slow-exchange region, plotted *vs.* temperature, and extrapolated through the intermediate-exchange region. Weighted averages of extrapolated shifts agreed well with experimental averages.

[15] A possible cause of this remarkable behavior could be electron-transfer catalysis of the intramolecular rearrangements by Co(II) impurity species. Although this possibility cannot be unequivocally disproven, it is considered improbable on the basis of the following observations: (i) line shapes at ambient temperature were the same for separate preparations of the complex and for varying degrees of purity; (ii) $Co(\alpha\text{-}C_3H_7T)_2$, prepared separately, is strongly absorbed on alumina and not eluted with chloroform, and therefore would be removed in the preparation of $Co(\alpha\text{-}RT)_3$; and (iii) methyl line shapes of $Co(\alpha\text{-}C_3H_5T)_3$ at 32° in $CDCl_3$ were unchanged by the addition of up to ~20 mol % $Co(\alpha\text{-}C_3H_7T)_2$.

(16) The trigonal twist is a conceptually simple but not unique way of describing the exchange pathway and produces different site interchanges than do the bond rupture processes analyzed elsewhere.[8]

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(19) See footnote 54 of ref 18.

(20) L. H. Pignolet, R. A. Lewis, and R. H. Holm, *J. Amer. Chem. Soc.*, **93**, 360 (1971); *Inorg. Chem.*, in press.

(21) NSF Predoctoral Fellow, 1969–1971.

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## Eupacunin, a Novel Antileukemic Sesquiterpene Lactone from *Eupatorium cuneifolium*[1,2]

*Sir:*

We wish to report on the isolation and structural elucidation of eupacunin (**1**), a novel germacranolide from *Eupatorium cuneifolium* (Tourn.) L.[3] Eupacunin has significant antileukemic and tumor inhibitory prop-

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(1) Tumor Inhibitors. LXVII. Part LXVI: S. M. Kupchan and A. J. Liepa, *Chem. Commun.*, 599 (1971).

(2) Supported by grants from the National Cancer Institute (CA-04500 and CA-11718), American Cancer Society (T-275), and Science Research Council, and a contract with Chemotherapy, National Cancer Institute (NIH 71-2099).

(3) Whole plant collected in Florida in 1966 and 1969. We thank Dr. Robert E. Perdue, Jr., USDA, Beltsville, Md., for supplying the plant material.