



Figure 2. Thermal interconversions of the  $(\text{CCF}_3)_6$  system.

Mass spectra (70 eV) of the four fluorocarbons are strikingly similar. In every case three peaks dominate the spectrum:  $m/e$  467 (loss of F), 417 (loss of  $\text{CF}_3$ ), and 69 ( $\text{CF}_3^+$ ). Though the base peak varies, the other two are always  $>50\%$  as intense. The parent peak increases in intensity from the prismane (4% of base) to the benzene (16% of base).

Highly strained fluorocarbons 1–3 appear to be the most stable (thermally) Dewar benzene,<sup>8</sup> benzvalene, and prismane<sup>9</sup> known at the present time. Steric effects are doubtless responsible in large measure for their impressive resistance to isomerization.<sup>1</sup> The Dewar benzene and benzvalene have half-lives at 234° of  $\sim 55$  and  $\sim 9$  min, respectively. It is interesting that their relative stability is opposite that found for the single other benzvalene–Dewar benzene pair which has been compared.<sup>10</sup> Haszeldine's group has reported that the prismane aromatizes at 170° at a rate intermediate between those of 1 and 2, but in our hands the major product from 3 was the Dewar isomer 1 ( $t_{1/2} \sim 7$  min at 234°).<sup>11</sup> All, or nearly all, of the benzene found could be accounted for by decomposition of 1 under the reaction conditions (see Figure 2).

Hexakis(trifluoromethyl)benzene is the first aromatic whose Dewar, benzvalene, and prismane isomers have all been obtained in pure form.<sup>14</sup> Thus these compounds provide a unique opportunity for studying the interrelationships of valence isomers of benzenes.

**Acknowledgments.** We wish to express our gratitude to Professor P. R. Shafer for valuable advice and for assistance with the  $^{19}\text{F}$  nmr work. Mr. David Cane of Harvard University kindly determined our mass spectra, and the National Science Foundation, the Petroleum Research Fund of the American Chemical Society, and the U. S. Army Research Office (Durham) provided generous financial support.

(8) The locked "Dewar" anthracene prepared by D. E. Applequist and R. Searle is excluded from consideration since its geometry prevents aromatization (*J. Amer. Chem. Soc.*, **86**, 1389 (1964)).

(9) Hexakis(pentafluoroethyl)prismane, comparable in stability to 3, is a possible exception.<sup>1</sup>

(10) H. G. Viehe, *Angew. Chem. Intern. Ed. Engl.*, **4**, 746 (1965).

(11) The other three prismanes whose thermal decomposition products have been reported give Dewar isomers,<sup>12</sup> exclusively in one case.<sup>13</sup>

(12) (a) K. E. Wilzbach and L. Kaplan, *J. Amer. Chem. Soc.*, **87**, 4004 (1965); D. M. Lemal and J. P. Lokensgard, *ibid.*, **88**, 5934 (1966); (b) W. Schäfer, R. Criegee, R. Askani, and H. Grüner, *Angew. Chem. Intern. Ed. Engl.*, **6**, 78 (1967).

(13) R. Criegee and R. Askani, *ibid.*, **5**, 519 (1966).

(14) In the tri-*t*-butyl and hexamethyl series all three ring systems have been found, but the prismane has not been obtained pure in the former nor the benzvalene in the latter series.<sup>12a</sup>

(15) Alfred P. Sloan Foundation Research Fellow, 1968–1970.

David M. Lemal,<sup>15</sup> James V. Staros, Volkhard Austel  
Department of Chemistry, Dartmouth College  
Hanover, New Hampshire 03755  
Received March 29, 1969

## The Absolute Configuration of the (–)-*cis*-Dichlorobis(ethylenediamine)ruthenium(III) Cation

Sir:

No ruthenium(III) complex has yet been assigned an absolute configuration. As a consequence of the resolutions<sup>1</sup> of both *cis*- $\text{RuCl}_2(\text{en})_2^+$  and *cis*- $\text{CoCl}_2(\text{en})_2^+$  with  $\text{Co}(\text{C}_2\text{O}_4)_2\text{en}^-$  we now show that the diastereoisomers (–)- $\text{RuCl}_2(\text{en})_2^+$ – $\text{Co}(\text{C}_2\text{O}_4)_2\text{en} \cdot \text{H}_2\text{O}$  and (+)  $\text{CoCl}_2(\text{en})_2^+$ – $\text{Co}(\text{C}_2\text{O}_4)_2\text{en} \cdot \text{H}_2\text{O}$  are isomorphous. (The signs refer to rotations in the sodium D line.) Making use of Jaeger's rule<sup>2</sup> relating configurations, as recently modified by Garbutt and Gillard,<sup>3</sup> the same absolute configuration can be assigned to both (–)- $\text{RuCl}_2(\text{en})_2^+$  and (+)- $\text{CoCl}_2(\text{en})_2^+$ . The configuration<sup>4</sup> of (+)- $\text{CoCl}_2(\text{en})_2^+$  has been related to the absolute  $D^*$  configuration of (+) $\text{Co}(\text{en})_3^{3+}$  so that (–)-*cis*- $\text{RuCl}_2(\text{en})_2^+$  is here given an absolute  $D^*$  configuration.

The diastereoisomer (–)- $\text{RuCl}_2(\text{en})_2^+$ –(–)- $\text{Co}(\text{C}_2\text{O}_4)_2\text{en} \cdot \text{H}_2\text{O}$  has already been described, but the mono- rather than the hemihydrate found previously was obtained.<sup>1</sup> The procedure for the Co(III) analog was as follows. Racemic  $\text{Na}[\text{Co}(\text{C}_2\text{O}_4)_2\text{en}]$  was prepared and resolved by known methods.<sup>5</sup> (–)- $\text{Na}[\text{Co}(\text{C}_2\text{O}_4)_2\text{en}] \cdot \text{H}_2\text{O}$  (0.21 g) in water (2 ml) was added to 0.37 g of ( $\pm$ )-*cis*- $[\text{CoCl}_2(\text{en})_2]\text{Cl}$  in water (8 ml) to give the purple diastereoisomer which was collected and washed with 50% ethanol. *Anal.* Calcd for  $\text{C}_{10}\text{H}_{28}\text{Cl}_2\text{N}_6\text{O}_9\text{Co}_2$ : C, 21.3; H, 4.6; N, 14.9. Found: C, 21.2; H, 4.5; N, 14.6. This diastereoisomer could be converted to (+)- $[\text{CoCl}_2(\text{en})_2]^+$  which had a molecular rotation of +2320 in the D line in good agreement with published values.<sup>6</sup> X-Ray data were obtained with Ni-filtered Cu  $K\alpha$  radiation. Bragg angles ( $\theta$ ) are given in Table I and confirm that the diastereoisomers are isomorphous.

Table I. Bragg angle Values for Ru(III) and Co(III) Diastereoisomers<sup>a</sup>

(+)- $\text{CoCl}_2(\text{en})_2^+$ –(–)- $\text{Co}(\text{C}_2\text{O}_4)_2\text{en} \cdot \text{H}_2\text{O}$		(–)- $\text{RuCl}_2(\text{en})_2^+$ –(–)- $\text{Co}(\text{C}_2\text{O}_4)_2\text{en} \cdot \text{H}_2\text{O}$	
6.80 s	11.53 m	6.80 m	11.45 m
7.20 w	12.39 w	7.18 m	12.35 m
7.70 vs	13.00 w	7.68 vs	12.90 w
8.30 m	13.90 s	8.28 m	13.80 m
8.84 m	14.60 w	8.90 m	14.60 m
9.15 m	18.00 w	9.10 w	17.92 w
9.60 m	18.60 w	9.64 m	18.50 w
10.60 s		10.60 s	

<sup>a</sup> s = strong, m = medium, w = weak.

**Acknowledgment.** A C.S.I.R.O. studentship to L. K. M. is gratefully acknowledged.

(1) J. A. Broomhead and L. A. P. Kane-Maguire, *J. Chem. Soc.*, **A**, 546 (1967).

(2) F. M. Jaeger, *Bull. Soc. Chim. France*, **4**, 1201 (1937).

(3) K. Garbutt and R. Gillard, *J. Chem. Soc.*, **A**, 802 (1966).

(4) R. D. Gillard and G. Wilkinson, *ibid.*, 1368 (1964).

(5) F. P. Dwyer, F. L. Garvan, and A. Shulman, *J. Amer. Chem. Soc.*, **81**, 290 (1959).

(6) J. P. Mathieu, *Compt. Rend.*, **199**, 278 (1934); **201**, 1183 (1935).

John A. Broomhead, Leon Kane-Maguire  
Chemistry Department, Australian National University  
Canberra, 2600, Australia  
Received February 10, 1969