Thermal Rearrangement of π-Cyclopentadienyl-π-dicarbollyl Derivatives of Cobalt

Moses K. Kaloustian, Richard J. Wiersema, and M. Frederick Hawthorne*

Contribution No. 2955 from the Department of Chemistry,
University of California, Los Angeles, California 90024.
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Abstract: Vapor-phase rearrangement of $(\pi\text{-}C_5H_5)Co[\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}]$ (**1a**), $(\pi\text{-}C_5H_5)Co[\pi\text{-}(3)\text{-}1,2\text{-}(CH_3)_2\text{-}1,2\text{-}B_9C_2H_9]$ (**2a**), and $(\pi\text{-}C_5H_5)Co[\pi\text{-}(3)\text{-}\mu\text{-}1,2\text{-}(CH_2)_3\text{-}1,2\text{-}B_9C_2H_9]$ (**3a**) at 400–700° yielded isomeric complexes **1b–g**, **2b–g**, **3d**, **3h**, and **3i**. These compounds incorporate all nine isomeric dicarbollyl ligands and are formed by the migration of the cage carbon atoms over the polyhedral surface. All isomers were separated by thick-layer chromatography and their structures determined on the basis of their chromatographic, electrochemical, and spectral (uv-visible, ^1H, and ^{11}B nmr) properties.

Polyhedral rearrangement of boranes, carboranes, and halocarboranes has been known for some time.[1] Interest in the rearrangement of metal complexes of the dicarbollyl ligand is of more recent origin. The first thermal rearrangement of dicarbollyl derivatives, *viz.* those of $[\pi\text{-}(3)\text{-}1,2\text{-}(CH_3)_2\text{-}1,2\text{-}B_9C_2H_9]_2Ni^{IV}$, $[\pi\text{-}(3)\text{-}1,2\text{-}B_9C_2H_{11}]_2Ni^{IV}$, and $[\pi\text{-}(3)\text{-}\mu\text{-}1,2\text{-}(CH_2)_3\text{-}1,2\text{-}B_9C_2H_9]_2Ni^{IV}$, were reported in 1970 by Warren and Hawthorne.[2] More recently, rearrangement of $3\text{-}MCH_2CH_3\text{-}1,2\text{-}B_9C_2H_{11}$ (M = Al, Ga)[3] and $3\text{-}Ge\text{-}1,2\text{-}B_9C_2H_{11}$[4] has been studied. In the rearrangement of these metallocarboranes, the 1,2-dicarbollyl moiety rearranges to the isomeric 1,7- and 1,6-dicarbollyl structures. Complexes with other isomeric dicarbollyl ligands were not observed. Since, at the present, only three (1,2, 1,7, and 1,12) of the possible nine dicarbollide ions can be obtained by the basic degradation of the parent $B_{10}C_2H_{12}$ carboranes[5] and there are no known synthetic pathways leading to the remaining dicarbollides, it was of interest to study the rearrangement of metallocarboranes to isomeric complexes incorporating the novel dicarbollyl ions. We now wish to report the detailed results of the thermal rearrangement of three monodicarbollyl complexes of cobalt: $(\pi\text{-}C_5H_5)Co(\pi\text{-}(3)\text{-}1,2\text{-}R_2\text{-}1,2\text{-}B_9C_2H_9)$, R = H (**1a**), R = CH_3 (**2a**), and $R_2 = (CH_2)_3$ (**3a**)[6,7] (Figure 1).

Results

The starting materials **1a**, **2a**, and **3a** were synthesized from the corresponding trimethylammonium 1,2-dicarbaundecaborate(−1) ions[5a,8] according to a modified procedure of Hawthorne, *et al.*[9] Sublimation of **1a** through a hot tube (400–500°) packed with glass wool led to varying amounts of isomeric $\mathrm{Co}H_2$ complexes, **1b–e**. Isolation and passage of **1c** through a tube packed with quartz wool at 600–700° produced, in addition to **1e**, two new isomers, **1f** and **1g**. Table I shows the effect of temperature on the isomer distribution in the rearrangement of **1a** and **1c**. Similarly, **2a** rearranged at 450–600° to give a mixture of isomeric complexes **2b–d**. At 650°, **2c** rearranged to give **2e–g**. Rearrangement of **3a** at 500° led to **3d** which at 600–650° rearranged to **3h** and **3i**.

Table I. Relative Amounts[a] of Isomeric $(\pi\text{-}C_5H_5)Co(\pi\text{-}(3)\text{-}B_9C_2H_{11})$ Complexes from the Rearrangement of **1a** and **1c**

T, °C	1a	1b	1c	1d	1e	1f	1g
		Rearrangement of 1a					
380	83	2	7	8			
410	45	11	27	17			
440	20	18	48	14			
470	4	24	64	5	3		
495	1	22	74	1	2		
		Rearrangement of 1c					
600		7	56		4	31	2
650		6	43		11	36	3
700		5	30		23	35	7

[a] By integration of cyclopentadienyl signals in the ^1H nmr spectra. The thermal instability of these compounds precluded thermolysis in a static system. The relative amounts of the various isomers, obtained under nonequilibrium conditions, reflect the preferred kinetic isomers and not necessarily the thermodynamically favored isomers.

Isomers of **1a** were separated by thick-layer chromatography on silica gel into five fractions using hexane–benzene as eluent.

$$\mathbf{1a} < \mathbf{1b} + \mathbf{1d} < \mathbf{1c} < \mathbf{1g} + \mathbf{1f} < \mathbf{1e}$$
$$\xrightarrow[\text{increasing } R_F]{}$$

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[1] For recent reviews see (a) E. L. Muetterties and W. H. Knoth, "Polyhedral Boranes," Marcel Dekker, New York, N. Y., 1968, pp 55–72; (b) R. N. Grimes, "Carboranes," Academic Press, New York, N. Y., 1970, pp 11–12, 156–161.

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

[3] D. A. T. Young, R. J. Wiersema, and M. F. Hawthorne, *ibid.*, **93**, 5687 (1971).

[4] T. Totani and M. F. Hawthorne, unpublished data.

[5] (a) M. F. Hawthorne, D. C. Young, P. M. Garrett, D. A. Owens, S. G. Schwerin, F. N. Tebbe, and P. A. Wegner, *J. Amer. Chem. Soc.*, **90**, 862 (1968); (b) D. A. Owen, private communication.

[6] For a preliminary account, see M. K. Kaloustian, R. J. Wiersema, and M. F. Hawthorne, *ibid.*, **93**, 4912 (1971).

[7] To simplify the nomenclature the following abbreviations are adopted here: $(\pi\text{-}C_5H_5)Co[\pi\text{-}(3)\text{-}B_9C_2H_{11}] \equiv \mathrm{Co}H_2$; $(\pi\text{-}C_5H_5)Co[\pi\text{-}(3)\text{-}(CH_3)_2\text{-}B_9C_2H_9] \equiv \mathrm{Co}Me_2$; $(\pi\text{-}C_5H_5)Co[\pi\text{-}(3)\text{-}\mu\text{-}(CH_2)_3\text{-}B_9C_2H_9] \equiv \mathrm{Co}TM$.

[8] T. E. Paxson, M. K. Kaloustian, G. M. Tom, R. J. Wiersema, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **94**, 4882 (1972).

[9] 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, *ibid.*, 90, 879 (1968).

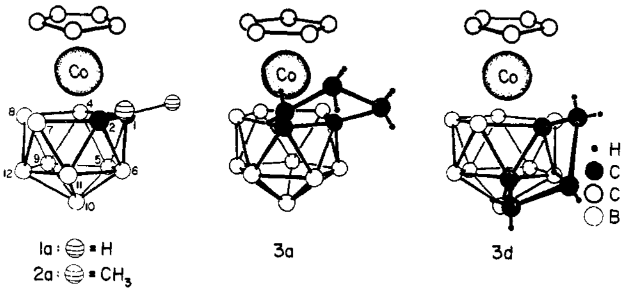

Figure 1. Proposed structures of π-cyclopentadienyl-π-(3)-1,2-dicarbollylcobalt(III) (**1a**), π-cyclopentadienyl-π-(3)-1,2-dimethyl-1,2-dicarbollylcobalt(III) (**2a**), π-cyclopentadienyl-π-(3)-μ-1,2-trimethylene-1,2-dicarbollylcobalt(III) (**3a**), and π-cyclopentadienyl-π-(3)-μ-1,6-trimethylene-1,6-dicarbollylcobalt(III)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

Isomers of **2a** were also separated into five fractions.

$$\mathbf{2a} < \mathbf{2b} + \mathbf{2d} < \mathbf{2c} < \mathbf{2g} + \mathbf{2f} < \mathbf{2e}$$

To separate **1b** from **1d**, **1g** from **1f**, **2b** from **2d**, and **2g** from **2f**, repeated elutions on thin-layer chromatograms (see Experimental Section) using hexane as eluent were carried out. The relative order of elution of the various complexes is as follows.

$$\mathbf{1b} < \mathbf{1d};\ \mathbf{1g} < \mathbf{1f};\ \mathbf{2b} < \mathbf{2d};\ \mathbf{2g} < \mathbf{2f}$$

Mixtures of **3a**, **3d**, **3h**, and **3i** were also separated by thick-layer chromatography also eluting with hexane.

All the $\mathrm{Co}H_2$, $\mathrm{Co}Me_2$, $\mathrm{Co}TM$ cobalt derivatives reported here are air-stable, yellow to orange compounds. Their R_f's, $E_{\mathrm{p}/2}$, and $\lambda_{\max}$ values are presented in Table II; the ^1H nmr data are given in Table III and the analytical data in Table IV. The infrared absorptions are listed in Table V. The 80.5-MHz ^{11}B spectra of the seven $\mathrm{Co}H_2$ complexes are shown in Figure 2 and the ^{11}B nmr data of the remaining complexes are given in Table VI.

Table II. R_f, $E_{\mathrm{p}/2}$, and $\lambda_{\max}$ Values of $\mathrm{Co}H_2$, $\mathrm{Co}Me_2$, and $\mathrm{Co}TM$ Complexes

	R_f[a]	$E_{\mathrm{p}/2}$, V[b]	$\lambda_{\max}$, mμ (log ε)[c]		
1a	0.01	−1.22	426 (2.60),	316 (3.35),	276 (4.52)
1b	0.20	−1.03	414 (2.47),	308 (3.37),	272 (4.47)
1c	0.45	−1.33	402 (2.53),	300 (3.34),	264 (4.50)
1d	0.22	−1.39	404 (2.46),	300 (3.41),	266 (4.43)
1e	0.65	−1.75	386 (2.45),	286 (3.34),	258 (4.58)
1f	0.57	−1.42	408 (2.54),	294 (3.35),	264 (4.57)
1g	0.56	−1.44	414 (2.51),	300 (3.42),	266 (4.42)
2a	0.14	−1.20	428 (2.75),	316 (3.38),	277 (5.47)
2b	0.26	−1.02	418[d]	323	281
2c	0.53	−1.38	406 (2.63),	308 (3.26),	265 (4.51)
2d	0.30	−1.40	410[d]	306	272
2e	0.69	−1.75	385 (2.50),	285 (3.30),	255 (4.61)
2f	0.61	−1.40	411 (2.64),	300 (3.28),	265 (4.61)
2g	0.58	−1.45	417[d]	308	272
3a	0.16	−1.14	440 (2.84),	320 (3.42),	281 (4.49)
3d	0.32	−1.43	402 (2.58),	306 (3.32),	266 (4.52)
3h	0.57	−1.70	386	292	256
3i	0.64	−1.80[e]	381[d]	290	263

[a] On E. Merck precoated silica gel F-25H (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 *vs.* sce. [c] In acetonitrile. [d] In cyclohexane. [e] At Hg electrode; remaining variables as in footnote *b*.

Discussion

A consideration of models indicates that there are nine possible isomeric dicarbollyl ligands (Figure 3); two of these, *viz.* the 1,6 and the 1,11, can exist as *dl* pairs. The dicarbollyl ions, and therefore the π-cyclopentadienylcobalt complexes derived from them, are either C_1 symmetry, *i.e.*, the boron atoms are in the ratio 1:1:1:1:1:1:1:1:1, or C_s symmetry, in which case the boron atoms are in the ratio of 2:2:2:1:1:1 or 2:2:2:2:1. The asymmetric 1,6 and 1,11 ligands and the corresponding $\mathrm{Co}H_2$ (and $\mathrm{Co}Me_2$) complexes have two types of carboranyl C–H's (C–CH_3's). The other seven isomers may have one type or two types of carboranyl C–H's (C–CH_3's) depending on the symmetry; thus the 1,2, 1,7, 5,6, and 5,11 isomers have one type of C–H (C–CH_3) whereas the 1,10, 1,12, and 5,10 complexes have two different C–H's (C–CH_3's). All of these complexes may have two, one, or no carbons in the open face of the icosahedral fragment. On the basis of the number of carbon atoms in the π-bonding face, and of the types of dicarbollyl C–H's (C–CH_3's) and B atoms, one can therefore group the $\mathrm{Co}H_2$ and $\mathrm{Co}Me_2$ isomers in five differentiable subsets (Table VII). The four $\mathrm{Co}TM$ complexes have the 1,2-, 1,6-, 5,6-, and 5,10-skeletal arrangements and belong to four of these five subsets. There is no unambiguous way of discerning the number of C atoms in the π-bonding face of the dicarbollyl ligands of the $\mathrm{Co}H_2$ and $\mathrm{Co}Me_2$ complexes; hence one cannot differentiate by ^{11}B and ^1H nmr spectroscopy between 1,10 and 1,12 on the one hand and 5,10 on the other; or, 1,2 and 1,7 *vs.* 5,6 and 5,11. In the $\mathrm{Co}TM$ series, it is the 1,2 and 5,6 isomers that cannot be differentiated by their proton or boron resonance spectra. However, further differentiation of these subsets is possible, indirectly, through correlation of R_f, $E_{\mathrm{p}/2}$, and $\lambda_{\max}$ values (*vide infra*). Within experimental error, the $E_{\mathrm{p}/2}$ values of the $\mathrm{Co}H_2$ are similar to the ones in the $\mathrm{Co}Me_2$ series (Figure 4) and the $\lambda_{\max}$

Table III. ^1H Chemical Shift Data of $\mathrm{Co}H_2$, $\mathrm{Co}Me_2$, and $\mathrm{Co}TM$ Complexes[a]

Compd	$C_5H_5^-$ (rel intensity)	Carboranyl substituent [H, CH_3, $(CH_2)_3$] (rel intensity)
1a	5.86 (5)	4.50 (2)
1b	5.90 (5)	2.90 (2)
1c	5.60 (5)	2.67 (1), 3.00 (1)
1d	5.58 (5)	3.27 (1), 3.85 (1)
1e	5.36 (5)	2.68 (2)
1f	5.63 (5)	2.34 (1), 3.04 (1)
1g	5.41 (5)	3.20 (1), 3175 (1)
2a	5.46 (5)	2.42 (6)
2b	5.46 (5)	1.60 (6)
2c	5.34 (5)	1.57 (3), 1.68 (3)
2d	5.35 (5)	1.88 (3), 2.03 (3)
2e	5.13 (5)	1.63 (6)
2f	5.35 (5)	1.25 (3), 1.43 (3)
2g	5.15 (5)	1.57 (3), 1.75 (3)
3a	5.53 (5)	2.63 (2), 2.83 (4)
3d	5.40 (5)	2.33 (6)
3h	5.26 (5)	2.33 (6)
3i	5.03 (5)	2.32 (6)

[a] Parts per million, downfield from TMS. $\mathrm{Co}H_2$ complexes **1a–g**, in acetone-d_6; $\mathrm{Co}Me_2$ and $\mathrm{Co}TM$ complexes in chloroform-*d*.

Table IV. Analytical Data for the Co*H*$_2$, Co*Me*$_2$, ad Co*TM* Isomers

Compound		Mp, °C	Calcd, % B	Calcd, % C	Calcd, % H	Calcd, % Co	Found, % B	Found, % C	Found, % H	Found, % Co
Co*H*$_2$	**1a**	246–248	37.94	32.79	6.29	22.98	37.89	33.01	6.14	22.88
	1b	239–239.5					37.61	32.60	6.25	22.84
	1c	152–153					38.03	33.63	6.66	21.24
	1d	146–148					37.80	33.32	6.36	21.66
	1e	116–116.5					37.82	33.39	6.44	21.64
	1f	159–159.5					37.91	33.50	6.46	21.64
	1g	128–130					*a*			
Co*Me*$_2$	**2a**	>267	34.20	37.99	7.08	20.71	34.15	37.81	6.93	20.81
	2b	240–242					*a*			
	2c	116–118					34.25	38.19	7.24	20.62
	2d	114–116					*a*			
	2e	84–85					*a*			
	2f	94.5–96					*a*			
	2g	115–116.5					*a*			
Co*TM*	**3a**	302–303.5	32.80	40.54	6.79	19.85	32.94	40.58	6.90	19.73
	3d	197–198					32.55	40.69	6.61	19.85
	3h	163–163.5					*a*			
	3i	130–132					*a*			

[a] Due to scarcity of samples molecular compositions were determined from the parent ion peak in mass spectra. All seven Co*H*$_2$ isomers manifested a mass spectral cutoff at *m/e* 258 which corresponds to the $^{11}B_9{}^{12}C_7{}^{1}H_{16}{}^{59}Co^+$ ion. All isomeric Co*Me*$_2$ had an *m/e* 286 ($^{11}B_9{}^{12}C_9{}^{1}H_{20}{}^{59}Co^+$), whereas the four Co*TM* complexes exhibited an *m/e* 298 ($^{11}B_9{}^{12}C_{10}{}^{1}H_{20}{}^{59}Co^+$).

(d–d transitions) values of **1a–g** correlate very well with those of **2a–g**. In addition, not only do the R_f's of members of the Co*H*$_2$ and Co*Me*$_2$ series vary in a parallel manner but there is a similarity of the high-field ^{11}B spectra as well (Figure 2 and Table VI). The correlation of $E_{p/2}$, λ_{max}, R_f values, and ^{11}B spectra of individual members of the **1a–g** series with those of the **2a–g** series strongly suggests that the Co*H*$_2$ complex has the same dicarbollyl skeleton as the corresponding member in the Co*Me*$_2$ series.

Table V. Infrared Spectra of the Co*H*$_2$, Co*Me*$_2$, and Co*TM* Isomers (Nujol Mulls)

Compound		Absorptions, cm^{-1}
Co*H*$_2$	**1a**	2540 (s), 1418 (m), 1193 (w), 1102 (s), 985 (m), 843 (s), 725 (m)
	1b	2575 (s), 1120 (m), 1045 (m), 1020 (m), 980 (m), 852 (s)
	1c (KBr)	2525 (s), 2526 (s), 1088 (m), 1040 (m), 1005 (m), 987 (w), 845 (s)
	1d	2540 (s), 1125 (m), 1042 (m), 1002 (m), 895 (m), 848 (s)
	1e	2620 (s), 2540 (s), 1060 (m), 1012 (s), 979 (m), 918 (m), 840 (s)
	1f	2590 (s), 975 (m), 892 (m), 840 (s)
	1g	2540 (s), 1120 (m), 940 (m), 840 (s)
Co*Me*$_2$	**2a**	2535 (s), 1012 (s), 855 (s)
	2c	2538 (s), 1004 (s), 938 (m), 912 (m), 888 (w), 849 (s)
	2e	2538 (s), 1190 (m), 995 (m), 932 (m), 920 (m), 839 (s)
	2f	2580 (s), 2540 (s), 1008 (s), 938 (m), 897 (m), 839 (s)
Co*TM*	**3a**	2520 (s), 1078 (m), 1011 (s), 880 (m), 851 (s)
	3d	2530 (s), 1010 (s), 898 (m), 871 (m), 840 (s)
	3h	2600 (s), 2550 (s), 1175 (m), 1009 (s), 844 (s)

Assignment of Structures

1a, 2a, 3a. These complexes (Figure 1) are thought to be isostructural with (π-C_5H_5)Fe[π-(3)-1,2-$B_9C_2H_{11}$], the "sandwich" structure[10] of which has been confirmed by a single-crystal X-ray diffraction study.[11]

1b, 2b. The R_f, infrared spectrum, and the melting point of **1b** were identical with those of authentic (π-C_5H_5)Co[π-(3)-1,7-$B_9C_2H_{11}$] (Figure 5) synthesized from potassium (3)-1,7-dicarbadodecahydroundecaborate(−1)[5a] according to the method of Hawthorne, *et al.*[9] The structure of **2b** follows from the above correlations.

Table VI. ^{11}B Chemical Shifts of Co*Me*$_2$ and Co*TM* Complexes[a]

2a	−4.9 (1), −0.8 (1), +8.9 (2), +19.7 (2), +28.5 (2), +31.01 (1)
2b	−3.6 (1), +1.4 (2), +8.7 (1), +24.1 (2), +25.5 (1), +28.5 (2)
2c	−0.6 (2), +2.4 (2), +8.3 (1), +19.9 (1), +26.3 (1), +28.1 (1), +30.2 (1)
2d	−5.6 (1), +3.8 (1), +7.9 (1), +9.7 (1), +11.7 (1), +21.1 (1), +27.4 (1), +27.9 (1), +32.4 (1)
2e	−1.6 (2), +1.9 (1), +2.5 (2), +3.9 (1), +11.7 (2), +12.9 (1)
2f	−0.3 (1), +1.6 (2), +3.3 (2), +12.9 (2), +14.7 (2)
2g	+0.3 (2), +2.0 (2), +9.6 (1), +13.7 (2), +16.7 (2)
3a[b]	−6.7 (1), −2.3 (1), +5.0 (2), +8.4 (2), +12.9 (3)
3d	−5.3 (1), −0.1 (3), +3.7 (1), +7.5 (1), +12.0 (1), +14.4 (2)
3h	−1.1 (2), −0.9 (1), +0.2 (1), +4.7 (2), +8.8 (1), +14.4 (2)
3i	−4.2 (1), −0.5 (2), +1.8 (2), +9.6 (2), +12.4 (2)

[a] Parts per million, relative to $BF_3 \cdot Et_2O$, chloroform-*d* solutions. [b] In acetone-d_6.

1c, 2c, 1d, 2d. Each of the 80.5-MHz ^{11}B spectra of **1c** and **1d** (Figure 2) showed nine different boron atoms. These compounds can have 1,11 and 1,6 arrangements (*vide supra*). It was shown previously[6] that **3d** has the structure in Figure 1. Since the R_f's of **1d** and **2d** (Table II) are similar to that of **3d** rather than to those

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(10) M. F. Hawthorne and R. L. Pilling, *J. Amer. Chem. Soc.*, **87**, 3987 (1965).

(11) A. Zalkin, D. H. Templeton, and T. E. Hopkins, *ibid.*, **87**, 3988 (1965).

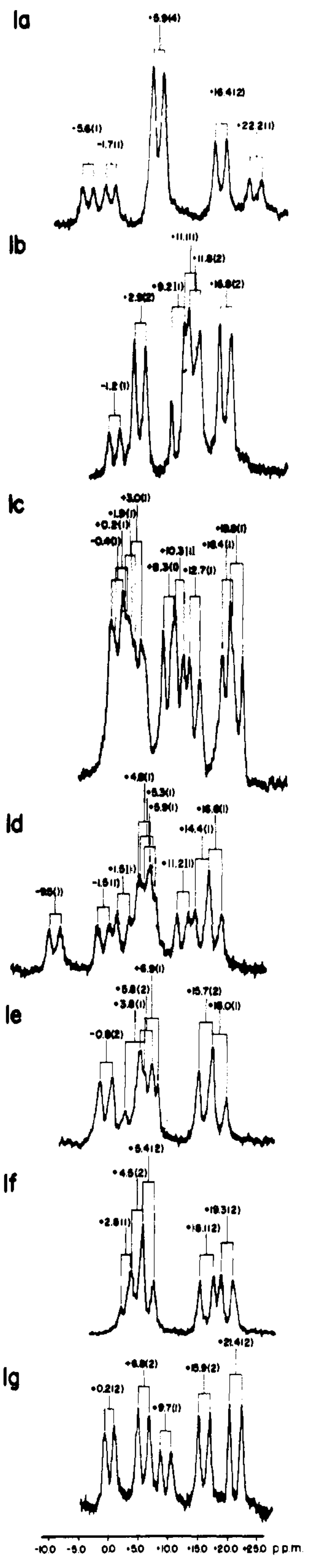

Figure 2. 80.5-MHz ^{11}B spectra of CoH_2 isomers **1a**-**g** in acetone-d_6.

of **1c** and **2c**, then **1d** and **2d** must be the 1,6 isomers.[12] Thus, by elimination, **1c** and **2c** must incorporate the 1,11-B_9C_2 framework. These assignments are reinforced by the observation that **1c** and **2c**, which are expected to be more stable than **1d** and **2d**, respectively, due to a greater separation of the electropositive carbon atoms of the 1,11-dicarbollyl ligand, become the predominant products of the rearrangement of **1a** and **2a** at *ca.* 600° (Table I). The proposed structures of these complexes are shown in Figures 1 and 5. Attempts at optical resolution of **1c** and **2c** by elution on various optically active absorbents were unsuccessful.

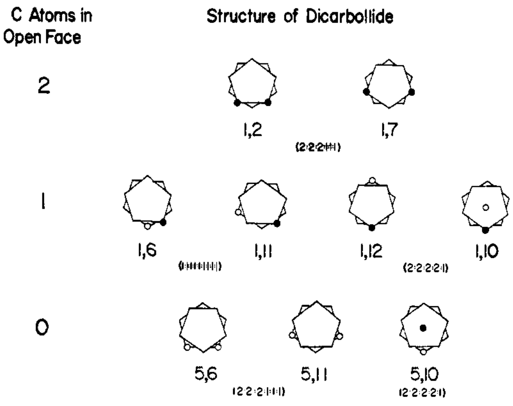

Figure 3. Projection formulas and relative ratios of boron atoms in the nine possible B_9C_2 skeletal arrangements.

Table VII. Classification of the CoH_2 and CoMe_2 Complexes

Isomers	Types of B's	Types of C–H or C–CH_3	No. of C atoms in π-bonding face
1,2 and 1,7	6	1	2
1,6 and 1,11	9	2	1
1,10 and 1,12	5	2	1
5,6 and 5,11	6	1	0
5,10	5	2	0

1e, 2e. The ^{11}B spectra of **1e** and **2e** showed six types of B atoms in the ratio of 2:1:2:1:2:1 (Figure 2, Table VI), and the ^1H nmr spectra revealed only one type of dicarbollyl C–H or C–CH_3 (Table III). According to Table VII, **1e** and **2e** have either the 5,6- or the 5,11-dicarbollyl ligands. Since **1e** (R_f = 0.65) moves faster than the 5,6-Co*TM* isomer (*vide infra*) **3h** (R_f = 0.57), it cannot be the 5,6 isomer. Consequently, **1e** and therefore **2e** (Figure 6) have the 5,11 structure. **1e** was reported to be the first metallocarborane with five boron atoms in the π-bonding face; **2e** is the analogous *dimethyl*dicarbollyl cobalt complex.[6]

1f, 1g, 2f, 2g. The $E_{p/2}$ values of **1a**–**e** and **2a**–**e** (Table II) can be correlated with the number of C atoms in the π-bonding face of the dicarbollyl fragments incorporated in these complexes. It appears that in the series **1a**, **1b** → **1c**, **1d** → **1e** and **2a**, **2b** → **2c**, **2d** → **2e**, as the number of metal bonding carbon atoms decreases (two → one → zero), the complexes are reduced with

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[12] The stepwise increase of R_f's 0.22 → 0.30 → 0.32 in the series **1d** → **2d** → **3d** is intelligible in terms of the enrichment of the dicarbollyl moiety by two methyl groups (**2d**) and the trimethylene group (**3d**), relative to two dicarbollyl C–H's (**1d**), and hence, the gradual increase in mobility with hexane–benzene. The same observation is true of the series of **1a** (R_f = 0.14) → **3a** (R_f = 0.16).

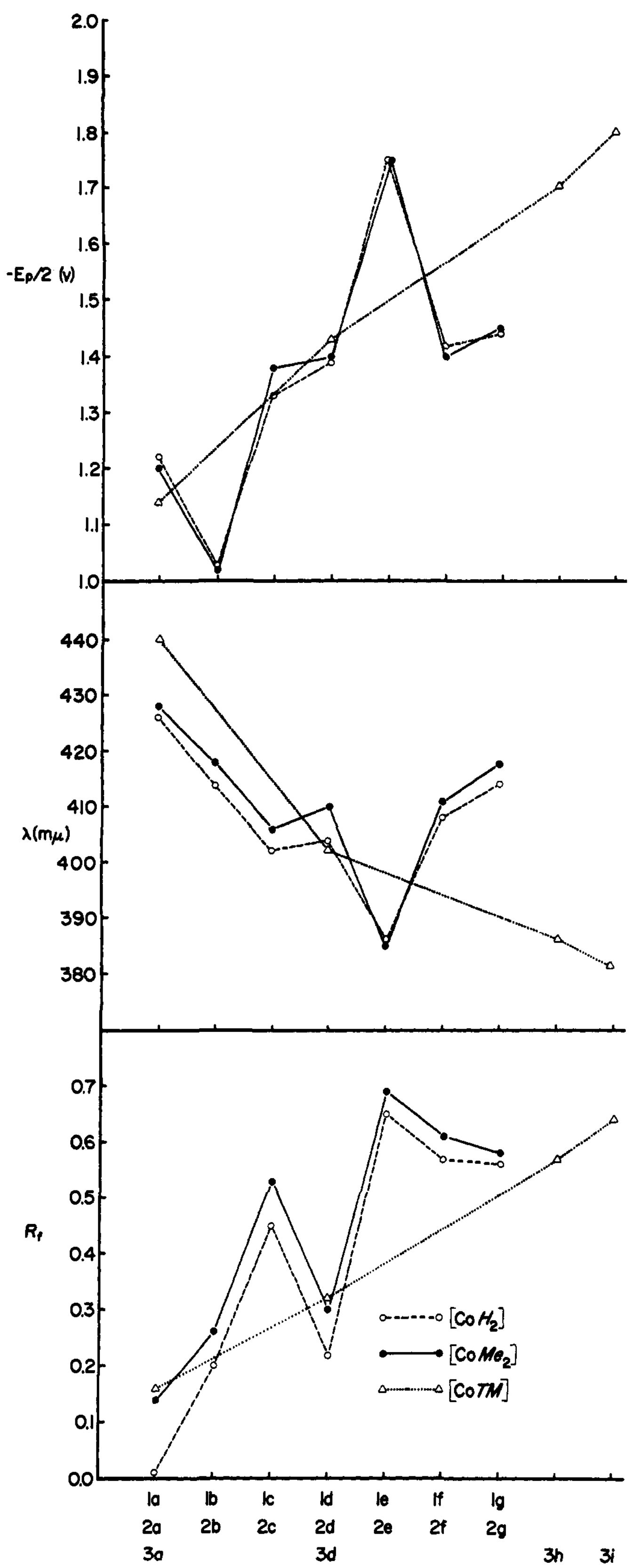

Figure 4. Correlations of $E_{p/2}$, λ_{max}, and R_f values of the CoH_2, $CoMe_2$, and $CoTM$ complexes.

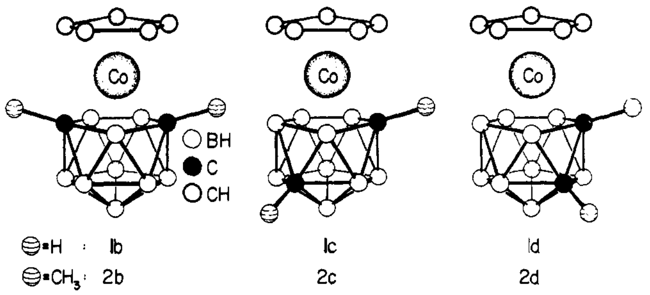

Figure 5. Proposed structures of isomers **1b–d** and **2b–d** resulting from the rearrangement of $(\pi\text{-}C_5H_5)Co(\pi\text{-}(3)\text{-}1,2\text{-}R_2\text{-}1,2\text{-}B_9C_2H_9)$ (R = H, CH_3) at 400–500°.

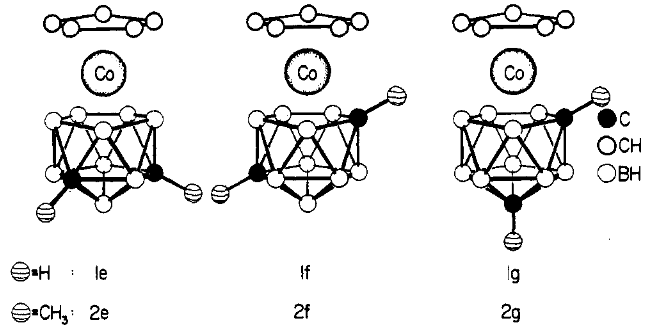

Figure 6. Proposed structures of isomers **1e–g** and **2e–g** resulting from the rearrangement of $(\pi\text{-}C_5H_5)Co(\pi\text{-}(3)\text{-}1,11\text{-}R_2\text{-}1,11\text{-}B_9C_2H_9)$ (R = H, CH_3) at 600–700°.

greater difficulty (−1.03, −1.22 → −1.33, −1.39 → −1.75). The similarity of $E_{p/2}$ of **1c** = −1.33 V) and **1d** (= −1.39 V), which have B_4C π-bonding faces, to those of **1f** and **1g** (= −1.42, −1.44 V, respectively) suggests that the latter two may also have B_4C π-bonding faces. The same argument applies to the $CoMe_2$ isomers **2f** and **2g**. On the basis of similar observations on the bisdicarbollyl complexes of nickel and palladium[2] and nickel(IV) complexes of $[1\text{-}(2)\text{-}B_{10}H_{10}\text{-}CH]^{3-}$, it has been suggested that "a B_4C bonding face donates more electron density to the metal atoms than the B_3C_2 face or that the former is superior to the latter in stabilizing the high formal oxidation state of 4+."[13] Our results are in agreement with this and indicate further that a B_5 face stabilizes a high positive charge (3+) even better than a B_4C open face.

In the series 1a → **1e** and 2a → **2e** the electronic spectra (Table II, Figure 4) reveal a gradual hypsochromic shift of the λ_{max} values (414–426 → 402–404 → 386) as the corresponding π-bonding faces change in the order $B_3C_2 \rightarrow B_4C \rightarrow B_5$. The similarity of the λ_{max} (d–d region) values of **1f** and **1g** (Table II) to those of **1c** and **1d** (B_4C faces) are in accordance with the above correlation of the $E_{p/2}$ values with the number of π-bonding dicarbollyl carbon atoms of the various isomers.

In view of the above correlations it is not unreasonable to assume that **1f**, **1g**, and hence **2f**, **2g**, all have one carbon atom in their metal bonding faces. These four complexes, therefore, do not have the 5,10 framework with a B_5 face. Since the ^{11}B spectra of **1f** and **1g** revealed nine borons in the ratio of 2:2:2:2:1, these complexes must have the 1,10- and 1,12-skeletal arrangements. Other things being equal, the 1,12-CoH_2 and

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(13) (a) D. E. Hyatt, J. L. Little, J. T. Moran, F. R. Scholer, and L. J. Todd, *J. Amer. Chem. Soc.*, **89**, 3342 (1967); (b) W. H. Knoth, *ibid.*, **89**, 3342 (1967).

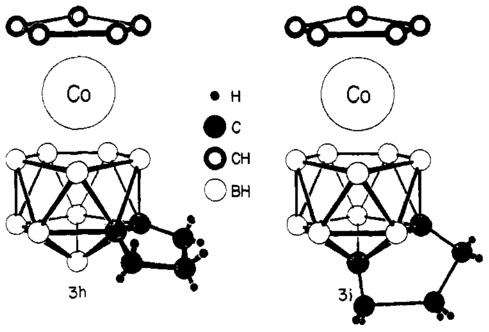


Figure 7. Proposed structures of Co*TM* isomers **3h** and **3i** resulting from the rearrangement of π-cyclopentadienyl-π-(3)-μ-1,6-trimethylene-1,6-dicarbollylcobalt(III) (**3d**).

-Co*Me*$_2$ complexes would be expected to be less polar (higher R_f) than the respective 1,10 complexes. The structural assignments of **1f**, **1g**, **2f**, and **2g** were made on the basis of the observed R_f's; *i.e.*, the ones with the greater R_f's (**1f** and **2f**, Table II) were assigned the structures. The synthesis of authentic $(\pi\text{-C}_5\text{H}_5)\text{Co}(\pi\text{-(3)-1,12-R}_2\text{-1,12-B}_9\text{C}_2\text{H}_9)$ (R = H, CH$_3$) from 1,12-$\text{B}_9\text{C}_2\text{H}_{11}{}^{2-}$ would enable the unambiguous differentiation between the 1,10 and 1,12 isomers.

3h, 3i. In addition to **3a** and **3d** there are only two Co*TM* complexes: the 5,6 and 5,10 structures. The structural assignments (Figure 7) of **3h** and **3i** follow from their ^{11}B spectra (Table VI). **3h** and **3i** are the third and fourth complexes with π-B$_5$ faces. It is interesting to note that the correlations of $\lambda_{\max}$ and $E_{\text{p/2}}$ values with the number of C atoms in the bonding face accommodates the observed values of all four Co*TM* complexes.

Mechanisms of Rearrangement

Polyhedral isomerizations of carboranes result in a greater separation of the carbon atoms, the driving force being the electrostatic repulsion between the electropositive C atoms.[14] The detailed pathways of these rearrangements, however, are not well understood. Three major mechanisms have been advanced to explain the observed rearrangements. According to Lipscomb's diamond–square–diamond (dsd)[15] mechanism, two contiguous triangular polyhedral faces stretch to a square face which may revert to the original form or, by an orthogonal return, generate two new triangles. For the rearrangement of Co*H*$_2$ and Co*Me*$_2$ complexes, this mechanism proceeds through a cuboctahedral intermediate and allows the following isomerizations.

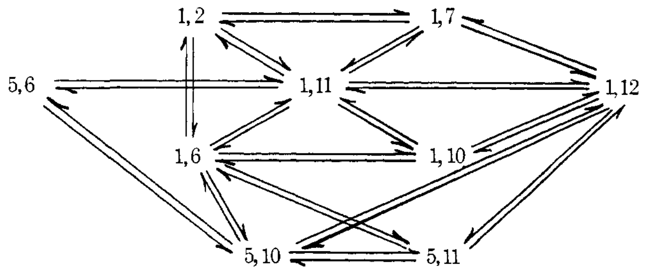
$$\begin{tikzcd}
1{,}2 \arrow[r, shift left] \arrow[d, shift left] & 1{,}6 \arrow[l, shift left] \arrow[r, shift left] & 5{,}6 \arrow[l, shift left] \arrow[d, shift left] \\
1{,}7 \arrow[u, shift left] \arrow[r, shift left] & 1{,}11 \arrow[l, shift left] \arrow[r, shift left] & 5{,}11 \arrow[l, shift left] \arrow[u, shift left] \\
1{,}10 \arrow[r, shift left] & 5{,}10 \arrow[l, shift left] & \\
 & 1{,}12 &
\end{tikzcd}$$

Thus, according to the dsd mechanism, the nine isomers can be grouped into three classes and no interclass crossing is possible between the six members of the first class, the two members of the second class, and the only member of the third. The dsd mechanism in its simplest form is inadequate in explaining our results since our studies of the Co*H*$_2$ and Co*Me*$_2$ systems have revealed the formation of five members of the first class, one of the second, and the only one in the third. For the Co*TM* complexes the dsd mechanism allows the following transformations.

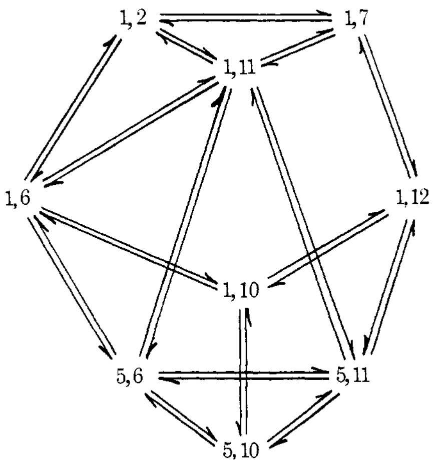
$$\begin{tikzcd}
1{,}2 \arrow[r, shift left] & 1{,}6 \arrow[l, shift left] \arrow[r, shift left] & 5{,}6 \arrow[l, shift left] \\
 & 5{,}10 &
\end{tikzcd}$$

The dsd mechanism again fails to account for the formation of the 5,10 derivative from any of the other three Co*TM* isomers.

A second mechanism has been suggested by Grafstein and Dvorak[16] and also by Zakharkin and Kalinin.[17] According to their pyramidal rotation mechanism, two icosahedral halves rotate in opposite directions. As applied to the Co*H*$_2$ and Co*Me*$_2$ systems, this mechanism allows the following interconversions.



In contrast to the dsd mechanism, this scheme allows interconversions between all nine isomers. Muetterties and Knoth[18] have proposed a third mechanism according to which a triangular face rotates while the remaining skeletal fragment pseudorotates simultaneously. As in the case of the previous mechanism, interconversions of all nine isomeric complexes are possible.



There are obvious differences of isomerization pathways between the last two mechanisms. Mention should also be made of Lipscomb's hybrid mechanism[19]

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[14] See ref 1b, p 11.

[15] W. N. Lipscomb, *Science*, **153**, 373 (1966), and references cited therein.

[16] D. Grafstein and J. Dvorak, *Inorg. Chem.*, 2, 1128 (1963).

[17] L. I. Zakharkin and V. N. Kalinin, *Dokl. Akad. Nauk SSSR*, **169**, 590 (1966).

[18] *Cf.* ref 1a, p 70.

[19] H. D. Kaesz, R. Bau, H. A. Beall, and W. N. Lipscomb, *J. Amer. Chem. Soc.*, **89**, 4218 (1967).

according to which triangular faces rotate in the cuboctahedral intermediate. Clearly, this would allow interconversions of all possible isomers.

In actuality, the observed kinetically controlled isomeric interconversions may employ any one or hybrid of the above three mechanisms. Clearly the simplest version of the dsd mechanism is inadequate to explain the results. The hybrid mechanism which allows triangular face rotation either in the ground state or cuboctahedral transition state is required in polyhedral rearrangements of metallocarboranes.

Conclusion

During the thermal rearrangement of Co*H*$_2$ and Co*Me*$_2$ complexes, the dicarbollyl C's migrate over the entire polyhedral surface. The absence of complexes having the 5,6 and 5,10 frameworks can be understood in terms of the unfavorable adjacent positioning of electropositive C atoms. In the Co*TM* series, however, the C's of the icosahedral fragment are "tied" together by the trimethylene bridge; consequently the 5,6 and 5,10 isomers are observed. On the other hand, the appearance of the 1,6 Co*H*$_2$, Co*Me*$_2$, and Co*TM* isomers which also have adjacent carbons signifies that the separation of carbon atoms is not the only driving force responsible for these rearrangements.

Dicarbollyl complexes with B$_5$ metal-bonding faces (*e.g.*, **1e**, **2e**, **3h**, and **3i**) *can* be synthesized. The experimental data indicate that as the coordination face changes from $B_3C_2 \rightarrow B_4C \rightarrow B_5$, the stability of the complexes increases in that order. This is reflected in the more negative $E_{\mathrm{p}/2}$'s (better stabilization of positive charge) and more energetic d–d transitions (larger ligand field).

The availability of such closely related dicarbollyl complexes opens a new area in the elucidation of structure–reactivity correlations. Furthermore, a better understanding of ^{11}B chemical shifts will ensue from the nmr data.

Experimental Section

Physical Measurements. Ultraviolet-visible spectra were recorded on a Beckman Model DB spectrophotometer. Infrared spectra were determined using a Perkin-Elmer Model 137 spectrophotometer. Proton nmr spectra were obtained on Varian A-60D or T-60 spectrometers; 80.5-MHz ^{11}B nmr spectra were recorded on an experimental superconducting spectrometer constructed by Professor F. A. L. Anet. Controlled-potential cyclic voltammetry was carried out using an instrument based on the design of Hawley.[20] Mass spectra were determined with an Associated Electrical Industries Model MS-9 spectrometer. Analyses were carried out by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y.

Materials. The synthesis of the dicarbadodecahydroundecaborate(−1) ions, (3)-1,2-$B_9C_2H_{12}^-$ and (3)-1,7-$B_9C_2H_{12}^-$, and their carbon-substituted dimethyl derivatives have been described previously.[5a] (3)-μ-1,2-$(CH_2)_3$-1,2-$B_9C_2H_{10}^-$ was made according to the procedure in ref 8. Cobaltic acetylacetonate was obtained from Research Organic/Inorganic Chemical Corp. Sodium hydride as a 56% dispersion in mineral oil was purchased from Metal Hydrides, Inc. Cyclopentadiene was freshly distilled by slow cracking of the dimer under a dry atmosphere. All tetrahydrofuran was freshly distilled from lithium aluminum hydride and collected under nitrogen. For ultraviolet-visible spectra, spectrograde acetonitrile and cyclohexane were used; for the cyclic voltammetry measurements, acetonitrile was distilled from P_2O_5 and then CaH_2.

Preparation of (π-C_5H_5)Co[π-(3)-1,2-$B_9C_2H_{11}$] (1a). The original procedure[9] was modified as follows. A cooled mixture of 81.2 mmol of Na_2(3)-1,2-$B_9C_2H_{11}$ and 189.0 mmol of NaC_5H_5 was added under nitrogen to 138.9 mmol of cobaltic acetylacetonate in 170 ml of tetrahydrofuran. The solution was refluxed for 15 min, stirred overnight at room temperature, and filtered (Celite), and the solvent was removed under reduced pressure. The residue was extracted with three 200-ml portions of hot benzene and the solution was cooled. An equal volume of hexane was added and the solution passed through a 2 × 12 in. column of silica gel eluting with 2 l. of hexane–benzene (1:1 v/v). The solvent was removed under reduced pressure and the product (3.35 g, 16.1%) recrystallized from CH_2Cl_2–hexane.

Preparation of (π-C_5H_5)Co[π-(3)-1,2-$(CH_3)_2$-$B_9C_2H_9$] (2a). A tetrahydrofuran solution of Na_2(3)-1,2-$(CH_3)_2$-$B_9C_2H_9$ and NaC_5H_5 prepared under nitrogen, from 30.0 g (135.5 mmol) of (Me_3NH)-[(3)-1,2-$(CH_3)_2$-$B_9C_2H_{10}$] and 22.4 g (339 mmol) of freshly cracked cyclopentadiene, was allowed to react with a refluxing mixture of cobaltic acetylacetonate (84.5 g, 237.3 mmol) in dry tetrahydrofuran. The mixture was stirred for 12 hr at room temperature and refluxed for 15 min. The cooled mixture was filtered through Celite and the Celite layer was washed with 100 ml of dry benzene. The combined solutions were concentrated under reduced pressure. The residue was taken up in 2 l. of 1:1 H_2O–C_6H_6. The phases were separated and the water was extracted with two 500-ml portions of benzene. The extracts were combined, dried over anhydrous magnesium sulfate, and concentrated to 500 ml, 500 ml of hexane was added, and the solution was filtered. The filtrate was chromatographed on a silica gel column, eluting with a 1:1 v/v benzene–hexane. Removal of the solvents followed by recrystallization in CH_2Cl_2–hexane produced 3.6 g (9.4%) of **2a**.

Preparation of (π-C_5H_5)Co[π-(3)-1,2-$(CH_2)_3$-$B_9C_2H_9$] (3a). According to the method described above for **1a**, 0.86 g (6.0%) of **3a** was prepared from 11.2 g (47.5 mmol) of [Me_3NH][(3)-μ-1,2-$(CH_2)_3$-$B_9C_2H_{10}$], 9.15 g (144.0 mmol) of cyclopentadiene, and 34.1 g (95.7 mmol) of cobalt(III) acetylacetonate.

Thermal Rearrangements. Below 490°. Each substrate (**1a**, **2a**, or **3a**) was placed in a 50-ml flask sealed to a 25-cm Pyrex tube (3-cm internal diameter) loosely packed with Corning Pyrex wool. A 500° thermometer was held against the tube with the thermometer bulb midway between the flask and the upper end of the tube, and the two were wrapped with two layers of electrical heating tape. The tube was fitted with a water-cooled sublimer connected to a high-vacuum line. The bulb was gradually submerged in a hot oil bath (150–170°) and the substrate slowly sublimed through the hot column.

Above 500°. Each compound to be rearranged (**1c**, **2c**, **3a**, and **3d**) was placed in a 50-ml flask sealed to a 18-cm quartz column (2.0-cm internal diameter) packed with quartz wool. A nichrome wire was wound around the tube and while a 3.2-ohm chromel–alumel thermocouple was held against the tube, the two were wrapped with asbestos tape. The two ends of the nichrome wire and the cold end of the thermocouple were connected to an Assembly Products Inc. recalibrated Sym-Ply-Trol temperature regulator. Temperature readings were monitored on the latter. The compounds were sublimed slowly as described above; the oil bath was maintained at 170–200°.

Chromatographic Separations. Mixtures from the Rearrangement of 1a and 2a (380–490°). Analytical thin-layer chromatography was carried out with benzene–hexane (3:2 v/v) as eluent. On a preparative scale, the mixtures were chromatographed on Mallinckrodt Chrom AR 1000 sheets eluting with benzene–hexane (1:1 v/v). In the Co*H*$_2$ series, the isomers were separated into three bands: **1a** < (**1b** + **1d**) < **1c** (increasing R_f left to right). The Co*Me*$_2$ isomers were similarly separated into three fractions: **2a** < (**2b** + **2d**) < **2c**. The (**1b** + **1d**), (**2b** + **2d**) mixtures were separated into their components by multiple elutions (hexane) on Merck precoated silica gel F-25H (0.25 mm) or Woelm 20 × 20 silica gel plates. Each compound was continuously extracted (Soxhlet) with hexane or chloroform, dried ($MgSO_4$), evaporated to dryness, and recrystallized or sublimed.

Mixtures from the Rearrangement of 1c and 2c (600–700°). Mixtures were analyzed by the eluting with benzene–hexane (1:3 v/v). Sample were separated, on a preparative scale, on Mallinckrodt Chrom AR 1000 sheets eluting once with hexane. In each of the Co*H*$_2$ and Co*Me*$_2$ series, five bands were obtained: **1b** < **1c** < (**1g** + **1f**) < **1e**; **2b** < **2c** < (**2g** + **2f**) < **2e**. **1g**, **1f**, **2g**, and **2f** were obtained from their respective binary mixtures by multiple elutions with hexane (see above). The compounds were isolated as described above.

Mixtures from the Rearrangement of 3a and 3d (500–650°). For analytical as well as preparative tlc, hexane was used as eluent (once).

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The rearrangement products (**3d**, **3h**, and **3l**) were isolated as described above for the CoH_2 isomers.

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Titanium-47 and Titanium-49 Nuclear Magnetic Resonance in Titanium(IV)-Halogen Compounds

R. G. Kidd,* R. W. Matthews, and H. G. Spinney

Contribution from the Department of Chemistry, University of Western Ontario, London, Ontario, Canada. *Received September 25, 1971*

Abstract: Chemical shift data for the ^{47}Ti and ^{49}Ti nmr of $TiCl_4$, $TiBr_4$, and TiF_6^{2-}, and binary mixtures of $TiCl_4$–$TiBr_4$, $TiCl_4$–TiI_4, have been determined. The order of increasing shielding of the titanium nucleus by the halogen ligands is I, Br < Cl. The resonance absorptions for $TiCl_4$ and $TiBr_4$ are unshifted on dilution of these compounds in inert solvents. This provides evidence for the existence of monomeric molecules in the neat liquids. The mixture of $TiCl_4$ and $TiBr_4$ showed just one resonance signal, the chemical shift of which varied linearly with the mole fraction of the components, indicating rapid exchange between the parent compounds and the mixed species $TiCl_3Br$, $TiCl_2Br_2$, and $TiClBr_3$.

Extensive chemical shift data for the nmr of various atoms in tetrahedral or pseudo-tetrahedral halogen-containing environments have been reported in recent years. Apparently without exception, the order of increasing shielding of the nucleus under investigations is Cl < Br < I. In particular, the nuclei for which this trend has been found are ^{11}B,[1,2] ^{13}C,[3–7] ^{27}Al,[8] ^{29}Si,[9,10] ^{31}P,[11,12] ^{71}Ga,[13] ^{115}In,[14] and ^{119}Sn.[15] While investigating the feasibility of using ^{47,49}Ti nmr to derive information on structure and bonding in titanium compounds, we have obtained surprising chemical shift data for the titanium(IV) tetrahalides. Our results show that the order of increasing nuclear magnetic shielding is anomalous, *viz.*, I, Br < Cl.

The natural abundances and sensitivities[16] (relative to ^{1}H at constant field) of the two stable isotopes of titanium with nonzero spins are: ^{47}Ti ($I = {}^5/_2$), 7.3%, 2.09×10^{-3}; ^{49}Ti ($I = {}^7/_2$), 5.5%, 3.76×10^{-3}. These properties restrict detection of nmr signals in liquids to neat liquids or very soluble compounds. The values of the nuclear quadrupole moments for these nuclei do not appear to have been determined. Previous workers have observed ^{47,49}Ti nmr signals in liquid $TiCl_4$,[17,18] aqueous H_2TiF_6,[17] and in the solids $SrTiO_3$, TiCo, TiFe, and TiH_2.[19] The gyromagnetic ratios of ^{47}Ti and ^{49}Ti are remarkably close. The ratio $\nu(^{49}\text{Ti})/\nu(^{47}\text{Ti})$ at constant field has been determined in $TiCl_4$ as 1.00026 ± 0.00002.[17,18]

Recently, there has been some discussion in the literature concerning the state of aggregation of liquid titanium(IV) tetrachloride. Griffiths[20] has interpreted the results of Raman studies to imply that $TiCl_4$ is dimeric in the liquid state and monomeric in solution in carbon tetrachloride. A subsequent detailed study[21] of the intensity pattern of the a_1 vibrational mode of $TiCl_4$ has provided evidence that $TiCl_4$ is monomeric both as a pure liquid and in cyclohexane solution. We have investigated this problem using ^{47,49}Ti nmr and obtained results consistent with the existence of monomeric units in liquid $TiCl_4$. Similar observations were made for the analogous titanium(IV) tetrabromide system.

The utility of the nmr method in determining the nature of the products of redistribution reactions has been amply demonstrated for a variety of systems (*e.g.*, $SnCl_4$–$SnBr_4$–SnI_4,[15] $POCl_3$–$POBr_3$,[10] and $AlCl_4^-$–$AlBr_4^-$–AlI_4^-[8]). Mixtures of $TiCl_4$ and $TiBr_4$ are known to contain an essentially random distribution of all possible species: $TiCl_4$, $TiCl_3Br$, $TiCl_2Br_2$, $TiClBr_3$ and $TiBr_4$.[21] We were unable to obtain ^{47,49}Ti chemi-

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