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THE UNIVERSITY OF ALBERTA

CRYSTAL STRUCTURE STUDIES OF SOME ORGANOMETALLIC COMPOUNDS

by

Ⓒ ROGER DUDLEY BALL

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled

CRYSTAL STRUCTURE STUDIES OF SOME
ORGANOMETALLIC COMPOUNDS

submitted by ROGER DUDLEY BALL in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

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ABSTRACTS

ABSTRACT

The crystal structures of $BrSn(Co(CO)_4)_3$, $(ac.ac.)_2SnCo_2(CO)_7$ and $C_6H_5GeCo_3(CO)_{11}$ were determined using X-ray diffraction techniques as a study into the ability of the group IVb elements (M) to form cobalt carbonyl compounds having MCo_3 or MCo_2 clusters containing Co-Co bonds. Tin, possibly because of its large size, prefers a cluster containing no Co-Co bonds and this was confirmed for the case of the $BrSn(Co(CO)_4)_3$ molecule. However, for the 6-Co-ordinate compound $(ac.ac.)_2SnCo_2(CO)_7$ a Co-Co bond is formed. A similar type of system also exists for the $C_6H_5GeCo_3(CO)_{11}$ molecule. Comparison of the Co-Co bond lengths in $Co_2(CO)_8$ with the latter two compounds indicates a trend towards shorter Co-Co distances with smaller bridging groups, the values being 2.52Å for $Co_2(CO)_8$, 2.546Å for $C_6H_5GeCo_3(CO)_{11}$ and 2.626Å for $(ac.ac.)_2SnCo_2(CO)_7$. Silicons inability to form a "closed" $MCo_3(CO)_9$ system indicates that the size of the group IVb element is not the only important factor involved. Comparisons between the group IVb series and the analogous VIb series are made.

The second part of the thesis consists of the crystal structures of the cis and trans isomers of

$Ru(CO)_4(GeCl_3)_2$. The unusual stability of the cis isomer had suggested the possibility of intramolecular halogen bridges. However, the structure analysis showed there were no such bridges. The $GeCl_3$ group is so oriented in the trans isomer as to lie very close to one potential minimum of a twelve-fold rotation axis. The internal consistency of bond lengths within each molecule is very good and the bond distances between the molecules compare well. Calculations from I.R. data show the π-acceptance ability of the CO and $GeCl_3$ groups to be similar and this is confirmed by structural evidence. The exchange of ^{13}CO is stereospecific and the possible reaction pathways point to a common reactive intermediate with a trigonal bipyramidal configuration.

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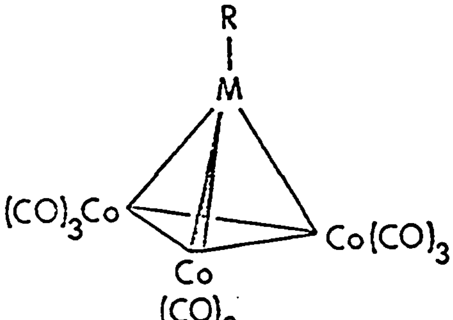
PART A

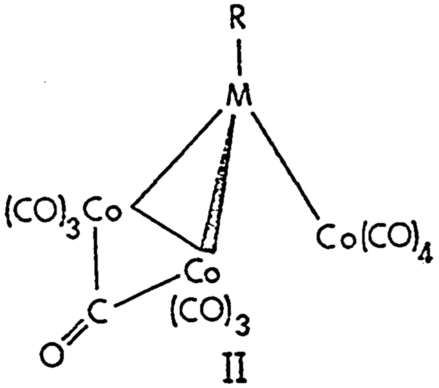
PART A

GENERAL INTRODUCTION

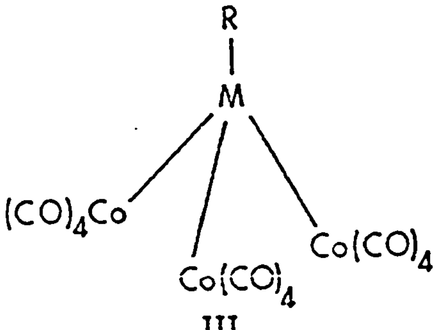
Since the preparation of the first trinuclear cobalt complex $(Co_3(CO)_9C_2H_3)^1$, a great deal of interest has been focussed on carbonyl compounds containing the structural fragment MCo_3 where M represents either one of the main group IV elements - C, Si, Ge, and Sn. Compounds of this type correspond to the stoichiometries $Co_3(CO)_9MR$, $Co_3(CO)_{11}MR$, and $Co_3(CO)_{12}MR$, for which the structures I, II and III, respectively, have been proposed.



I



II



III

The first structural type, I, consists of a triangular arrangement of $Co(CO)_3$ groups connected by equidistant Co-Co σ-bonds, with an apical M group being symmetrically co-ordinated (in the ideal case) to each of the cobalts. In II only one Co-Co bond remains and this is bridged by a carbonyl group. Finally, in III, we have a system which contains no Co-Co bonds. Each of the group IV elements (C, Si, Ge and Sn) has the ability to form one or more of these three basic structures, but the preference for, and facility of formation of, any particular one of these structures change markedly within the group.

Carbon appears to form compounds of type I only. Evidence in favour of type I for the complex $Co_3(CO)_9C_2H_3$ was largely based on I.R. studies and eventually confirmed in an X-ray analysis by Dahl *et al.*[2] Carbon seems to prefer being bonded to a "closed" cobalt cluster system (I), there being no reports in which carbon has been bonded to either of the "open" cobalt cluster systems (II or III). An analogous Si compound ($CH_2 = CHSiCo_3(CO)_9$) is claimed to have been prepared by Kettle *et al.*[3], but efforts to reproduce their results have resulted only in the formation of $CH_2 = CHSiCo_3(CO)_{11}$[4] with a postulated structure similar to II. Germanium, however, has been shown to form compounds of all three structural types[4], $C_6H_5GeCo_3(CO)_9$ (I), $C_6H_5GeCo_3(CO)_{11}$ (II), and $C_6H_5GeCo_3(CO)_{12}$ (III). Crystals of $C_6H_5GeCo_3(CO)_9$ are not nearly as stable as the carbon analogues and $C_6H_5GeCo_3(CO)_{12}$ could not be isolated owing to its rapid loss of carbon monoxide to reform $C_6H_5GeCo_3(CO)_{11}$. Attempts to prepare tin analogues have resulted in compounds of the type $R\text{-}Sn(Co(CO)_4)_3$ (III)[5]. These compounds do not possess a Co-Co metal bond and it was presumed that the Sn atom would display tetrahedral co-ordination with a $Co\hat{Sn}Co$ angle of 109°. Thus the molecular dimensions would be such that no mutual interference could take place between the carbonyl moieties of the separate $Co(CO)_4$ groups. The structural determinations of $ClSn(Mn(CO)_5)_3$[6] and $Sn(Fe(CO)_4)_4$[7] support these conjectures. There has been but one report of the preparation of a 4-co-ordinate tin compound containing the $Co_3(CO)_9$ cluster (I) and this report was never substantiated[11]. However, Graham *et al.*[8] have prepared the novel 6-co-ordinate compound $(C_5H_7O_2)_2SnCo_2(CO)_7$ for which they proposed from I.R. and mass spectral evidence a structure containing a Co-Co metal bond and a bridging carbonyl group (similar to II). Thus it would appear that by making the tin 6-co-ordinate the two $Co(CO)_4$ moieties make close enough approaches for the elimination of a CO group and the formation of a Co-Co bond.

It is very tempting to relate the facility with which these compounds can be made to the covalent radii of the group IV elements. From this type of argument one might expect the group IV elements of smallest covalent radii to more readily form "closed" cobalt cluster systems. However, germanium (cov. radius = 1.22Å) will form a "closed" cobalt cluster system, whereas silicon (cov. radius = 1.17Å) forms this type of system with great reluctance if at all.

A similar series of "closed" cluster compounds of general formulae $MCo_3(CO)_9$ and $MCo_2Fe(CO)_9$ has been prepared by Dahl using the group VI elements S, Se, and Te[9,10]. A comparison between this series and the similar main group IV series should prove to be of interest.

The preference of some group IV elements for a "closed" cobalt cluster system is still not fully understood. Various effects, including size and steric repulsions, could help explain the anomalies in the group IV series, but until more data are available on these systems no firm conclusions can be drawn.

To this effect the following 3-D crystal structure analyses were undertaken.

CHAPTER I

The Crystal and Molecular Structures of $BrSn(Co(CO)_4)_3$

INTRODUCTION

As part of an investigation[5] into the ability of group IVb elements to form cobalt carbonyl cluster compounds containing the $MCo_3(CO)_9$ (M = a group IVb element) nucleus, tin was found to give a different structural type from those observed for the elements carbon and silicon. From mass spectral and I.R. studies[5] tin was shown to form a molecule with a $Sn(Co(CO)_4)_3$ nucleus which contained no Co-Co bonds. To confirm the postulated structure for compounds of this type, a single crystal X-ray analysis of $BrSn(Co(CO)_4)_3$ was undertaken.

EXPERIMENTAL

Dark red hexagonal shaped needles of $BrSn(Co(CO)_4)_3$ were prepared by D.J. Patmore[5] from the reaction of tin(IV)bromide with $Co_2(CO)_8$ in T.H.F. The compound was recrystallized from n-pentane.

Weissenberg photographs for the layers $0k\ell$, $1k\ell$ and hk0, hk1 showed 6/m diffraction symmetry and systematic absences 00ℓ for ℓ odd. Together with consideration of the molecular symmetry, the space group was uniquely defined as $P6_3$ with the Sn-atoms of the molecules sitting on three-fold axes at the special positions 1/3, 2/3, z and 2/3, 1/3, 1/2 + z. The lattice parameters were obtained from precession photographs using MoK_α radiation and the errors determined using the method of Patterson and Love[26]: a = 10.20(1), c = 11.81(2). The density was determined by flotation methods using an aqueous solution of $ZnBr_2$ with the experimentally observed density of $2.20 g.cm^{-3}$ agreeing well with the calculated density of $2.22 g.cm^{-3}$ for a unit cell volume of $1065.1 Å^3$, Z = 2 and a molecular weight of 711.51.

A suitable crystal was mounted about the c-axis and the layers hkn ($0 \leq n \leq 7$) collected on a Nonius Weissenberg camera using the multiple film technique.

To minimize the absorption problem Zr filtered MoK_α radiation ($\mu = 52.8$ cm^{-1}) was used in preference to CuK_α radiation ($\mu = 201.4$ cm^{-1}). In order to obtain measurements of all the observed reflections, three exposures of 24 hours, 10 hours and 3 hours were necessary for each layer. Each reflection was measured visually by comparison with a previously prepared scale which had a barely visible reflection for its unit. For the purposes of interlayer scaling, a second crystal was mounted about the a-axis and the layers $nk\ell$ ($0 \leqslant n \leqslant 3$) collected using the same techniques. Corrections for Lorentz and polarization effects were made and an absorption correction applied to each set of data. The transmission factor range for both data sets was small (0.29 - 0.34). Since $P6_3$ is a non-centrosymmetric space group, consideration should be given to the hand of each crystal before data from separate crystals can be combined. For a centrosymmetric crystal the relation $|Fhk\ell| = |F\bar{h}\bar{k}\bar{\ell}|$ holds by virtue of the symmetry. For a non-centrosymmetric crystal the same relation is true provided the imaginary component $\Delta f''$ of the anomalous dispersion term is negligible (Friedel's Law). For this molecule, however, $\Delta f''$ is not negligible and Friedel's Law does not hold ($F_{hk\ell} \neq F_{\bar{h}\bar{k}\bar{\ell}}$). In consequence, with non-centrosymmetric crystals it is often the practice to measure the reflections in only one half of reciprocal space where all reflections have, say, ℓ non-negative (c being the polar axis). Since the polar axis in $P6_3$ is the c-axis, it is convenient to consider all reflections having ℓ positive as consisting of one hand while the second hand has ℓ negative. While the data collected about the polar c-axis are consistent, having all ℓ either positive or negative, the data about the a-axis consist of reflections with both hands. Since the least squares program available did not have the facility to apply the $\Delta f''$ correction to the appropriate scattering factors, the data about the a-axis which contained both hands were averaged and combined with the c-axis data using the method of Rae[64]. This gave 339 unique reflections.

STRUCTURE SOLUTION AND REFINEMENT

The two Sn atoms sit at the special positions 1/3, 2/3, 0; 2/3, 1/3, 1/2. A Patterson map revealed the positions of the Br and Co atoms. The remaining carbonyl groups had their positions determined using difference Fourier techniques. The atomic scattering factors calculated by Cromer and Waber[27] were employed and the real part ($\Delta f'$) of the anomalous dispersion correction applied to the Sn ($\Delta f' = -0.8$), Br ($\Delta f' = -0.3$) and Co ($\Delta f' = 0.3$), the $\Delta f'$ values being obtained from the usual source[28].

The atoms were initially assigned variable isotropic temperature factors and the full matrix least squares refinement converged with the usual discrepancy factors $R_1 = \sum||Fo|-|Fc||/\sum|Fo|$ and R_2 (or weighted R factor) $= \left\{\sum w(|Fo|-|Fc|)^2/\sum wFo^2\right\}^{\frac{1}{2}}$) at values of .10 and .12 respectively. Unit weights were used. An examination of the electron density difference map indicated that the heavy atoms could be allowed to refine anisotropically. The general expression for anisotropic thermal vibrations is $\exp-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}\ell^2 + 2\beta_{12}hk + 2\beta_{23}k\ell + 2\beta_{31}h\ell)$. However, the Sn and Br atoms lie in positions of special symmetry and certain restrictions are placed on their thermal motion[2]. These are $\beta_{11} = \beta_{33} = 2\beta_{12}$, $\beta_{13} = \beta_{23} = 0$, and the anisotropic temperature factor expression now becomes $\exp-(\beta_{11}(h^2 + k^2 + hk) + \beta_{33}\ell^2)$. Three cycles of refinement made $R_1 = .085$ and $R_2 = .099$. A weighting scheme of the form $w = a^2/(a^2 + (F-b)^2)$ with $a = 15$ and $b = 50$ ensured Cruickshank's criterion[32] that $w\Delta^2$ should be invariant with F.

The carbonyl atoms were not assigned anisotropic temperature factors because of the insufficient amount of data. The final residuals were $R_1 = .081$ and $R_2 = .082$ with no parameter shifting more than 0.2 of its estimated standard deviation. No reflections were considered to be suffering from secondary extinction. A final electron density map revealed a peak of $1.7e^-$ near the Sn atom and one of $1.2e^-$ near the Br atom. Several peaks of $0.6 - 0.8e^-/\text{Å}^3$ were located near the carbonyl groups and could be attributed to the anisotropic motion of these groups. Otherwise, all the residual peaks were less than $0.7e^-/\text{Å}^3$.

At a later date an attempt was made to collect a consistent set of data on a diffractometer in order to make the appropriate anomalous dispersion correction and hence eliminate a systematic error from the data.

However, no suitable crystals were available and attempts to make more were unsuccessful.

Table I

Observed and calculated structure amplitudes (x10) in electrons for $BrSn(Co(CO)_4)_3$

K	L	FO	FC
		H = 0	
0	4	236	206
0	6	28	20
0	8	57	55
0	10	39	36
0	14	25	27
		H = 1	
0	3	70	59
0	4	122	105
0	5	72	75
0	6	28	24
0	7	14	14
0	8	25	25
0	9	27	24
0	10	21	21
0	11	18	20
1	2	52	50
1	3	108	91
1	4	112	95
1	5	42	45
1	6	86	84
1	7	46	47
1	8	55	53
1	9	23	26
1	10	51	50
2	0	52	50
2	1	132	122
2	2	100	101
2	3	44	42
2	4	56	59
2	5	99	86
2	6	93	91
2	7	23	19
2	8	69	69
2	9	41	41
2	10	42	44
3	0	64	60
3	1	73	68
3	2	16	13
3	3	32	34
3	4	34	36
3	5	57	56
3	6	39	34
3	7	22	25
3	8	25	26
3	9	40	40
4	0	81	68
4	1	47	49
4	2	24	29
4	3	47	48
4	4	69	75
4	5	24	25
4	6	46	49
4	7	26	25
4	8	39	40
4	10	26	30
5	0	19	20
5	1	21	24
5	2	20	18
5	3	22	27
5	4	26	30
5	5	28	32
5	6	41	34
5	7	23	26
5	8	23	24
5	9	20	25
6	0	39	40
6	1	19	16
6	2	34	31
6	4	28	31
6	5	34	39
6	7	27	27
6	9	23	27
7	2	11	13
7	4	22	24
7	6	36	26
8	0	32	26
8	2	26	23
8	4	15	14
8	5	22	29
8	7	23	22
		H = 2	
0	1	56	55
0	2	21	18
0	3	40	35
0	4	20	19
0	5	111	109
0	6	23	22
0	7	49	49
0	9	79	75
0	10	16	21
0	11	17	19
0	13	18	20
1	0	90	98
1	1	85	82
1	2	99	96
1	3	49	49
1	4	51	53
1	5	98	95
1	6	27	23
1	7	33	36
1	9	56	57
1	11	16	20
2	0	114	113
2	2	55	58
2	3	16	16
2	4	72	72
2	6	53	53
2	8	31	32
2	10	27	33
3	0	93	92
3	1	30	30
3	2	49	46
3	3	38	43
3	4	62	64
3	5	81	82
3	7	50	51
3	9	53	51
3	11	29	24
4	0	14	15
4	1	30	30
4	2	54	54
4	3	12	21
4	4	39	40
4	5	32	35
4	6	55	47
4	7	22	21
5	0	73	71
5	2	40	39
5	4	46	46
5	6	14	13
6	0	25	25
6	1	34	38
6	2	23	24
6	3	32	32
6	4	16	15
6	5	22	26
7	1	22	24
7	2	12	14
7	4	16	20
7	5	20	21
7	6	20	20
9	1	19	20
		H = 3	
0	0	75	79
0	1	101	96
0	2	51	51
0	3	34	35
0	4	88	83
0	5	15	20
0	6	37	33
0	7	15	12
0	8	26	25
0	10	30	34
1	0	66	67
1	1	129	137
1	2	37	35
1	3	100	100
1	4	58	59
1	5	53	53
1	7	28	26
1	8	19	16
2	0	11	10
2	1	75	81
2	3	44	47
2	4	38	38
2	5	51	55
2	6	28	26
2	7	16	14
3	0	56	53
3	1	21	19
3	2	6	10
3	3	25	20
3	4	47	46
3	5	10	18
3	6	50	50
3	8	29	34
3	10	28	31
4	0	33	32
4	1	50	54
4	2	19	21
4	3	31	34
4	4	33	29
4	5	26	27
5	0	39	40
5	1	74	71
5	2	35	35
5	3	60	60
5	4	29	28
5	5	32	34
5	6	15	16
6	0	36	37
6	2	34	32
6	4	25	28
6	6	16	16
7	6	17	15
8	2	9	13
9	2	14	17
		H = 4	
0	0	72	65
0	1	92	92
0	2	55	55
0	3	82	91
0	4	44	44
0	5	60	65
0	7	23	21
1	0	135	152
1	2	87	86
1	4	81	82
1	6	38	32
1	8	18	17
2	1	57	54
2	2	27	25
2	3	35	35
2	4	35	38
2	5	49	51
2	6	34	36
2	7	21	21
3	0	50	49
3	1	19	19
3	2	29	27
3	3	21	25
3	4	28	28
3	5	53	54
3	7	30	31
3	9	28	32
4	0	57	54
4	2	44	44
4	4	35	35
5	0	9	16
5	1	29	30
5	3	22	26
5	4	12	19
5	5	13	23
5	7	20	10
6	0	13	18
6	2	12	16
6	5	14	20
7	1	18	14
7	5	15	15
		H = 5	
0	0	61	57
0	1	55	54
0	2	44	43
0	3	37	39
0	4	39	39
0	5	46	46
0	7	15	16
1	0	31	32
1	1	49	51
1	3	20	22
1	4	20	22
1	5	42	45
1	6	26	16
1	7	23	21
2	1	51	51
2	2	22	21
2	3	38	42
2	4	35	36
2	5	33	37
2	6	53	42
2	7	16	20
2	8	23	30
3	1	22	26
3	2	7	14
3	4	17	20
3	5	22	25
3	6	29	24
3	7	17	16
4	1	19	21
4	2	18	14
4	3	19	19
4	4	20	21
4	5	13	18
4	6	31	24
5	4	17	19
5	6	29	21
6	1	14	14
		H = 6	
0	0	18	18
0	1	43	43
0	2	36	36
0	3	51	53
0	4	44	48
0	5	36	36
0	6	58	44
0	7	27	28
0	8	28	31
1	0	20	18
1	1	23	21
1	2	22	16
1	3	27	26
1	5	34	33
1	7	20	21
2	0	29	26
2	1	22	22
2	2	24	23
2	3	21	18
2	4	22	22
2	5	16	20
3	0	28	25
3	1	22	21
3	2	23	20
3	4	25	24
3	6	28	19
4	0	30	27
4	2	19	20
4	5	19	24
4	7	25	21
5	1	18	19
6	0	34	25
6	2	25	21
		H = 7	
0	1	35	36
0	2	11	14
0	3	23	25
0	4	11	18
0	5	23	26
0	6	29	24
1	0	58	57
1	2	46	45
1	4	33	37
2	0	28	30
2	1	38	41
2	2	23	23
2	3	31	33
2	4	21	19
2	5	19	18
3	1	8	17
5	1	15	20
		H = 8	
0	1	28	30
0	3	20	21
0	4	10	14
0	5	20	20
1	0	18	22
1	1	34	35
1	2	19	18
1	3	27	29
1	4	17	16
2	0	30	27
2	2	25	21
2	4	21	21
2	5	12	4
3	2	9	12
		H = 9	
0	4	8	16
1	2	13	13
1	5	12	15

Table II

Final Atomic Positional and Thermal Parameters for $BrSn(Co(CO)_4)_3$

Atom	x/a	y/b	z/c	B
Sn	0.6666	0.3333	0.50	-
Br	0.6666	0.3333	0.7131(8)	-
Co	0.4023(6)	0.2908(6)	0.4421(6)	-
C1	0.2361(72)	0.2651(65)	0.4020(44)	8.2(1.3)
O1	0.1121(61)	0.2201(51)	0.3731(40)	10.9(1.2)
C2	0.4659(50)	0.4791(64)	0.4772(50)	7.5(1.2)
O2	0.5057(38)	0.6113(38)	0.4866(38)	8.8(8)
C3	0.4286(44)	0.2390(47)	0.3141(39)	4.3(8)
O3	0.4508(34)	0.1804(35)	0.2261(35)	6.9(8)
C4	0.3186(59)	0.1668(59)	0.5563(39)	5.6(1.1)
O4	0.2747(50)	0.0767(50)	0.6304(45)	10.4(1.1)

Numbers in parentheses are estimated standard deviations occurring in the last digits listed.

Table III

Anisotropic Temperature Factors
for the Sn, Br and Co Atoms ($x10^4$)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Sn	132(10)	132(10)	69(4)	66(5)	0	0
Br	396(34)	396(34)	56(7)	198(17)	0	0
Co	117(8)	143(8)	82(5)	58(7)	25(6)	9(6)

Numbers in parentheses are estimated standard deviations occurring in the last digits listed.

Figure 1

A perspective view of the $BrSn(Co(CO)_4)_3$ molecule with 50% probability thermal ellipsoids

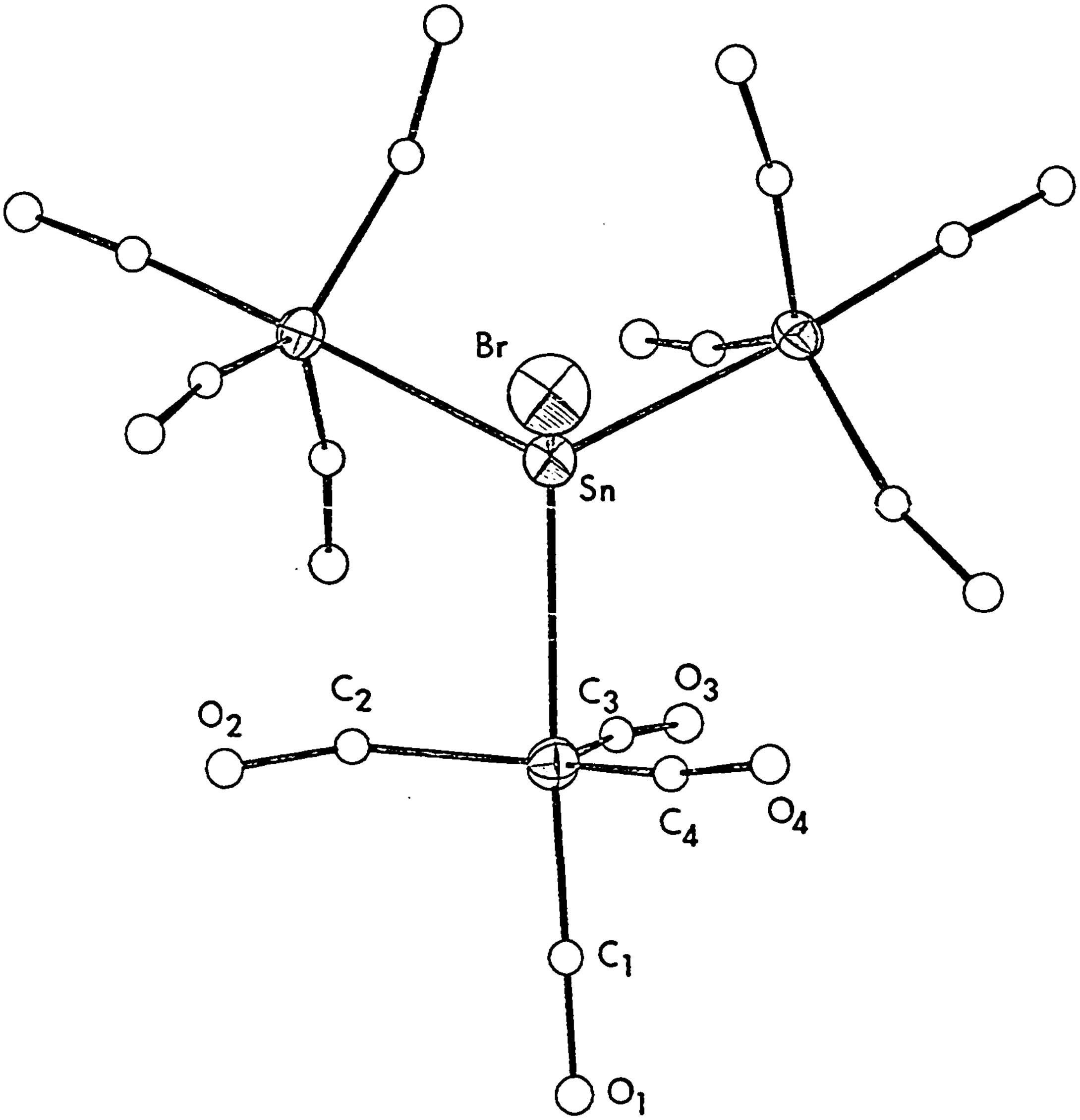

Br
Sn
C2
O2
C3
O3
C4
O4
C1
O1

Table IV

Intramolecular Bond Lengths and Angles of $BrSn(Co(CO)_4)_3$

Atoms	Distance(Å)
Sn-Br	2.52(5)
Sn-Co	2.602(6)
Co-C1	1.74(6)
Co-C2	1.81(6)
Co-C3	1.71(5)
Co-C4	1.73(5)
C1-O1	1.19(8)
C2-O2	1.17(7)
C3-O3	1.20(6)
C4-O4	1.25(7)

Atoms	Angles(°)
Co-$\hat{\mathrm{Sn}}$-Co	112.5(2)
Co-$\hat{\mathrm{Sn}}$-Br	104.8(2)
Sn-$\hat{\mathrm{Co}}$-C1	176(4)
Sn-$\hat{\mathrm{Co}}$-C2	86(4)
Sn-$\hat{\mathrm{Co}}$-C3	86(3)
Sn-$\hat{\mathrm{Co}}$-C4	89(3)

Numbers in parentheses are estimated standard deviations occurring in the last digits listed.

DISCUSSION

A perspective view of the molecule is depicted in Figure 1. The molecule possesses triad symmetry, with the tin and bromine atoms located on the c-axis. The structure consists of a distorted tetrahedron consisting of the Br atom and the three $Co(CO)_4$ groups, each σ-bonded to a central Sn atom. Each of the cobalt atoms, which are equivalent by space group symmetry, attains a closed-shell electronic configuration through bonds to the four carbonyl groups and the tin atom. The four CO groups each donate two electrons and the Sn atom one electron which together with the twenty-seven electrons of the Co atom allow the Co to attain the Kr noble-gas configuration. The intramolecular angles about the Sn atom show significant distortions from the ideal tetrahedral value of ~109° with a Br-$\hat{\mathrm{Sn}}$-Co angle of 104.8° and Co-$\hat{\mathrm{Sn}}$-Co angles of 112.5°. These distortions are a reflection of the mutual repulsion forces between the carbonyls of adjacent $Co(CO)_4$ groups. It is these repulsions which prevent the molecule in the crystalline state from having the idealized C_{3v} symmetry observed in solution I.R. work[5]. The Sn-$\hat{\mathrm{Co}}$-C axial angle is 176° and the Sn-$\hat{\mathrm{Co}}$-C equatorial angles are all less than 90° and have a mean value of 87°. However, the Sn-Ĉo-C4 angle is somewhat larger at 89° than the Sn-Ĉo-C2 and Sn-Ĉo-C3 angles which are both at 86°. This larger angle is probably due to the mutual repulsion forces between the bromine atom and this carbonyl group which is more closely situated to the bromine atom than the other carbonyl groups. The intramolecular Br-O4 distance is 3.68Å (Van der Waals contact being 3.35Å) with all the other intramolecular Br-O contacts being >4Å.

The displacement of the equatorial carbonyl groups towards the substituent group, in this case the Sn atom, has been well authenticated. There are several factors which may explain this experimentally observed displacement. Intermolecular interactions within the crystal is an unlikely explanation because of the magnitude and general occurrence of the carbonyl displacement towards the substituent group. Another argument is based upon the steric requirements of the axial carbonyl group and the trans substituent group being unequal. For a molecule of the type $HCo(CO)_4$ it is easy to show that the steric requirements of the axial carbonyl group are greater than those for the hydrogen atom. However, for other substituents the use of Van der Waals radii often does not definitely show whether the equatorial carbonyl groups should be bent away or towards the substituent group. In the present structure the average carbon-carbon contact is 2.6Å and the average tin to equatorial carbon contact is 3.1Å. Both of these contacts are considerably shorter than the sum of Van der Waals radii for these atoms (C = 1.7Å[68], Sn = 2.2Å[69]). Bennett and Mason[70] have suggested from symmetry arguments that the out of plane displacements could be caused by a difference in π-acceptor capacity of the substituent as compared to the axial carbonyl group, the equatorial groups being bent toward the weaker π-acceptor. MacDiarmid *et al.*[71] believe that the above interaction may account, at least in part, for the displacement of the equatorial groups in some compounds, but that an intramolecular bonding interaction between the equatorial carbonyls and the substituent group may well play an important role. M.O. calculations on the molecules $HCo(CO)_4$ and $R_3SiCo(CO)_4$ (R = F, Cl) predict a large bonding interaction between the equatorial carbonyl and the respective H and Si atoms. The above authors postulate that analogous types of interaction might exist in a variety of other transition metals and their derivatives.

Before discussing the bond lengths, the error introduced by neglecting the imaginary anomalous dispersion correction ($\Delta f''$) will be considered. Templeton *et al.*[72] have recently pointed out the serious co-ordinate errors which can result from the neglect of the imaginary component $\Delta f''$ of the anomalous scattering in polar space groups. For this molecule the symmetry of the space group $P6_3$ gives a cancellation of the effect on the x and y co-ordinates, but there is a systematic biasing of the z components of interatomic vectors with one or both atoms suffering from anomalous dispersion. Unless the $\Delta f''$ contribution (which is always positive) is considered, the anomalous scatterer will appear to be closer to the X-ray source and detector than is actually the case, giving significant shifts in the z co-ordinate. Cruickshank and McDonald[55] have recently discussed polar dispersion errors in detail and have produced a formula which calculates the co-ordinate error Δz introduced by excluding the $\Delta f''$ term in the calculation

$$\Delta z = \frac{1}{\pi \mathrm{Smax}} \left(\frac{\Delta f''}{|f|}\right)_{1/2\mathrm{Smax}}$$

where $S = 2\sin\theta/\lambda$, $|f|$ is the modulus of the complex atomic scattering factor and the quantity $\left(\frac{\Delta f''}{|f|}\right)$ is taken as the phase shift due to anomalous scattering, evaluated at $S = 1/2S\text{max}$. Using the $\Delta f''$ values of $1.7e^-$ for Sn, $1.0e^-$ for Co and $2.5e^-$ for Br, the Δz values for these atoms were calculated to be 0.013Å, 0.023Å and 0.045Å for the respective atoms. Those distances which have interatomic vectors aligned in the z direction will suffer most from this systematic error. The Sn-Br distance would be expected to have the greatest error. However, the distance of 2.52(5)Å lies within the range of the previously observed values of 2.51Å for 4-bromo-1,2,3,4-tetraphenyl-cis, cis-1,3-butadienyldimethyltinbromide[58], 2.55Å in $SnBr_2$[68] and 2.46Å (average)[68] in $SnBr_4$, CH_3SnBr_3, $(CH_3)_2SnBr_2$ and $(CH_3)_3SnBr$. The Sn-Co distance is 2.60Å. The mean value for the Co-C distances is 1.75Å with all distances agreeing within 1σ of this value. The C-O mean distance is 1.20Å with all the distances once more agreeing within 1σ of this value.

The crystallographic study confirmed the structure postulated from I.R. evidence by Graham *et al.*[5] It would appear that tin cobalt carbonyl cluster compounds are reluctant to form systems involving a Co-Co bond. One exception is the Co-Co bond formed in the sterically crowded six-co-ordinate tin molecule (ac.ac.)$_2$SnCo$_2$(CO)$_7$. However, the above authors have observed in relatively high abundance the RSnCo$_3$(CO)$_{11}{}^+$ (R = Me, C_6H_5) ions in their mass spectral work on molecules of the type RSn(Co(CO)$_4$)$_3$ for which they predicted a structure similar to that of the $C_6H_5GeCo_3(CO)_{11}$ molecule[12] containing a Co-Co bond with a bridging CO group.

CHAPTER II

The Crystal and Molecular Structures of $(C_5H_7O_2)_2SnCo_2(CO)_7$

INTRODUCTION

There have been no reported cases in which 4-co-ordinate tin forms cobalt carbonyl cluster compounds containing Co-Co bonds. However, when bis(2,4-pentadionato)dichlorotin(IV) was reacted with the tetracarbonylcobaltate(-1) anion, among other products crystals of $(C_5H_7O_2)_2SnCo_2(CO)_7$ were formed[13]. Mass spectral and I.R. work showed this 6-co-ordinate tin compound to have a Co-Co bond bridged by a carbonyl group. This molecule was the prototype for main group IV elements bonded to a Co-Co bond with the exception of the parent cobalt carbonyl $Co_2(CO)_8$. In order to study the trends, especially the Co-Co bond length, in molecules of this type a single crystal X-ray analysis of $(C_5H_7O_2)_2SnCo_2(CO)_7$ was undertaken.

EXPERIMENTAL

Red crystals of $(ac.ac.)_2SnCo_2(CO)_7$ were prepared from the reaction of $NaCo(CO)_4$ with a solution of $(ac.ac.)_2SnCl_2$ in T.H.F. at room temperatures by D.J. Patmore[12,13]. Recrystallization from the same solvent produced well-formed needles of triangular cross-section.

The preliminary Weissenberg ($0k\ell$ and $1k\ell$ levels) and precession ($h0\ell$ and $hk0$ levels) photographs showed mmm Laué symmetry and the following systematic absences $0k\ell$ for $k \neq 2n$, $h0\ell$ for $\ell \neq 2n$, $hk0$ for $k \neq 2n$ uniquely defined the space group as Pbca (No. 61). The lattice constants were measured from precession photographs using MoK_α radiation and the errors determined using the method of Patterson and Love[26]: $a = 13.88\ (\pm.01)$, $b = 29.34\ (\pm.02)$, $c = 11.53\ (\pm.01)$. The density was determined by flotation using Clerici's solution. The experimentally observed density of 1.80 agrees with the calculated density of 1.80 for a unit cell volume of $4698\mathring{A}^3$, $Z = 8$ and a molecular weight of 634.8.

The crystal was mounted about the a-axis and the layers $nk\ell$ ($0 \leq n \leq 11$) collected on a Pailred Linear Diffractometer using crystal monochromatized MoK_α radiation. Since similar crystals had shown signs of surface oxidation, the crystal was mounted in a Lindeman glass capillary and sealed under an inert atmosphere of nitrogen. To minimize absorption, MoK_{α} radiation (μ = 24.6 cm^{-1}) was used in preference to CuK_{α} (μ = 199.8 cm^{-1}). At the completion of the fourth layer of data collection, the Mo tube burnt out and subsequent layers were collected with a "new" tube. The zero layer data were recollected using the "new" tube and together with the zero layer data from the "old" tube used to calculate a scale factor between the two sets of data. Each reflection was scanned once with a scan speed of 1°/min. being employed for the "old" tube data. The "new" tube data were scanned at a speed of 2.5°/min. since the diffracted beam intensity was a factor of 2.5 greater than that for the "old" tube. A stationary 24 second background count was taken on either side of the scan with the scan width being gradually increased from 1.4° up to 3.2° as the peak profiles broadened with increasing equi-inclination angles. A set of standard reflections collected at the commencement of each new layer showed variations consistent with fluctuations in the electronic circuits rather than with crystal decomposition.

The intensity I was calculated for each reflection assuming a linear change in background between the two limits of the scan. The reflections were rejected on the basis of two criteria: (1) $I < 0$, and (2) $I < 2\sigma I$. Lorentz and polarization corrections were applied to the remaining 1408 reflections and standard deviations calculated using the expression $\sigma(I) = [P + (t_1/t_2)^2(B_1+B_2) + (pI)^2]^{1/2}$ where P is the total integrated peak count obtained in time t_1, B_1 and B_2 are the background counts obtained in time t_2, and $I = P - t_1/t_2(B_1+B_2)$. The p term takes into account the indeterminant errors, including machine instability and any non-isotropic effect which may cause variations in the reflection intensities. Since the ratio of maximum to minimum transmission factors for the 1408 reflections is only 1.13, no absorption correction was applied.

STRUCTURE SOLUTION AND REFINEMENT

A three-dimensional Patterson map revealed the expected triangular arrangement of the tin and two cobalt atoms. By using difference Fourier techniques, the remaining carbon and oxygen atoms were located and the structure refined using full matrix least squares calculations. The atomic scattering factors calculated by Cromer and Waber[27] were employed for atoms other than hydrogen with anomalous dispersion corrections for the tin and cobalt atoms being included in Fc[28]. The atomic scattering factors used for hydrogen were those experimentally determined by Mason and Robertson[29].

All atoms were initially assigned variable isotropic temperature factors, and after four cycles of full matrix least squares refinement the usual discrepancy factors $R_1 = \sum||Fo|-|Fc||/\sum|Fo|$ and R_2 (or weighted R factor) $= \left\{\sum w(|Fo|-|Fc|)^2/\sum wFo^2\right\}^{\frac{1}{2}}$ were .086 and .094 respectively. The function minimized during the least squares refinement was $\sum w(|Fo|-|Fc|)^2$ where $|Fo|$ is the observed structure amplitude, $|Fc|$ is the calculated structure factor amplitude, and the weighting factor $w = 1/(\sigma F)^2$.

An electron density difference map was now calculated and the residual electron densities indicated that the heavy atoms could be given anisotropic temperature factors. The calculated positions of the two hydrogen atoms on the two acetylacetonate groups were included in the last cycles of refinement and assigned temperature factors one unit higher than the adjacent carbon atom.

During the final cycle of least squares refinement, no parameter shifted by more than one-ninth of its estimated standard deviation and $R_1 = .059$ and $R_2 = .057$. An electron density difference map based on the final parameters contained only three peaks ($1.1e^-/\mathring{A}^3$, $.95e^-/\mathring{A}^3$, $.75e^-/\mathring{A}^3$) with electron densities higher than $0.6e^-/\mathring{A}^3$, and these could be assigned to the anisotropic motion of carbonyl moieties. The experimental weighting scheme satisfied, within acceptable limits, Cruickshank's criterion[32] and a comparison of the final observed and calculated structure factor amplitudes did not suggest that a correction for extinction was necessary. The final standard deviation for an observation of unit weight was 2.198. The expected value is unity and the discrepancy between the two reflects the error introduced into the model by not allowing the light atoms to have anisotropic vibrations, or by assuming a too small p factor.

Table V

Observed and calculated structure amplitudes (x10)

in electrons for (ac.ac.)$_2$SnCo$_2$(CO)$_7$

Table VI

Final Atomic Positional and Thermal Parameters

Atom	x	y	z	B(Å^2)
Sn	0.2380(1)	0.1142(1)	0.1020(1)	4.4*
Co$_1$	0.1317(2)	0.1639(1)	-0.0287(2)	4.4*
Co$_2$	0.2994(2)	0.1348(1)	-0.1036(2)	4.6*
C1	0.1695(4)	0.1235(6)	-0.1433(16)	5.8(.5)
O1	0.1316(9)	0.0997(5)	-0.2169(12)	7.8(.4)
C2	0.0796(16)	0.1976(8)	-0.1350(20)	8.3(.6)
O2	0.0409(16)	0.2179(6)	-0.2088(15)	11.1(.5)
C3	0.0345(16)	0.1349(7)	0.0295(18)	7.3(.5)
O3	-0.0338(11)	0.1167(5)	0.0621(13)	8.7(.4)
C4	0.1606(15)	0.2108(8)	0.0537(19)	7.8(.6)
O4	0.1851(10)	0.2438(6)	0.1067(14)	10.0(.4)
C5	0.3830(15)	0.1702(7)	-0.0366(18)	6.8(.5)
O5	0.4401(11)	0.1963(5)	0.0025(12)	8.3(.4)
C6	0.3465(14)	0.0817(7)	-0.1068(18)	7.0(.5)
O6	0.3787(11)	0.0439(5)	-0.1120(13)	9.4(.4)
C7	0.3228(16)	0.1563(8)	-0.2409(21)	8.3(.6)
O7	0.3348(12)	0.1684(6)	-0.3361(15)	10.8(.5)
O8	0.1776(8)	0.0487(4)	0.0602(9)	5.1(.3)
O9	0.3532(7)	0.0763(4)	0.1665(10)	5.1(.3)
O10	0.3070(8)	0.1647(4)	0.2041(10)	5.5(.3)
O11	0.1606(11)	0.1006(3)	0.2532(10)	5.2(.3)
C8	0.1683(12)	0.1201(6)	0.3568(15)	5.4(.4)
C9	0.0946(13)	0.0983(7)	0.4427(17)	6.7(.5)
C10	0.2265(13)	0.1544(6)	0.3801(16)	6.2(.4)
C11	0.2893(14)	0.1769(7)	0.3122(18)	6.3(.5)
C12	0.3531(14)	0.2171(7)	0.3545(17)	7.0(.5)
C13	0.3599(12)	0.0338(6)	0.1890(14)	4.9(.4)
C14	0.4498(12)	0.0181(6)	0.2518(17)	5.7(.4)
C15	0.2868(12)	0.0004(6)	0.1609(15)	5.4(.4)
C16	0.2071(12)	0.0106(6)	0.0990(16)	5.0(.4)
C17	0.1436(13)	-0.0310(6)	0.0623(15)	6.2(.5)
H1	0.2280	0.1650	0.4630	7.8
H2	0.3040	-0.0100	-0.0610	6.1

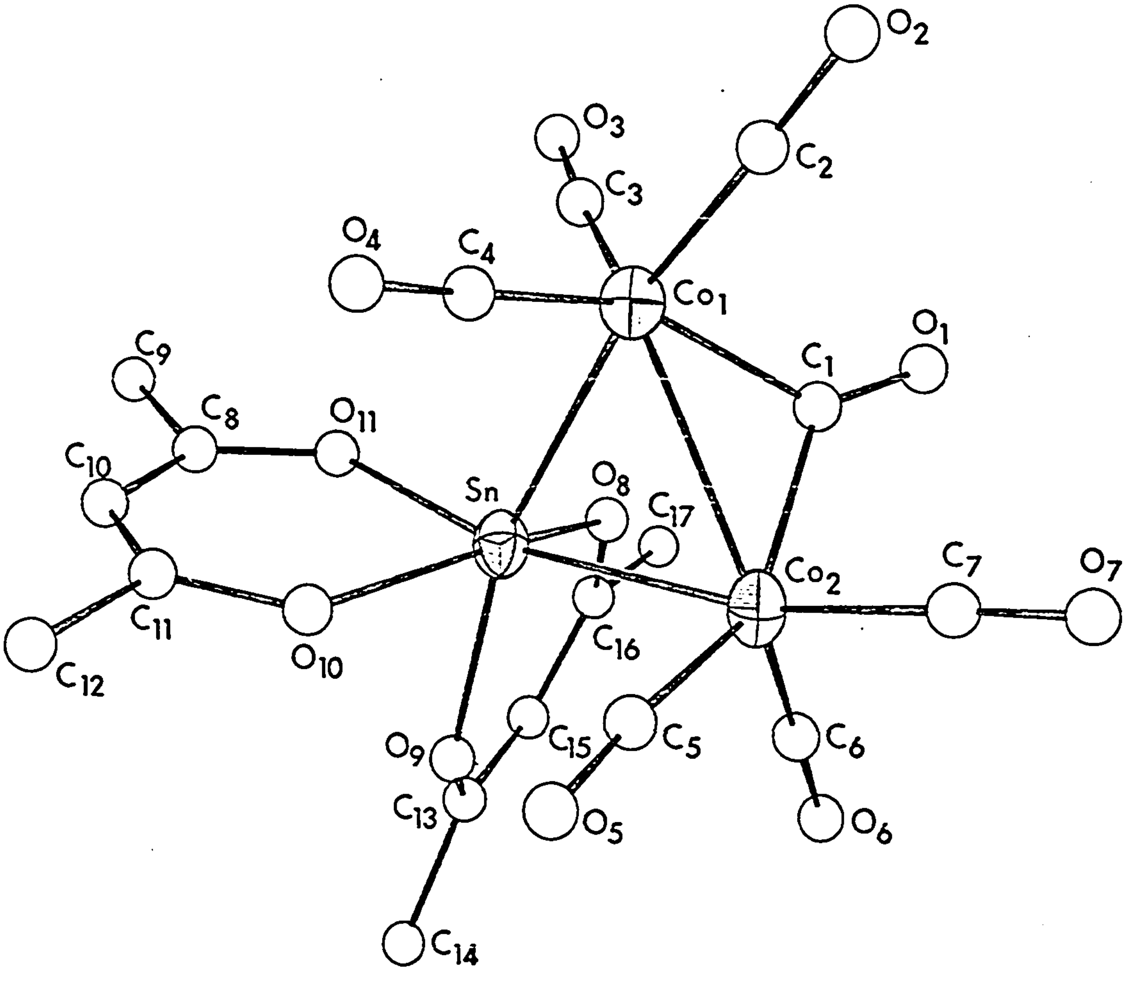
* These values of B are the equivalent isotropic thermal parameters corresponding to the anisotropic thermal vibration tensors having the following components (x10^{-5}):

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co$_1$	672(17)	102(4)	844(25)	28(6)	19(16)	10(9)
Sn	721(9)	109(2)	719(10)	6(3)	6(3)	27(5)
Co$_2$	708(17)	138(4)	691(22)	62(6)	47(18)	24(10)

Numbers in parentheses are estimated standard deviations occurring in the last digits listed.

Figure 2

A perspective view of the $(ac.ac.)_2SnCo_2(CO)_7$ molecule, the anisotropic atoms having 50% probability thermal ellipsoids



O2
O3
C2
C3
O4
C4
Co1
O1
C9
C1
C8
O11
C10
Sn
O8
C17
C7
O7
Co2
C11
C16
C12
O10
C15
C5
C6
O9
C13
O5
O6
C14

Table VII

Intramolecular Distances*

Atoms	Distances (Å)
Sn-Co$_1$	2.564(3)
Sn-Co$_2$	2.591(3)
Sn-O8	2.15(1)
Sn-O9	2.09(1)
Sn-O10	2.12(1)
Sn-O11	2.09(1)
Co$_1$-Co$_2$	2.626(4)
Co$_1$-C1	1.85(2)
Co$_1$-C2	1.73(2)
Co$_1$-C3	1.73(2)
Co$_1$-C4	1.72(2)
Co$_2$-C1	1.89(2)
Co$_2$-C5	1.74(2)
Co$_2$-C6	1.69(2)
Co$_2$-C7	1.74(2)
C1-O1	1.22(2)
C2-O2	1.17(2)
C3-O3	1.15(2)
C4-O4	1.19(2)
C5-O5	1.19(2)
C6-O6	1.20(2)
C7-O7	1.17(2)
O8-C16	1.27(2)
O9-C13	1.28(2)
C15-C13	1.35(2)
C15-C16	1.45(2)
C16-C17	1.56(2)
C13-C14	1.51(2)
O10-C11	1.32(2)
O11-C8	1.33(2)
C10-C8	1.32(2)
C10-C11	1.34(2)
C8-C9	1.56(2)
C11-C12	1.56(2)

* Numbers in parentheses are estimated standard deviations occurring in the last digits listed.

Table VIII

Intramolecular Angles

Atoms	Angles(°)	Atoms	Angles(°)
$Sn-\hat{Co}_1-Co_2$	59.88(9)	$Sn-\hat{O}8-C16$	126(1.0)
$Sn-\hat{Co}_2-Co_1$	58.88(8)	$O8-\hat{C}16-C17$	114(1.5)
$Co_1-\hat{Sn}-Co_2$	61.24(9)	$O8-\hat{C}16-C15$	130(1.6)
		$C16-\hat{C}15-C13$	123(1.7)
$Co_1-\hat{Sn}-O8$	98.7(3)	$C15-\hat{C}13-O9$	124(1.6)
$Co_1-\hat{Sn}-O9$	162.6(3)	$C14-\hat{C}13-O9$	117(1.5)
$Co_1-\hat{Sn}-O10$	100.9(3)	$Sn-\hat{O}9-C13$	131(1.0)
$Co_1-\hat{Sn}-O11$	107.7(3)		
$Co_2-\hat{Sn}-O8$	97.6(3)		
$Co_2-\hat{Sn}-O9$	101.4(3)	$Sn-\hat{O}10-C11$	129(1.2)
$Co_2-\hat{Sn}-O10$	101.3(3)	$O10-\hat{C}11-C12$	133(1.7)
$Co_2-\hat{Sn}-O11$	168.2(3)	$O10-\hat{C}11-C10$	123(1.9)
$O8-\hat{Sn}-O9$	84.4(4)	$C11-\hat{C}10-C8$	131(2.0)
$O8-\hat{Sn}-O10$	157.6(4)	$C10-\hat{C}8-O11$	124(1.8)
$O8-\hat{Sn}-O11$	79.4(4)	$O11-\hat{C}8-C9$	110(1.5)
$O9-\hat{Sn}-O10$	80.2(4)	$Sn-\hat{O}11-C8$	129(1.1)
$O9-\hat{Sn}-O11$	89.7(4)		
$O10-\hat{Sn}-O11$	84.4(4)		
$Co_1-\hat{C}1-Co_2$	89.2(9)		
$Sn-\hat{Co}_1-C1$	83.9(6)	$Co_1-\hat{C}1-O1$	138(1.5)
$Sn-\hat{Co}_1-C2$	168.6(7)	$Co_1-\hat{C}2-O2$	176(2.1)
$Sn-\hat{Co}_1-C3$	86.6(7)	$Co_1-\hat{C}3-O3$	175(2.0)
$Sn-\hat{Co}_1-C4$	89.7(7)	$Co_1-\hat{C}4-O4$	176(2.0)
$Sn-\hat{Co}_2-C1$	82.4(5)	$Co_2-\hat{C}1-O1$	133(1.5)
$Sn-\hat{Co}_2-C5$	87.3(7)	$Co_2-\hat{C}5-O5$	175(1.9)
$Sn-\hat{Co}_2-C6$	86.1(7)	$Co_2-\hat{C}6-O6$	178(2.0)
$Sn-\hat{Co}_2-C7$	168.9(7)	$Co_2-\hat{C}7-O7$	175(2.2)
$C4-\hat{Co}_1-C3$	111(1)	$C5-\hat{Co}_2-C6$	108(1)
$C4-\hat{Co}_1-C2$	92(1)	$C5-\hat{Co}_2-C7$	94(1)
$C3-\hat{Co}_1-C2$	103(1)	$C6-\hat{Co}_2-C7$	104(1)
$C1-\hat{Co}_1-C3$	100.6(9)	$C1-\hat{Co}_2-C6$	101.7(9)
$C1-\hat{Co}_1-C4$	147.2(9)	$C1-\hat{Co}_2-C5$	148.1(9)
$C1-\hat{Co}_1-C2$	88.7(9)	$C1-\hat{Co}_2-C7$	91.2(9)

Dihedral angle between planes defined by $Co_1-Cl-Co_2$ and $Co_1-Sn-Co_2$ = 113.0°.

Numbers in parentheses are estimated standard deviations occurring in the last digits listed.

Table IX

Angles in Chelate Rings

Atoms	Angles	Atoms	Angles
Sn-$\hat{\mathrm{O}}$8-C16	125.5(1.1)	Sn-$\hat{\mathrm{O}}$10-C11	128.9(1.2)
O8-$\hat{\mathrm{C}}$16-C15	130.0(1.6)	O10-$\hat{\mathrm{C}}$11-C10	122.6(1.9)
C16-$\hat{\mathrm{C}}$15-C13	123.1(1.7)	C11-$\hat{\mathrm{C}}$10-C8	130.8(2.0)
C15-$\hat{\mathrm{C}}$13-O9	123.9(1.6)	C10-$\hat{\mathrm{C}}$8-O11	124.1(1.8)
C13-$\hat{\mathrm{O}}$9-Sn	130.7(1.0)	C8-$\hat{\mathrm{O}}$11-Sn	128.8(1.1)

Numbers in parentheses are estimated standard deviations occurring in the last digits listed.

DISCUSSION

The molecular structure consists of a 6-coordinate tin atom having two acetylacetonate groups and a $Co_2(CO)_7$ group functioning as bidentate ligands. The Sn-Co-Co cluster approximates an equilateral triangle with the three bond angles being close to 60° (±1.3°). The two Sn-Co distances of 2.564(3)Å and 2.591(3)Å differ by the significant amount of 7σ. In absolute terms, the Δ of .027Å is probably large enough not to be attributed simply to systematic errors. The reason for the difference is not clear. If these Sn-Co bonds undergo asymmetric distortions in order to more readily accommodate the $Sn(ac.ac.)_2$ group, then some significantly close contacts might be expected between the members of the chelate rings and the carbonyl groups. However, there are no close contacts and the two chelate groups have virtually identical steric environments. The Sn-Co distances tend to be somewhat shorter than the other reported values of 2.66Å for $Ph_2Sn(Co(CO)_4)(Mn(CO)_5)$[15] and 2.61Å for $BrSn(Co(CO)_4)_3$[14]. The Co-Co distance (2.626Å) is considerably longer than the corresponding average distances in $CH_3CCO_3(CO)_9$ (2.47Å)[2] and in $Co_2(CO)_8$ (2.52Å)[31], but slightly shorter than that observed in $SCo_3(CO)_9$[16] (2.637Å). The Co-Co distances were observed to vary from 2.43Å → 2.55Å in the following cobalt carbonyl cluster compounds:

$CH_3CCo_3(CO)_9$[2], $(SC_2H_5)_4Co_6(CO)_{11}$[22],

$[SCo_3(CO)_7]_2S_2$[4], $(SC_2H_5)Co_5(CO)_{10}$[21],

$(C_2H_5S)_5Co_3(CO)_4$[20], $Co_4(CO)_{12}$[17,19],

and $FeCo_2(CO)_9S$[9].

One longer Co-Co distance has been reported for the compound $SCo_3(CO)_9$[16] (2.637(7)Å), but in this molecule the sulphur has an unpaired electron which Strouse and Dahl[9] have shown to exist in an anti-bonding metal orbital and this is thought to account for the exceptionally long distances observed for this compound. Since comparisons between the $SCo_3(CO)_9$ molecule and the tin molecule are scarcely valid due to the different systems involved, the long Co-Co distance in the tin compound may be primarily attributed to the large size of the tin atom. Further discussion on the trends in Co-Co distances for group IVb cobalt carbonyl cluster systems is undertaken in Chapter III.

The bridging carbonyl group subtends an angle of 89.2° at the Co-Co bond, a value which is somewhat greater than 83.6° obtained for $C_6H_5GeCo_3(CO)_{11}$[12]. The larger angle is a result of the longer Co-Co distance observed in the Sn compound. The bridging C to Co distances agree within one standard deviation of the mean value 1.87(2)Å. This distance is a little shorter than the equivalent distance of 1.92Å found in $Co_2(CO)_8$[31]. Another interesting structural feature is the dihedral angle of 113° between the $SnCo_1Co_2$ plane and the Co_1Co_2 bridging carbonyl plane. It should be of interest to compare this dihedral angle with the one determined in $C_6H_5GeCo_2(CO)_{11}$[12].

The geometries of the two $Co(CO)_3$ groups compare nicely, there being no significant differences in the bond angles and lengths or the orientation of the $Co(CO)_3$ groups about the Co-Co bond. The mean Co-C distance of 1.73Å is somewhat shorter than the more usually observed value of between 1.78Å - 1.80Å for cobalt carbonyl cluster compounds.

The geometry of the chelate groups shows some unusual features. The two Sn-O distances which are trans to the Sn-Co bond tend to be shorter at 2.09(1)Å than the average distance for the other two Sn-O bonds of 2.14(1)Å. The four C-C distances have a mean value of 1.37Å. The calculated r.m.s. value for the distances is .06Å, a value which does not agree well with the estimated error of .02Å from ORFFE[73]. Hence these distances may not be treated as a single population. However, these bond length variations show no consistent pattern and it is likely that the data are suffering from a systematic error. Similarly, the r.m.s. value for the mean C-O distance of the chelate groups is .03Å, a value which is somewhat larger than the value of .02Å calculated from ORFFE.

A review[15] on 13 monomeric structures containing these chelates gave the average length of the C-C (excluding $C-CH_3$) bond as 1.39Å which is approximately equal to the C-C distance in benzene. The average C-O distance from this review was 1.28Å. The mean $C-CH_3$ distance of 1.54Å is only slightly longer than the average reported value of 1.52Å. There is no convincing structural evidence for an acetylacetone ring having bond lengths significantly distorted from those expected for a delocalized system. However, from N.M.R. studies Kawasaki *et al.*[23] noted that for the molecules $X_2Sn(ac.ac.)_2$ (X = Cl, Br and I) two distinct methyl resonances were received. This implied that the methyl groups are in different environments, i.e., the acetylacetonate rings have a distorted structure containing somewhat localized bonds. If $Cl_2Sn(ac.ac.)_2$ were trans and symmetrical bonding were obtained, the compound would have D_{2h} symmetry and all of the methyl groups would be equivalent. However, Davison *et al.*[24] have shown that the coincident bonds in the infrared and Raman spectra, particularly those in the low-frequency region attributable to Sn-O and Sn-Cl vibrations, imply the absence of a centre of inversion and consequently the C_2 symmetry of cis-$Cl_2Sn(ac.ac.)_2$. This cis structure has two non-equivalent methyl groups which give rise to the two distinct methyl resonances. These two peaks collapse to a single signal at higher temperatures, and Davison[24] explains this as being due to the conversion of one enantiomorph of the cis molecule to the other at a rate which is fast on the N.M.R. time scale, rather than a rapid exchange of somewhat localized bonds. Davison proposes two possible mechanisms for this configurational change. Based on the observation that the γ-proton to Sn coupling is apparent before, during and after the coalescence of the two methyl protons, he proposes a non-dissociative mechanism involving a "twist" mechanism via a C_{2v} intermediate. A second possibility is conversion through a 5-co-ordinate intermediate. The N.M.R. spectrum for $(ac.ac.)_2SnCo_2(CO)_7$ did not display the split methyl proton splitting that was observed for $(ac.ac.)_2SnCl_2$. However, since the splitting is not expected to be large, it may have been obscured by quadruple broadening of the signal causes by the cobalt atoms. Another possibility, as suggested by Graham *et al.*[13] is that either of the averaging mechanisms aforementioned could be operating at lower temperatures.

CHAPTER III

The Crystal and Molecular Structures of $C_6H_5\text{-}GeCo_3(CO)_{11}$

INTRODUCTION

The reaction of $C_6H_5GeH_3$ with $Co_2(CO)_8$ in n-hexane at room temperature affords the compound $C_6H_5GeCo_3(CO)_{11}$[4]. The solution I.R. showed there to be two peaks in the bridging carbonyl region, indicating that two possible isomers for the compound could exist, one isomer having the bridging carbonyl group bent away from the phenyl group, and the other towards the phenyl group. The facility with which the cobalt-cobalt bridging carbonyl compounds form is thought to be related to the size of the bridging component and considerable variations in the Co-Co distances are expected. In order to determine the structure of the molecule $C_6H_5GeCo_3(CO)_7$ and further study the trends in Co-Co bond lengths, a 3-D X-ray analysis was undertaken.

EXPERIMENTAL

Orange crystals of $C_6H_5GeCo_3(CO)_{11}$ were prepared in Dr. Graham's laboratory by the reaction of $C_6H_5GeH_3$ with $Co_2(CO)_8$ in hexane at room temperatures[4]. Well-formed needle shaped crystals were obtained after recrystallization from the same solvent.

Optical and preliminary X-ray examination of the crystals showed 2/m Laué symmetry and the observed systematic absences $(h0\ell)\ \ell = 2n+1$, $(0k0)\ k = 2n+1$ uniquely defined the monoclinic space-group as $P2_1/c$. The lattice constants were measured from precession photographs using MoK_α radiation and the errors determined using the method of Patterson and Love[26]: $a = 9.173\ (\pm.004)$, $b = 13.203\ (\pm.007)$, $c = 18.98\ (\pm.01)$, $\beta = 105.07°\ (\pm.05)$. The density was determined by flotation using Clerici's solution. The experimentally observed density of 1.91 agrees well with the calculated density of 1.90 for a unit cell volume of 2220Å^3, $Z = 4$, and a molecular weight of 634.6.

The crystal was mounted about the b-axis and using a Pailred Linear Diffractometer all the reflections lying within one quarter of a sphere of reciprocal space corresponding to a d-spacing of $\geqslant 1\text{Å}$ were collected. To minimize the absorption problem, crystal monochromatized Mok_α radiation ($\mu = 37\ cm^{-1}$) was used in preference to CuK_α radiation ($\mu = 200\ cm^{-1}$) and a crystal with a small μR (range .29 → .59) chosen. Since similar crystals had been observed to decompose slowly on exposure to air, the crystal was mounted on a thin glass fibre and sealed in a Lindeman glass capillary (diam. = .3mm) under an inert atmosphere of nitrogen. Each reflection was scanned once at a scan speed of 1°/min. with a stationary 20 second background count being taken on either side of the scan. The scan width was gradually increased from 1.6° for the zero layer up to 4.0° for the higher layers to allow for the broadening peak profiles with larger equi-inclination angles. A set of standard reflections collected at the beginning of each new layer indicated that no decomposition correction was necessary.

Reflections were rejected on the basis of two criteria: (1) $I \leqslant 0$, and (2) $I < 2\sigma I$. Lorentz and polarization corrections were applied to the remaining 1927 reflections and standard deviations calculated using the expression $\sigma(I) = [P + (t_1/t_2)^2(B_1+B_2) + (\ pI\ )^2]^{\frac{1}{2}}$ where P is the total integrated peak count obtained in time t_1, B_1 and B_2 are the background counts obtained in time t_2, and $I = P - t_1/t_2(B_1+B_2)$. The p term takes into account the indeterminant errors, including machine instability, and prevents ridiculously high weights from being given to strong reflections.

STRUCTURE SOLUTION AND REFINEMENT

The positions of the germanium atom and the three cobalt atoms were obtained from the Patterson map. The remaining carbon and oxygen positions were readily determined from a difference Fourier and the structure refined using conventional full matrix least squares calculations. The atomic scattering factors calculated by Cromer and Waber[27] were employed, for atoms other than hydrogen, with anomalous disperson corrections[28] for the germanium and cobalt atoms being included in Fc. The atomic scattering factors used for hydrogen were those experimentally determined by Mason and Robertson[29].

The function minimized during the full matrix least squares refinement was $\sum w(|Fo|-|Fc|)^2$ where $|Fo|$ is the observed structure amplitude, $|Fc|$ is the calculated structure factor amplitude and the weighting factor $w = 1/(\sigma F)^2$. Initially all atoms were assigned variable isotropic thermal parameters and after four cycles of refinement of the 129 variables (scale factor plus three positional and one thermal parameter per atom), the usual discrepancy factors $R_1 = \sum||Fo|-|Fc||/\sum|Fo|$ and R_2 (or weighted R factor) = $\left\{\sum w(|Fo|-|Fc|)^2/\sum wFo^2\right\}^{\frac{1}{2}}$ were 10.0% and 9.4%

respectively. At this stage of the refinement the data were corrected for absorption and the heavy atoms allowed to refine anisotropically. In order to save computer time and storage, ensuing refinements were carried out with the phenyl group as a rigid body restricted to its well known geometry (D_{6h} symmetry, C=C = 1.392Å). Next the C-H distance in the phenyl group was assumed to be 1.0Å and the hydrogen atoms were introduced at their five calculated positions. Each H-atom was assigned a temperature factor one unit higher than the adjacent carbon atom.

During the final cycle of least squares refinement no parameter shifted by more than one half of its estimated standard deviation and R_1 = 7.4%, and R_2 = 6.4%. The final standard deviation for an observation of unit weight was 2.745, rather higher than the expected value of unity. There are two main reasons for this occurrence:

(1) The theoretical model did not take into account the anisotropic vibrations of the light atoms.

(2) The value of p used in the expression for determining the weights could have been made larger, e.g., .05.

The final difference map contained five peaks with electron density from $.74e^-/\mathring{A}^3$ up to $.95e^-/\mathring{A}^3$. These peaks could be attributed to the anisotropic vibrations of the carbonyl moieties. All the remaining peaks showed electron densities less than $.70e^-/\mathring{A}^3$.

The correlation matrix indicated that there is a high correlation (.86) between two of the angles used to define the orientation of the rigid body. This is a consequence of the particular coordinate system used but is not sufficiently high to give trouble.

A comparison of the final observed and calculated structure factors indicated that no reflections were suffering appreciably from secondary extinction.

Table X

Observed and calculated structure amplitudes (x10) in electrons for $C_6H_5GeCo_3(CO)_{11}$

Table XI

Final Atomic Positional and Thermal Parameters

Atom	x	y	z	B(Å^2)
Ge	.2319(2)	.2362(1)	.1680(1)	3.1
Co$_1$	-.0097(2)	.1792(1)	.1777(1)	3.0
Co$_2$	.1769(2)	.0631(1)	.1386(1)	2.9
Co$_3$	.2576(2)	.3661(1)	.0795(1)	3.7
C1	.3004(27)	.4623(18)	.0251(11)	9.3(.6)
O1	.3307(19)	.5267(13)	-.0097(9)	11.9(.5)
C2	.4231(23)	.3032(13)	.0823(9)	6.3(.4)
O2	.5353(16)	.2594(9)	.0806(6)	8.0(.3)
C3	.2391(19)	.4471(12)	.1466(9)	5.9(.4)
O3	.2193(14)	.5023(9)	.1930(6)	7.7(.3)
C4	.0841(22)	.3329(12)	.0167(9)	6.3(.4)
O4	-.0301(16)	.3237(9)	-.0256(7)	8.2(.3)
C5	.2682(20)	.0574(12)	.0700(9)	6.0(.4)
O5	.3293(14)	.0537(8)	.0225(6)	6.9(.3)
C6	.3158(18)	.0269(11)	.2219(8)	4.9(.4)
O6	.3897(15)	.0002(8)	.2764(7)	7.9(.3)
C7	.0778(18)	-.0558(12)	.1316(8)	4.9(.3)
O7	.0106(14)	-.1274(9)	.1309(6)	7.1(.3)
C8	-.0097(18)	.1257(11)	.0856(8)	10.8(.4)
O8	-.0833(13)	.1238(7)	.0224(5)	5.8(.3)
C9	-.0718(19)	.3015(13)	.1626(8)	5.7(.4)
O9	-.1168(15)	.3857(10)	.1562(6)	8.1(.3)
C10	-.1811(20)	.1138(11)	.1651(8)	5.1(.4)
O10	-.2972(13)	.0711(8)	.1529(5)	6.3(.3)
C11	.0593(17)	.1539(10)	.2735(8)	4.2(.3)
O11	.1039(13)	.1376(8)	.3353(6)	6.7(.3)

Continued over......

Table XI (Continued)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ge	822(22)	482(9)	211(5)	6(14)	-17(8)	-17(6)
Co_1	720(31)	495(13)	217(7)	33(18)	26(11)	-14(8)
Co_2	858(30)	409(11)	210(6)	13(17)	12(11)	-22(7)
Co_3	954(35)	553(14)	273(7)	-44(19)	0(13)	79(8)

Rigid Bodies

Phenyl Ring

Atom	x	y	z	$B(\text{Å}^2)$
C12	.3858(25)	.2653(7)	.2593(8)	3.3(.3)
C13	.5317(19)	.2279(7)	.2681(9)	4.4(.3)
C14	.6409(18)	.2431(7)	.3337(4)	5.6(.4)
C15	.6043(25)	.2957(7)	.3905(8)	5.8(.4)
C16	.4584(19)	.3331(7)	.3817(9)	5.3(.4)
C17	.3492(18)	.3179(7)	.3161(4)	4.4(.3)
D	2.109(.006)			
E	2.59(.01)			
F	.28(.01)			

Hydrogen Ring

Atom	x	y	z	$B(\text{Å}^2)$
H13	.5589	.1955	.2249	5.4
H14	.7484	.2209	.3370	6.6
H15	.6856	.3049	.4370	6.8
H16	.4332	.3636	.4250	6.3
H17	.2437	.3382	.3129	5.4
D	2.066			
E	2.622			
F	1.346			

Numbers in parentheses are estimated standard deviations occurring in the last digits listed.

Figure 3

A perspective view of the $C_6H_5GeCo_3(CO)_{11}$ molecule, the anisotropic atoms having 50% probability thermal ellipsoids

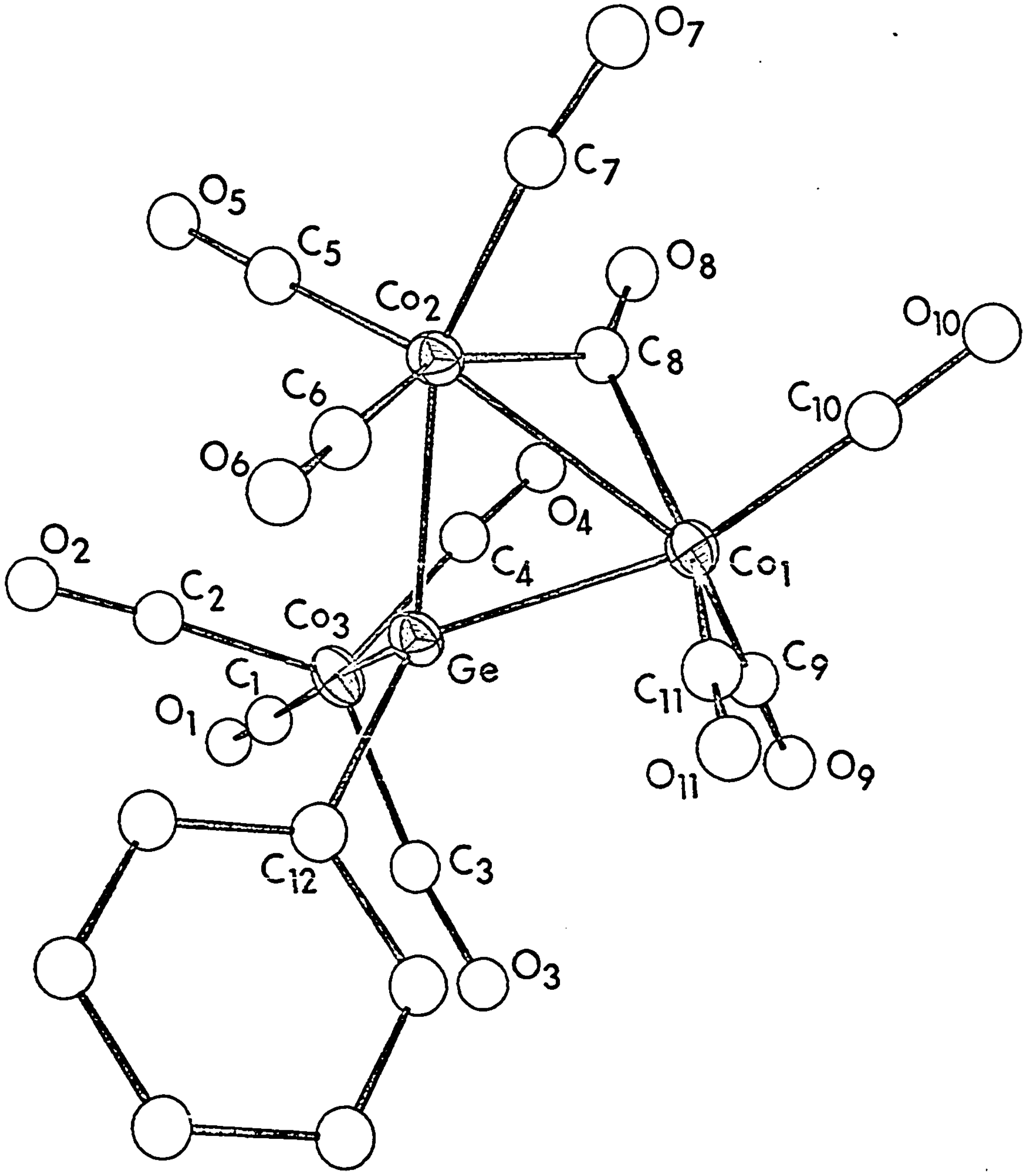

O7
C7
O5
C5
O8
Co2
O10
C8
C6
C10
O6
O4
O2
C4
Co1
C2
Co3
C1
Ge
C9
C11
O1
O11
O9
C12
C3
O3

Table XII

Intramolecular Distances in C_6H_5-$GeCo_3(CO)_{11}$*

Atoms	Distances (Å)
Ge-Co_1	2.392(3)
Ge-Co_2	2.375(3)
Ge-Co_3	2.456(3)
Ge-C12	1.967(8)
Co_1-Co_2	2.546(3)
Co_1-C8	1.89(1)
Co_1-C9	1.71(2)
Co_1-C10	1.76(2)
Co_1-C11	1.79(2)
Co_2-C8	1.93(1)
Co_2-C5	1.72(2)
Co_2-C6	1.82(2)
Co_2-C7	1.80(2)
Co_3-C1	1.75(2)
Co_3-C2	1.72(2)
Co_3-C3	1.71(2)
Co_3-C4	1.78(2)
C1-O1	1.15(2)
C2-O2	1.19(2)
C3-O3	1.19(2)
C4-O4	1.15(2)
C5-O5	1.18(2)
C6-O6	1.14(2)
C7-O7	1.13(2)
C8-O8	1.21(1)
C9-O9	1.18(2)
C10-O10	1.17(2)
C11-O11	1.16(1)

* Numbers in parentheses are estimated standard deviations occurring in the last digits listed.

Table XIII

Intramolecular Angles in $C_6H_5-GeCo_3(CO)_{11}$

Atoms	Angles (°)	Atoms	Angles (°)
$Co_2-\hat{Ge}-Co_1$	64.57(8)	$Co_1-\hat{C}8-O8$	142(1.2)
$Ge-\hat{Co}_1-Co_2$	57.40(8)	$Co_1-\hat{C}9-O9$	176(1.5)
$Ge-\hat{Co}_2-Co_1$	58.03(7)	$Co_1-\hat{C}10-O10$	176(1.4)
		$Co_1-\hat{C}11-O11$	180(1.3)
$C12-\hat{Ge}-Co_2$	117.0(3)		
$C12-\hat{Ge}-Co_1$	117.5(3)	$Co_2-\hat{C}8-O8$	134(1.2)
$C12-\hat{Ge}-Co_3$	107.0(3)	$Co_2-\hat{C}5-O5$	179(1.4)
$Co_2-\hat{Ge}-Co_3$	124.29(9)	$Co_2-\hat{C}6-O6$	173(1.5)
$Co_1-\hat{Ge}-Co_3$	121.9(1)	$Co_2-\hat{C}7-O7$	175(1.4)
$Ge-\hat{Co}_1-C8$	79.8(5)	$Co_3-\hat{C}1-O1$	179(2.0)
$Ge-\hat{Co}_1-C9$	88.0(6)	$Co_3-\hat{C}2-O2$	177(1.5)
$Ge-\hat{Co}_1-C10$	163.7(5)	$Co_3-\hat{C}3-O3$	177(1.6)
$Ge-\hat{Co}_1-C11$	92.7(5)	$Co_3-\hat{C}4-O4$	172(1.6)
$Ge-\hat{Co}_2-C8$	79.4(4)	$Ge-\hat{Co}_3-C1$	171.9(7)
$Ge-\hat{Co}_2-C5$	96.0(5)	$Ge-\hat{Co}_3-C2$	83.3(5)
$Ge-\hat{Co}_2-C6$	89.5(5)	$Ge-\hat{Co}_3-C3$	83.2(5)
$Ge-\hat{Co}_2-C7$	158.2(5)	$Ge-\hat{Co}_3-C4$	93.3(5)
$C6-\hat{Co}_2-C5$	106.1(7)	$C11-\hat{Co}_1-C9$	111.1(7)
$C6-\hat{Co}_2-C7$	93.5(6)	$C11-\hat{Co}_1-C10$	96.5(7)
$C5-\hat{Co}_2-C7$	103.9(7)	$C9-\hat{Co}_1-C10$	101.2(8)
$C8-\hat{Co}_2-C5$	99.4(7)	$C8-\hat{Co}_1-C9$	106.2(6)
$C8-\hat{Co}_2-C6$	153.2(6)	$C8-\hat{Co}_1-C11$	141.7(6)
$C8-\hat{Co}_2-C7$	88.4(6)	$C8-\hat{Co}_1-C10$	84.6(7)

Dihedral angle between the planes defined by $Co_1-C8-Co_2$ and $Co_1-Ge-Co_2$ = 95.0°.

Numbers in parentheses are estimated standard deviations occurring in the last digits listed.

DISCUSSION

The molecule was found to consist of a distorted tetrahedron about the germanium atom, with two of the cobalt atoms being bridged to give a $Co_2(CO)_7$ moiety similar to that found in $(ac.ac.)_2SnCo_2(CO)_7$[35]. The observation in the solution I.R. spectrum for this compound of two carbonyl stretching bands in the bridging carbonyl region (one peak at 1850 cm^{-1} with a weak shoulder at 1835 cm^{-1})[4] indicated that the compound could exist as two isomers, one isomer having the bridging carbonyl bent away and the other towards the phenyl group. This compound consists of the former isomer with the dihedral angle between the Co-Co-CO plane and the CoCoGe plane being 95°. This angle is somewhat smaller than observed for the 6-co-ordinate tin compound $(ac.ac.)_2SnCo_2(CO)_7$ which has a dihedral angle of 113°. Why the bridging cobalts should prefer this dihedral angle to be 18° less in the Ge system is not clear. There appear to be no steric reasons for this decrease in the dihedral angle for the germanium molecule, since the bridging carbonyl groups make no significant Van der Waals close contact in either structure.

The Co-Co bond length of 2.546(3)Å is significantly shorter than that for the $(ac.ac.)_2SnCo_2(CO)_7$

molecule (2.626(4)) which might be expected since the germanium atom (cov. radius = 1.22Å) is smaller than the tin atom (cov. radius = 1.39Å). It should be pointed out that the covalent radius for tin was determined from the tetrahedrally co-ordinated tin molecule $((C_6H_5)_2Sn)_6$[30], and one might expect some variation from this value in 6-co-ordinate tin structures. A comparison of the Co-Co distance in the $Co_2(CO)_7$ moiety with that in dicobalt octacarbonyl (2.52Å)[31] shows a small but significant increase for the germanium bridged molecule. The Co-Co distances for the non-bridged species tend to be long, being 2.661(3)Å in $Co_2(CO)_6(P(C_6H_5)_3)_2$[36], 2.667(6)Å in $Co_2(CO)_6[P(OC_6H_5)_3]_2$[37], 2.67(11)Å in $Co_2(CO)_6[P(n\text{-}C_4H_9)_3]_2$[38,39], and as long as 2.74Å in $Co_2(CHCH_3)_{10}^{4+}$[40]. It is interesting to note that the Co-Co distance in the $Co_2(CO)_6[PR_3]_2$ series is relatively insensitive to the nature of the attached ligand. From the available data it would appear that bridged systems of this type have Co-Co bond lengths which are considerably shorter than those for non-bridged systems. It is also apparent that the Co-Co distance increases as the size of group IVb bridging group increases, being 2.52Å for $Co_2(CO)_8$[31] which has two bridging carbonyl groups, 2.546(3) for

$C_6H_5GeCo_2(CO)_{11}$ which has one carbonyl and a germanium atom bridging the Co-Co bond, and 2.626(4) for $(ac.ac.)_2SnCo_2(CO)_7$[35] which has a carbonyl group and a tin atom bridging the Co-Co bond. In the similar Fe-Fe system[41,42,43], it has been observed that when the Fe-Fe bond is bridged by either a sulphur or a germanium atom the distances tend to be greater than those observed in a non-bridged system. When, however, the Fe-Fe bond is bridged by a carbonyl group, the Fe-Fe distance tends to be somewhat less than that observed in a non-bridged system.

Although the Ge-Co distances of 2.392(3) and 2.375(3) are different in a statistical sense, σ for $\Delta = .004\text{Å}$ and $^{\Delta}/\sigma \sim 4$, the absolute error is very small and could possibly be accounted for from systematic errors in the data. The two cobalt bridging carbonyl distances both agree within 2σ of the mean value 1.91(1)Å.

For the $(ac.ac.)_2SnCo_2(CO)_7$ molecule the $Co(CO)_3$ groups are eclipsed when viewed down the Co-Co bond. However, for the $C_6H_5GeCo_3(CO)_{11}$ molecule the $Co(CO)_3$ groups are slightly rotated with respect to one another. No contacts less than the Van der Waals distances are made, and one might speculate that this distortion might make for the easier accommodation of the large Ge-atom, although no such distortions were observed for the 6-co-ordinate Sn compound. The Co-C distances in the $Co(CO)_3$ groups show considerable variations ranging from 1.71 → 1.82Å. The estimated standard deviation of 0.04Å compared with the experimentally determined value of .02Å would indicate, if this latter value σ can be believed, that we are not dealing with a single population of Co-C distances. The two carbonyls which are trans to the Co-Co bond have Co-C distances of 1.71Å and 1.72Å, both considerably shorter than the mean value of 1.79Å observed for the remaining carbonyls on the $Co(CO)_3$ moieties. The shortest Co-C distance in the $(ac.ac.)_2SnCo_2(CO)_7$ molecule was also trans to the Co-Co bond. When looking at such small differences in bond length, very accurate structural determinations are needed. For comparison purposes, many of the structures in the literature are of poor resolution due either to disorder problems, the low precision of film data, or the lack of accurate corrections for systematic errors such as absorption, extinction and anomalous dispersion. The Co-C distances in the terminal $Co(CO)_4$ group also have a considerable range, 1.71 → 1.78. The two equatorial carbonyl groups which are bent up towards the Ge show Co-C distances of 1.71Å and 1.72Å. The equatorial carbonyl which is bent away from the germanium has a Co-C distance of 1.78Å. These values, however, do not vary from the mean value of 1.74Å for the $Co(CO)_4$ moiety by a significant amount. If the mean values of the Co-C distances within the $Co_2(CO)_7$ groups are compared for the structures $Co_2(CO)_8$, $C_6H_5GeCo_3(CO)_{11}$ and $(ac.ac.)_2SnCo_2(CO)_7$, a trend for shorter Co-C (terminal) distances as the group IVb element increases in size is apparent, being 1.80Å, 1.765Å and 1.725Å for these molecules respectively. A small decrease in the cobalt to bridging carbonyl carbon distance is also apparent, being 1.92Å, 1.91Å and 1.87Å for the respective molecules. These trends probably indicate an increase in the amount of π-bonding taking place between the cobalts and the carbonyl groups as we ascend the group IVb series. The mean C-O distance for the terminal carbonyls of 1.16(2)Å agrees well with 1.18(2)Å for the $(ac.ac.)_2SnCo_2(CO)_7$ molecule, and 1.17Å for the $Co_2(CO)_8$ molecule. The bridging C-O distance of 1.21(2)Å agrees well with 1.22(2)Å, and 1.21Å for the above two molecules respectively.

Although the three structures determined in this part of the thesis have added considerably to our knowledge of the molecular dimensions of these cobalt cluster compounds and the trend for longer Co-Co bonds with the increasing size of the main group IVb bridging group noted, more data need to be collected before any firm conclusions can be drawn as to the ability of the MCo_3 nucleus to form a "closed" system.

A similar series of "closed" cluster compounds containing the group VIb elements, S, Se and Te, has been prepared by Dahl:

$SCo_3(CO)_9$[9,16] $SeCo_3(CO)_9$[9]

$SCo_2Fe(CO)_9$[9] $SeCo_2Fe(CO)_9$[9] $TeCo_2Fe(CO)_9$[10]

It is of interest to note that whereas Te (cov. radius = 1.37Å compared with Sn = 1.39Å)[46] is able to form a "closed" system with $FeCo_2(CO)_9$, attempts to make $TeCo_3(CO)_9$[10] have not been successful. Structural studies by Dahl[9,16] of the paramagnetic complex $SCo_3(CO)_9$ and its isomorphous diamagnetic analogue $SCo_2Fe(CO)_9$ showed that the formal removal of an unpaired electron by substitution of an iron for a cobalt atom has resulted in a remarkable shortening of the average Co-Co distance from 2.637(7)Å in $Co_3(CO)_9S$

to 2.554(7)Å in $SFeCo_2(CO)_9$. From e.s.r. studies Dahl[9] has shown the unpaired electron in the $SCo_3(CO)_9$ molecule to lie in a molecular orbital comprised primarily of an antibonding combination of d-orbitals essentially localized in the plane of the cobalts. Apart from the unpaired electron, the molecular geometry of these group VIb cobalt cluster compounds may be substantially influenced by a lone pair effect[18]. The lone pair of electrons on S, Se and Te may well repulse the metals strongly enough to give rise to the "closed" systems. Since the covalent radii of Sn(1.39Å) and Te(1.37Å) are very close and the size of the Co and Fe atoms are comparable, the one obvious factor which might really favour the formation of $TeCo_2Fe(CO)_9$, but not the formation of the analogous hypothetical $R\text{-}SnCo_3(CO)_9$ molecule, are the repulsion forces from the lone pair of electrons on the Te atom. The possibility of making the anion $SnCo_3(CO)_9^-$ is not an unreasonable idea. The lone pair on the Sn atom would have a similar effect to the lone pair on the analogous $TeCo_2Fe(CO)_9$ molecule, with any excessive charge on the tin atom being redistributed over the carbonyl groups. However, efforts to isolate the analogous P, As and Sb group Vb[36] molecules have not been successful, although the possibility of their forming as intermediates cannot be discounted.

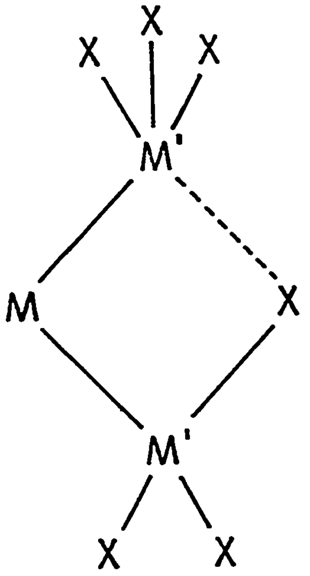
When this study was undertaken, it was naively believed that the ability of the group IVb elements to form closed cluster carbonyl structures was related purely to the size of the element involved. The inability of silicons to form a "closed" $MCo_3(CO)_9$ system, however, would indicate that facets other than size are of importance. That one of these facets may be a subtle electronic effect is evidenced in the observed inability of the group Vb elements to form the closed $MCo_3(CO)_9$ system which is isoelectronic with the group VIb $MCo_2Fe(CO)_9$ compounds. The bonding schemes within these molecules must be very complex and the use of simple stick bonds to describe them inadequate. A more detailed knowledge of the molecular electronic energy levels might greatly facilitate the elucidation of the kinds of bonding involved within these structures.

PART B

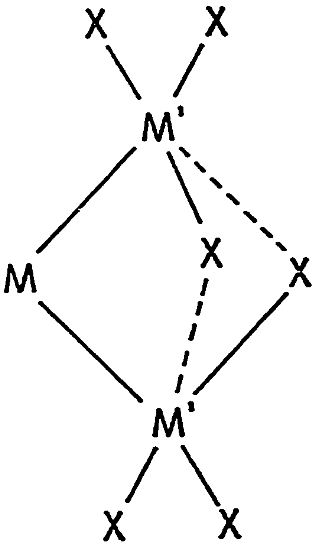
PART B

GENERAL INTRODUCTION

Compounds of the type $M(CO)_4(M'X_3)_2$ (where M = Fe, Ru, Os; M' = Si, Ge, Sn; X = Cl, Br, I, alkyl or aryl) have been found to exist as cis and/or trans isomers[47,48,49,50,51]. There are several factors which can affect the relative stability of the cis and trans isomers. A consideration of π-bonding abilities for the ligands CO and $M'X_3$ suggests that any discrepancy (either $CO >> M'X_3$ or $M'X_3 >> CO$) would favour the cis isomer. These relative π-bonding abilities would be expected to vary with M, M', and X. The other major factor influencing the preferred geometry involves intramolecular repulsions. Thus the investigations of Stone *et al.*[47,51] on trialkyl and triaryl, silyl and stannyl derivatives of $Ru(CO)_4$, where definite equilibria were established, showed increasing preference for the trans structure as the bulkiness of the $M'R_3$ group increased. However, when X = a halogen in the cis compounds, an additional interaction may be possible but attractive in nature rather than repulsive. This is due to the potential to form intramolecular halogen bridges of the type suggested by Graham *et al.*[49,52,53,54], for example:



or



While the formation of weak halogen bridges was demonstrated in bipy(OC)$_3$ClMoSnCH$_3$Cl$_2$[57] and 4-bromo-1,2,3,4-tetraphenyl-cis,cis-1,3-butadienyl dimethyl tin bromide, as yet there is no direct confirmation that cis M'X$_3$ groups do interact in this way.

Of particular interest was the synthesis and isolation of both the cis and trans isomers of bis(trichlorogermanyl) tetra carbonyl ruthenium (Ru(CO)$_4$(GeCl$_3$)$_2$) where the spectroscopic properties suggested that the π acceptor properties of GeCl$_3$ were comparable with those of carbon monoxide. The unusual solubility properties of the cis and trans isomers raised the serious question that the cis and trans isomers might contain intra and intermolecular halogen to Ge bridge bonding respectively. From dipole moment considerations the cis isomer would be expected to be more soluble in polar organic solvents, but the reverse is true. It was also found that the cis isomer melts at 95°, whereas the trans isomer decomposes without melting only at temperatures greater than 200°. The current structural study was undertaken to investigate these features.

CHAPTER IV

The Crystal and Molecular Structures of
trans-$Ru(CO)_4(GeCl_3)_2$
and
cis-$Ru(CO)_4(GeCl_3)_2$

EXPERIMENTAL

(a) Trans-$Ru(CO)_4(Ge(Cl_3))_2$

The white well formed crystals kindly supplied by Dr. W.A.G. Graham were found to be suitable for an X-ray diffraction study. The preliminary photography - CuK_α Weissenbergs $0k\ell$, $1k\ell$, $2k\ell$, and MoK_α precession $h0\ell$, $0k\ell$ - showed the crystal to be monoclinic, and the systematic absences - $0k0$ for $k = 2n+1$, and $h0\ell$ for $h+\ell = 2n+1$ - suggested the non-standard space group $P2_1/n$. The lattice parameters and their e.s.d.'s were obtained as $a = 9.1518(9)\text{Å}$, $b = 10.025(1)\text{Å}$, $c = 8.3988(8)\text{Å}$, $\beta = 94.84(1)°$ by a least squares analysis using data from 12 high angle reflections that had been accurately centred on a Picker four-circle diffractometer using $CuK_{\alpha 1}$ radiation ($\lambda = 1.54051\text{Å}$). The observed density ($2.40\ g/cm^3$) is in good agreement with that calculated ($2.39\ g/cm^3$) for $Z = 2$, and hence the molecules are situated at sites of symmetry $\bar{1}$. The crystal used in this study was a small centrosymmetric prism with well formed $\bar{1}10$, $10\bar{1}$, 011, and 110 faces and their respective centrosymmetrically related faces $1\bar{1}0$, $\bar{1}01$, $0\bar{1}\bar{1}$, and $\bar{1}\bar{1}0$. The perpendicular distances between each of these faces and its centrosymmetrically related mate were .0178 cm, .0122 cm, .024 cm and .0190 cm respectively. The crystal was mounted with a* coincident with the ø axis of a Picker manual four-circle diffractometer. Intensity data were collected using MoK_{α} radiation that had been monochromatized by a graphite crystal (002 reflecting plane) to minimize absorption corrections $-CuK_{\alpha}$ $\mu = 223.0$ cm^{-1} and MoK_{α} $\mu = 58.6$ cm^{-1}. The coupled $w/2\theta$ scanning technique was used from $2\theta = -1.5°$ to $2\theta = +1.5°$ with a scan rate of 2°/min. and a 2θ maximum limit of 45°. Backgrounds were estimated from a linear interpolation of two 30 sec. stationary crystal stationary counter measurements made at the limits of the scan. As a check on the absorption correction, three h00 reflections having 2θ values of 8.9°, 17.9° and 36.2° were measured over a range of 0 - 180° in ø at intervals of 10°. Six reflections with a good range of 2θ values were measured periodically throughout the data collection and showed no evidence for decomposition, the deviations being ±1%. The data were corrected for Lorentz polarization effects and reduced to structure factor amplitudes with standard deviations estimated as previously described. An absorption correction was applied with the transmission factor range being 0.40 → 0.45. The ø-scan data, after the absorption correction, showed an internal consistency of ±3%. Of the 806 independent reflections measured, 667 were estimated to be significantly above background using a criterion $I/\sigma(I) \geqslant 3.0$ where $\sigma(I)$ was calculated using pure counting statistics.

(b) Cis-$Ru(CO)_4(GeCl_3)_2$

The white crystals were kindly prepared by R.K. Pomeroy and supplied by Dr. Graham. A suitable crystal was only obtained after the compound had been sublimed in a sealed tube at 40°C. for two weeks. The preliminary photography showed the crystal to be monoclinic with the systematic absence 0k0 for k = 2n+1, which suggested either $P2_1$ or $P2_1/m$ as the possible space group. The lattice parameters and their e.s.d.'s were obtained as a = 9.759(5), b = 12.608(10), c = 12.878(9) and β = 91.57(1)° with their e.s.d.'s being obtained from 11 high angle reflections as previously described. The observed density of 2.40 g/cm^{-3} is in good agreement with the calculated value of 2.39 g/cm^{-3} for Z = 4. The crystal used for the intensity data was bound by the faces 101, $\bar{1}0\bar{1}$, $\bar{1}01$, $10\bar{1}$, 001, $00\bar{1}$, 010 and $0\bar{1}0$, and had approximate dimensions .12 mm x .09 mm x .12 mm. The crystal was mounted with b* coincident with the ø-axis of a Picker manual four-circle diffractometer. The same methods as for the trans compound were used for the data collection of the cis isomer with MoK$_\alpha$ radiation ($\mu = 57.8$ cm^{-1}) being used in preference to CuK$_\alpha$ radiation ($\mu = 220.0$ cm^{-1}). As a check for decomposition six reflections having a good range of 2θ values were measured periodically and showed no evidence for decomposition, the deviations being ±1.5%. As a check on the absorption correction three reflections having 2θ values of 12.9°, 19.5° and 32.7° were measured over a range of 0 - 180° in ϕ at intervals of 10°. Lorentz, polarization and absorption effects were corrected for, and the data reduced to structure amplitudes with standard deviations estimated as previously described. The transmission factor range for the absorption correction was $0.47 \rightarrow 0.65$. The ϕ-scan data, after the absorption correction, showed an internal consistency of ±3%. Of the 1752 independent reflections measured, 1087 were estimated to be significantly above background using the criterion $I/\sigma(I) \geqslant 2.0$ where $\sigma(I)$ was calculated using pure counting statistics.

STRUCTURE SOLUTION AND REFINEMENT

(a) Trans-$Ru(CO)_4(GeCl_3)_2$

$P2_1/n$ is a non-standard space group and the general positions were derived as:

x,y,z	½+x, ½-y, ½+z
$\bar{x},\bar{y},\bar{z}$	½-x, ½+y, ½-z

The site symmetry of the molecule being , the two Ru atoms were one set of special positions located at special positions 0,0,0; ½,½,½. To determine the position of the Ge atom, consideration was given to the vectors, other than the origin, and their multiplicities, in order to obtain a consistent solution. The vectors with their respective multiplicities are:

Atoms	Vectors	Multiplicity	Vectors	Multiplicity
Ru-Ru	½,½,½	2		
Ru-Ge	x,y,z	2	½+x,½+y,½+z	2
	$x,\bar{y},z$	2	½+x,½-y,½+z	2
	$\bar{x},y,\bar{z}$	2	½-x,½+y,½-z	2
	$\bar{x},\bar{y},\bar{z}$	2	½-x,½-y,½-z	2
Ge-Ge	2x,2y,2z	1	½,½-2y,½	2
	2x,-2y,2z	1	½,½+2y,½	2
	-2x,2y,-2z	1	½-2x,½,½-2z	2
	-2x,-2y,-2z	1	½+2x,½,½+2z	2

The values of $x = 0.00$, $y = 0.17$, $z = 0.21$ gave a consistent solution. The electron density map computed using structure factors phased by the Ge and Ru atoms (R = 35%) allowed the location of all remaining atoms.

The atomic scattering factors of Cromer and Waber[27] were employed with anomalous dispersion[28] corrections being applied to the Ge, Ru and Cl atoms. During the course of refinement, three molecular models where the function minimized was $\sum w(|F_{obs}|-|F_{calc}|)^2$ where $w = 1/\sigma F^2$ were tested:

(1) all atoms isotropic $R_1 = 6.7\%$, $R_2 = 8.6\%$ (R_1 defined as $= \sum||Fo|-|Fc||/\sum|Fo|$ and R_2 (or weighted R-factor) $= \left\{\sum w(|Fo|-|Fc|)^2/\sum wFo^2\right\}^{\frac{1}{2}}$);

(2) ruthenium, germanium and chlorine atoms anisotropic, carbon and oxygen atoms isotropic $R_1 = 3.5\%$, $R_2 = 4.5\%$; and

(3) all atoms anisotropic $R_1 = 2.8\%$, $R_2 = 3.8\%$.

The introduction of anisotropic thermal parameters was justified by electron density difference maps and by the Hamilton statistical test. The poor agreement of the strong reflections ($|F_{obs}|<|F_{calc}|$) suggested that the crystals suffered from extinction and that a correction was necessary. The calculated structure factors were modified by the term $1/(1 + \beta(2\theta).C.I)$

as suggested by Zachariasen[59] where I was the raw intensity and C was the secondary extinction parameter which was treated as a variable in subsequent refinements. The $\beta(2\theta)$ terms were not calculated accurately and this can be briefly justified. The $\beta(2\theta)$ term contains a polarization term and a shape (absorption) term, modified for the Picker monochromator geometry. Over the range of 2θ covered in this experiment, the polarization term changes from 1.0 to 1.17 and for a spherical crystal of $\mu r \sim 0.7$ the $\beta(2\theta)$ value is virtually independent of 2θ, i.e., absorption in this region offsets the variation introduced by the polarization term. Since the transmission factors vary from 0.40 → 0.45, which are larger than those found for a sphere of $\mu r = 0.7$, it was felt that the true $\beta(2\theta)$ would all lie inside the range 1 to 1.17. Initially, then, $\beta(2\theta)$ was set to 1.0 for all reflections, and full matrix refinement converged to $R_1 = 1.91\%$, $R_2 = 2.41\%$ with a value for C of $.1063 \times 10^{-5}$. The largest correction to Fcalc based on the final reduced values was 20%. The refinement was repeated with $\beta(2\theta)$ terms calculated using the polarization contribution only, and converged to $R_1 = 1.94\%$, $R_2 = 2.45\%$ with a value for $C = 0.1118 \times 10^{-5}$. Either refinement is acceptable, and the maximum error introduced in the final calculated structure factors is estimated to be less than 4% and on an average must be considerably better. In view of the assumptions made, all thermal parameters must be considered to be less reliable than is indicated. The results of the refinement for which $\beta(2\theta) = 1$ for all reflections is reported. While the parameters from the refinements of the two approaches to the extinction correction agree well, a comparison of these parameters with those from the refinement without the extinction correction shows some interesting features. As expected, the main effect is in the thermal parameters where the βij's all increase in magnitude as a result of the extinction correction. The co-ordinates of the heavy atoms Ge and Cl (Ru being fixed cannot be affected) show little difference, but some large differences do show up in the light atom co-ordinates. For carbon and oxygen the average discrepancy is 1.1σ where σ is taken as the standard deviation from the final refinement including an extinction correction. The final value for the standard deviation of an observation of unit weight was 0.91, suggesting that the P factor used in the $\sigma(F)$ calculation was slightly too high. An investigation of the variation of $w\Delta^2$ for ranges of Fobs and $\sin\theta/\lambda$ was consistent with the weighting scheme being acceptable on a relative scale. The final difference map showed the greatest residual electron density to be $0.16e^-/\mathring{A}^3$.

(b) Cis-$Ru(CO)_4(GeCl_3)_2$

A statistical analysis of the data suggested that the structure was non-centrosymmetric, and the space group $P2_1$ was assumed for the initial solution and subsequently confirmed by refinement. The asymmetric unit then contained two independent molecules. The Patterson showed a very large vector at ½,0,½ which suggested that the two independent molecules were related by a pseudo B-face centering. Systematic weaknesses in the data ($hk\ell$ for $h+\ell = 2n+1$) were consistent with this suggestion. The approximation of the structure to the space group $B2_1$ lead to an ambiguity in the solution for the co-ordinates of the ruthenium and germanium atoms. This ambiguity is simply related to the correct identification of the true and pseudo 2_1 axes. A careful investigation of the Patterson map showed a preference for one solution, but the alternative was also tested in the early stages of refinement. To improve the phasing the calculated positions of the CO groups were introduced into both models. The preferred model refined to R_1 = 28%, and an electron density difference map revealed the positions of the Cl atoms. The alternate solution proved to be a false minimum that failed to reduce $R_1 < 35\%$. Associated with the correct solution several false minima occur for the Cl and CO atom groups because of the semi-special co-ordinate relationships of the Ru and Ge atoms within each molecule. The refinement was very slow due to the high correlation between the parameters of the two molecules at this stage. Several of the Cl atoms refined to false positions. The errant atoms were repositioned using electron density difference maps and their new geometry checked for sensibility. The structure was refined with isotropic temperature factors to R_1 = 7.1%, R_2 = 7.7%. The electron density maps suggested the use of anisotropic temperature factors for the heavy atoms, and the structure was refined to give R_1 = 4.09%, R_2 = 4.13%. The effects of the polar dispersion error were investigated using the solution $x\bar{y}z$, and the refinement once again converged to R_1 = 4.08%, R_2 = 4.15%. A Hamilton[56] statistical test did show a preference for the first model where the consistency of the Re-Ge distances was better. The formula of Cruickshank and McDonald[55] estimates the error invoked by neglecting the $\Delta f''$ anomalous dispersion term in a polar space group. For the Ru and Ge co-ordinates along the y co-ordinate the error between the right and wrong models is estimated to be 0.04Å which is in good agreement with the average value of 0.03Å observed. The second model was just rejected at the .01 significance level when all the data were included in the calculations. However, the significance for the first model improves when the comparison is done using only those data that are theoretically sensitive to the change of hand (i.e., $h0\ell$'s omitted).

An electron density difference map based on the final parameters contained no residual peaks greater than $0.6e^-/\text{Å}^3$, and these peaks could be assigned to the anisotropic motion of the carbonyl moieties. The final standard deviation for an observation of unit weight was 1.09 which is in good agreement with the expected value of unity. The experimental weighting scheme satisfied, within acceptable limits Cruickshank's criterion[32] and a comparison of the final observed and calculated structure factor amplitudes did not suggest that a correction for extinction was necessary. An investigation of the correlation coefficients shows no large correlation between the parameters of the two molecules of the asymmetric unit.

Table XIV

Observed and calculated structure amplitudes (x10) in electrons for trans-$Ru(CO)_4(GeCl_3)_2$

Table XV

Observed and calculated structure amplitudes (x10) in electrons for cis-$Ru(CO)_4(GeCl_3)_2$

```
R   [illegible]
L   [illegible]
FO  [illegible]
FC  [illegible]
R   [illegible]
L   [illegible]
FO  [illegible]
FC  [illegible]
R   [illegible]
L   [illegible]
FO  [illegible]
FC  [illegible]
R   [illegible]
L   [illegible]
FO  [illegible]
FC  [illegible]
R   [illegible]
L   [illegible]
FO  [illegible]
FC  [illegible]
R   [illegible]
L   [illegible]
FO  [illegible]
FC  [illegible]
R   [illegible]
L   [illegible]
FO  [illegible]
FC  [illegible]
R   [illegible]
L   [illegible]
FO  [illegible]
FC  [illegible]
R   [illegible]
L   [illegible]
FO  [illegible]
FC  [illegible]
```

Table XVI

Final Atomic Co-ordinates and Isotropic Temperature Factors of Trans-$Ru(CO)_4(GeCl_3)_2$

Atom	x	y	z	B(Å^2)
Ru	0.0	0.0	0.0	2.22
Ge	-0.00568(5)	0.16971(5)	0.21377(6)	2.71
Cl_1	0.01991(19)	0.37406(15)	0.14589(19)	5.09
Cl_2	0.16309(16)	0.14574(16)	0.40742(18)	4.86
Cl_3	-0.20348(17)	0.16794(16)	0.33553(19)	4.81
C1	-0.2155(7)	-0.0174(5)	-0.0066(6)	3.06
C2	-0.0264(5)	0.1386(5)	-0.1679(7)	2.91
O1	-0.3370(5)	-0.0277(4)	-0.0119(5)	4.97
O2	-0.0426(5)	0.2161(4)	-0.2630(5)	4.57

Anisotropic Temperature Factors ($x10^5$)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ru	629(9)	548(7)	797(11)	28(6)	81(7)	-19(6)
Ge	881(9)	620(7)	897(11)	9(6)	81(6)	-88(6)
Cl_1	2370(32)	661(17)	1572(28)	-237(18)	-3(24)	54(17)
Cl_2	1368(23)	1453(23)	1326(27)	132(19)	-415(20)	-91(20)
Cl_3	1226(21)	1346(22)	1788(29)	24(18)	612(19)	-319(21)
C1	1033(98)	605(64)	1117(95)	-31(59)	102(73)	54(59)
C2	689(73)	838(73)	1079(95)	61(58)	200(66)	-250(74)
O1	659(59)	1557(64)	2235(91)	-919(50)	75(55)	242(58)
O2	1622(68)	1061(53)	1373(69)	7(49)	58(58)	433(58)

Numbers in parentheses are estimated standard deviations occurring in the last digits listed.

Table XVII

Final Atomic Co-ordinates and Isotropic Temperature Factors for Cis-Ru(CO)$_4$(GeCl$_3$)$_2$

Atom	x	y	z	B(Å^2)
Ru$_1$	0.45282(24)	0.0	0.16628(18)	2.88(8)*
Ru$_2$	-0.03844(23)	-0.01134(31)	-0.31807(19)	2.93(9)*
Ge$_1$	0.43687(33)	-0.02650(41)	0.35614(25)	4.09(13)*
Ge$_2$	0.48235(36)	0.19387(39)	0.18929(30)	4.23(14)*
Ge$_3$	-0.00281(32)	0.01805(38)	-0.12909(25)	3.71(13)*
Ge$_4$	-0.00246(32)	0.17871(33)	-0.35153(25)	3.61(13)*
Cl$_1$	0.2548(8)	0.0342(9)	0.4228(6)	5.8(4)*
Cl$_2$	0.5976(9)	0.0469(10)	0.4473(8)	7.5(5)*
Cl$_3$	0.4473(10)	-0.1869(10)	0.4036(8)	8.1(5)*
Cl$_4$	0.4308(10)	0.2726(9)	0.3290(7)	7.0(4)*
Cl$_5$	0.6820(10)	0.2498(10)	0.1583(11)	9.7(6)*
Cl$_6$	0.35670(12)	0.2863(9)	0.0795(8)	7.3(5)*
Cl$_7$	0.2057(9)	0.2321(8)	-0.3664(8)	6.1(4)*
Cl$_8$	-0.0983(10)	0.2295(8)	-0.4967(7)	6.4(4)*
Cl$_9$	-0.0858(9)	0.2930(8)	-0.2443(7)	5.0(3)*
Cl$_{10}$	-0.1693(9)	0.0831(9)	-0.0441(7)	6.3(4)*
Cl$_{11}$	0.0481(11)	-0.1213(9)	-0.04150(8)	7.6(5)*
Cl$_{12}$	0.1586(10)	0.1263(9)	-0.0896(7)	6.4(4)*
C1	0.6543(36)	-0.0193(34)	0.1854(27)	6.7(9)
C2	0.2498(28)	0.0310(26)	0.1639(20)	3.7(7)
C3	0.4235(37)	-0.1534(33)	0.1528(29)	6.0(9)
C4	0.4699(26)	0.0254(27)	0.0166(23)	3.9(7)
C5	0.1571(32)	-0.0319(29)	-0.3233(25)	5.2(8)
C6	-0.2293(32)	0.0204(32)	-0.3002(25)	6.1(9)
C7	-0.0642(24)	-0.0260(25)	-0.4678(22)	3.0(6)
C8	-0.0626(39)	-0.1594(36)	-0.2874(31)	7.0(1.0)
O1	0.7646(25)	-0.0251(25)	0.2025(21)	8.7(7)
O2	0.1416(22)	0.0451(18)	0.1632(15)	5.3(5)
O3	0.4155	-0.2406(29)	0.1370(24)	10.0(9)
O4	0.4799(19)	0.0376(19)	-0.0733(17)	5.4(5)
O5	0.2760(21)	-0.0373(20)	-0.3220(16)	6.2(6)
O6	-0.3427(21)	0.0450(18)	-0.2903(16)	5.3(5)
O7	-0.0759(20)	-0.0384(19)	-0.5553(17)	5.3(5)
O8	-0.0772(24)	-0.2468(23)	-0.2724(19)	6.6(7)

Numbers in parentheses are estimated standard deviations occurring in the last digits listed.

* The anisotropic temperature factors for these atoms are listed in Table XVIII.

Table XVIII

Anisotropic Temperature Factors ($x10^5$) for Cis-$Ru(CO)_4(GeCl_3)_2$

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ru_1	897(29)	509(27)	460(20)	-31(26)	69(18)	3(20)
Ru_2	901(29)	384(26)	473(19)	24(26)	78(18)	17(22)
Ge_1	1101(43)	1019(42)	473(26)	39(41)	56(27)	131(30)
Ge_2	1380(54)	680(38)	689(31)	-299(40)	175(32)	-209(30)
Ge_3	1177(42)	659(35)	475(25)	136(35)	74(26)	55(26)
Ge_4	1045(45)	472(30)	560(27)	9(34)	53(28)	21(26)
Cl_1	1584(125)	1726(125)	493(59)	265(102)	159(72)	13(81)
Cl_2	1756(146)	1794(149)	959(89)	20(124)	-748(92)	-164(99)
Cl_3	1836(159)	1326(116)	1173(96)	47(108)	-181(96)	523(92)
Cl_4	2318(174)	1115(107)	941(86)	381(115)	-65(96)	346(85)
Cl_5	1785(171)	1236(129)	3008(187)	-792(120)	1161(142)	-843(130)
Cl_6	3298(210)	793(93)	1009(91)	-203(122)	-241(112)	243(80)
Cl_7	1313(123)	913(101)	1353(101)	102(96)	262(84)	112(83)
Cl_8	2306(149)	780(86)	692(71)	-220(99)	-264(83)	324(68)
Cl_9	1935(144)	613(76)	774(72)	292(91)	165(82)	-154(66)
Cl_{10}	1878(145)	1346(105)	649(77)	291(106)	224(80)	-76(74)
Cl_{11}	3197(210)	980(102)	771(86)	780(125)	112(105)	329(78)
Cl_{12}						

Numbers in parentheses are estimated standard deviations occurring in the last digits listed.

DISCUSSION

(a) Trans-$Ru(CO)_4(GeCl_3)_2$

The complex has the expected octahedral configuration, and a perspective view is shown in Figure 4. There are no intermolecular bridges between the chlorine and germanium atoms, and indeed all the intermolecular contacts are consistent with a normal molecular crystal. A second view (Figure 5) of the molecule down the Ge-Ru-Ge axis shows the relative orientations of the $GeCl_3$ and $Ru(CO)_4$ groups. This arrangement is very close to one potential minimum of a twelve-fold barrier that would arise from intramolecular repulsion between the chlorine atoms and carbonyl groups. Detailed bond lengths and angles are given in Tables XVI through to XIX. Riding corrections have been applied to all the bond lengths in order to account for the shortening of the bond distances brought about by assuming that anisotropic thermal motion can be described as an ellipsoid. The internal consistency of bond lengths and angles is very good and is in agreement with the standard deviations as obtained from ORFFE.

(b) Cis-$Ru(CO)_4(GeCl_3)_2$

A perspective view of one molecule is given in

Figure 4

A perspective view of the trans-Ru(CO)$_4$(GeCl$_3$)$_2$ molecule with 50% probability thermal ellipsoids

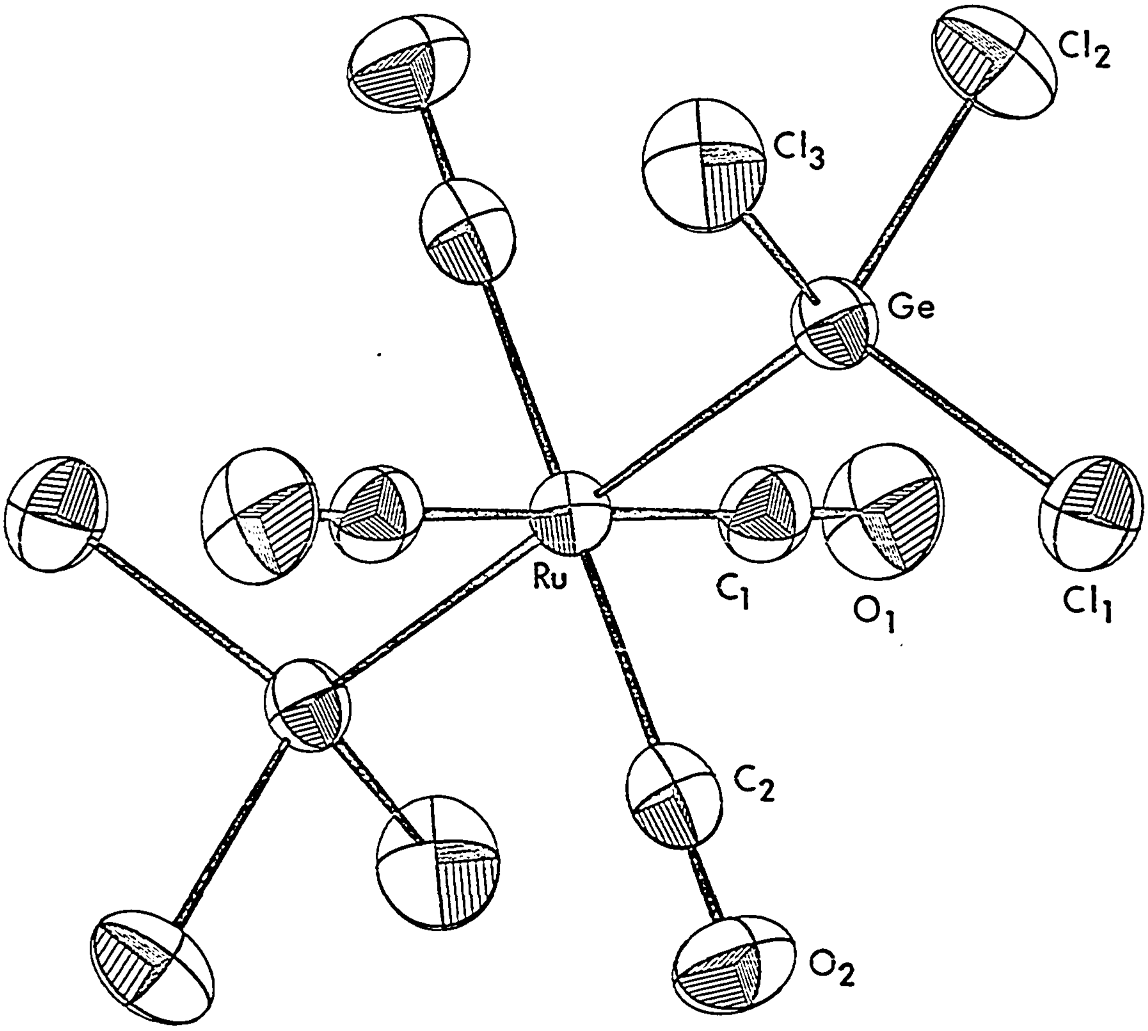

Cl2
Cl3
Ge
Ru
C1
O1
Cl1
C2
O2

Figure 5

A view down the Ge-Ru axis of the

trans-$Ru(CO)_4(GeCl_3)_2$ molecule

displaying the twelve-fold rotation barrier

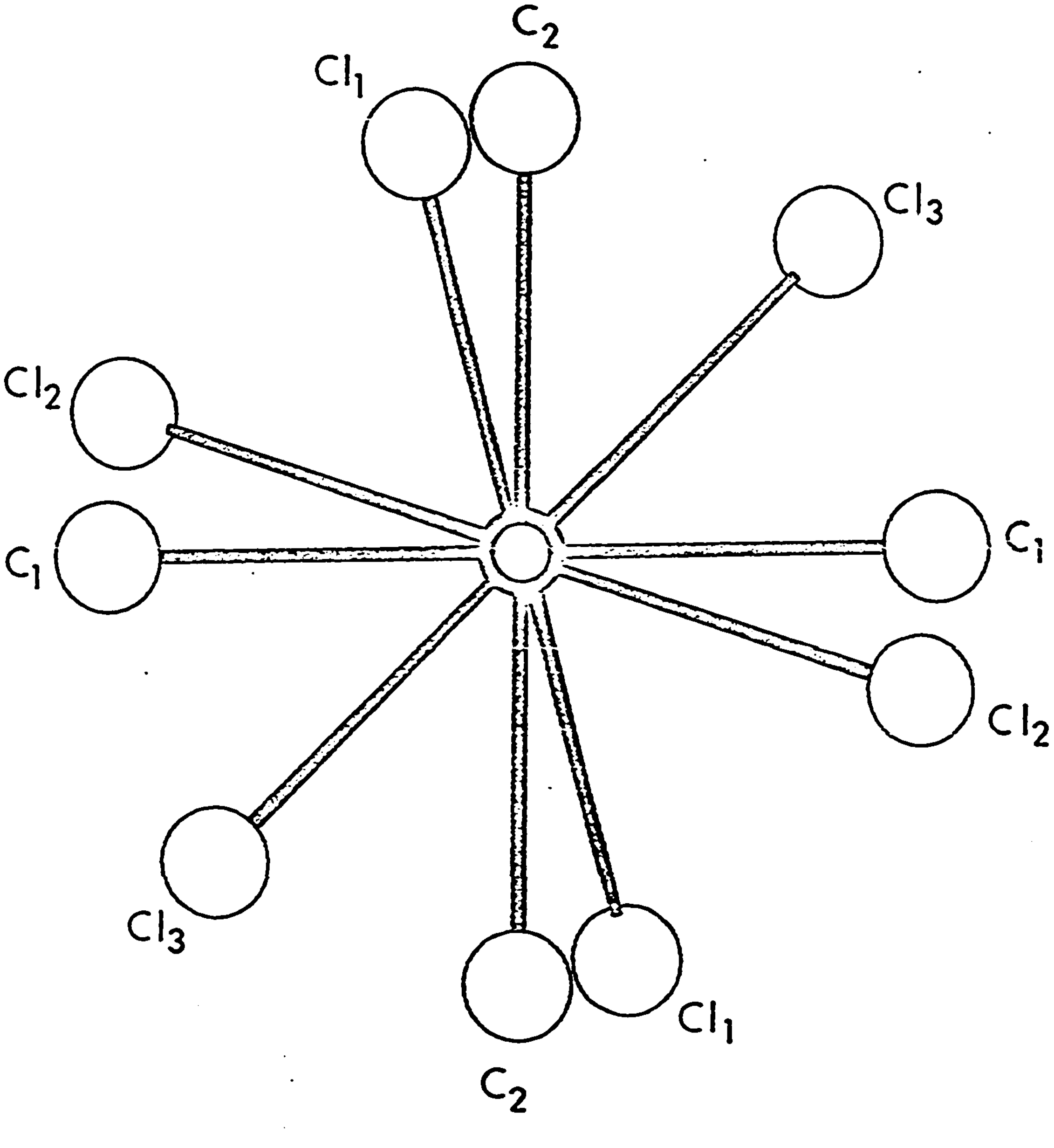

C$_2$
Cl$_1$
Cl$_3$
Cl$_2$
C$_1$
C$_1$
Cl$_2$
Cl$_3$
Cl$_1$
C$_2$

Table XIX

Bond Lengths of Trans-Ru(CO)$_4$(GeCl$_3$)$_2$ With and Without Riding Corrections

Atoms	Corrected Distance (Å)	Uncorrected Distance (Å)
Ru-Ge	2.4807(7)	2.4772(5)
Ru-C1	1.980(6)	1.976(6)
Ru-C2	1.981(6)	1.980(6)
Ge-Cl$_1$	2.166(2)	2.145(2)
Ge-Cl$_2$	2.179(2)	2.160(2)
Ge-Cl$_3$	2.171(2)	2.153(2)
C1-O1	1.154(7)	1.114(6)
C2-O2	1.151(7)	1.115(6)

Numbers in parentheses are estimated standard deviations occurring in the last digits listed.

Table XX

Intramolecular Angles of trans-$\text{Ru(CO)}_4(\text{GeCl}_3)_2$

Atoms	Angle(°)	Atoms	Angle(°)
Ge-$\widehat{\text{Ru}}$-C1	90.0(1)	Ru-$\widehat{\text{C1}}$-O1	179.3(5)
Ge-$\widehat{\text{Ru}}$-C2	89.8(1)	Ru-$\widehat{\text{C2}}$-O2	179.3(5)
Ru-$\widehat{\text{Ge}}$-Cl_1	117.00(5)	Cl_1-$\widehat{\text{Ge}}$-Cl_2	102.67(7)
Ru-$\widehat{\text{Ge}}$-Cl_2	114.33(5)	Cl_2-$\widehat{\text{Ge}}$-Cl_3	102.58(6)
Ru-$\widehat{\text{Ge}}$-Cl_3	114.11(5)	Cl_1-$\widehat{\text{Ge}}$-Cl_3	104.43(7)
		C1-Ru-C2	88.9(2)

Numbers in parentheses are estimated standard deviations occurring in the last digits listed.

Table XXI

Intramolecular Non-Bonded Contacts (<4.0Å) of Trans-$Ru(CO)_4(GeCl_3)_2$

Atoms	Distances	Atoms	Distances
Cl_1-Cl_2	3.361(2)	Cl_2-C2	3.668(5)
Cl_1-Cl_3	3.397(2)	Cl_2-O1	3.983(5)
Cl_2-Cl_3	3.366(2)	Cl_2-O2	3.952(5)
Cl_1-C2	3.536(3)	Cl_3-C1	3.416(5)
Cl_1-O2	3.781(5)	Cl_3-O1	3.640(5)
Cl_2-C1	3.673(5)		

Numbers in parentheses are estimated standard deviations occurring in the last digits listed.

Table XXII

Intermolecular Non-Bonded Contacts (<3.6Å) for Trans-Ru(CO)$_4$(GeCl$_3$)$_2$

Atom	Distance	Symmetry Position of Second Atom
Cl_1-O1	3.422	½+x, ½-y, ½+z
Cl_1-Cl_1	3.516	-x, 1-y, -z
Cl_2-O2	3.446	½+x, ½-y, ½+z
Cl_3-O2	3.352	x-½, ½-y, ½+z
Cl_3-O1	3.399	-½-x, ½+y, ½-z
Cl_3-C2	3.533	-½-x, ½-y, ½+z
Cl_3-C1	3.570	-½-x, ½+y, ½-z
Cl_3-O2	3.596	x, y, 1+z
O1-O1	3.057	-x-1, -y, -z
O1-O2	3.322	-½-x, -½+y, -½-z

Figure 6. The ruthenium has the expected octahedral co-ordination. There is no intramolecular chlorine bridge between germanium atoms in either molecule of the asymmetric unit. A calculation of all the intermolecular distances shows no contacts that are significantly shorter than those predicted by Van der Waals radii, and hence they are not discussed but are listed for completeness in Tables XXV and XXVI. The intramolecular distances and angles of interest are collected in Tables XXIII and XXIV.

At this point it is convenient to discuss the agreement of the geometry of the two independent molecules, as in subsequent discussion of the comparisons of the cis and trans isomers average values will be used. It is interesting to note that taking the distances alone, false and opposite impressions can be obtained from two distinct molecules, i.e., in molecule one Ru-C (for CO trans to CO) > Ru-C (CO trans to $GeCl_3$), the reverse being true for the molecule two. However, in neither case is the difference significant, and indeed an analysis of all eight Ru-C distances shows that they can be treated as a single population with an estimated standard deviation of .03Å on each observation, a value that is in good agreement with

Figure 6

A perspective view of the cis-Ru(CO)$_4$(GeCl$_3$)$_2$ molecule with the anisotropic atoms having 50% probability thermal ellipsoids

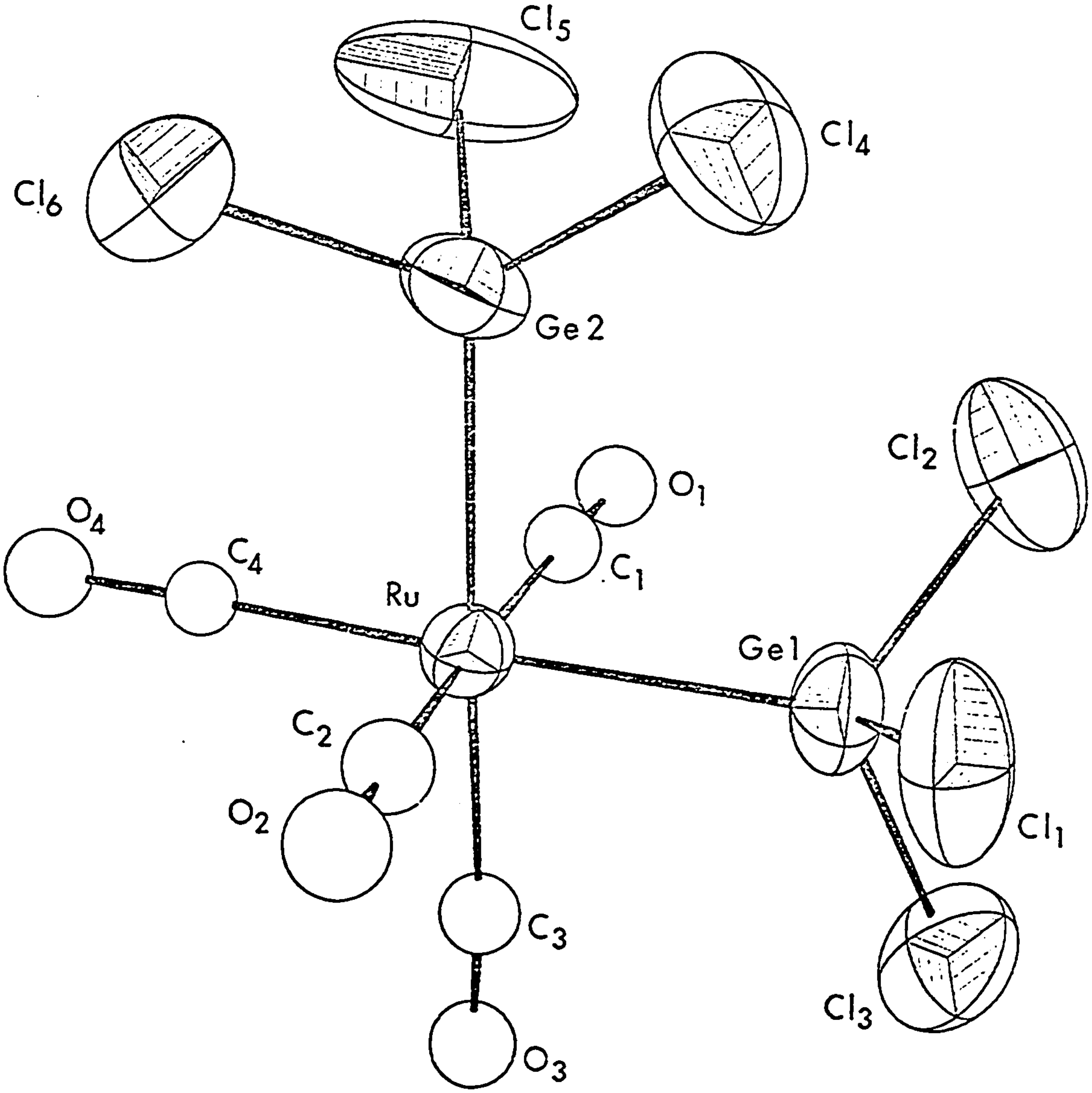

Cl5
Cl4
Cl6
Ge2
Cl2
O1
O4
C4
C1
Ru
Ge1
C2
O2
Cl1
C3
Cl3
O3

Table XXIII

Bond Lengths of Cis-Ru(CO)$_4$(GeCl$_3$)$_2$ With and Without Riding Corrections

Atoms	Corrected Distance (Å)	Uncorrected Distance (Å)
Ru$_1$-Ge$_1$	2.487(5)	2.477(4)
Ru$_1$-Ge$_2$	2.488(6)	2.478(5)
Ru$_2$-Ge$_3$	2.484(6)	2.477(5)
Ru$_2$-Ge$_4$	2.466(5)	2.461(4)
Ge$_1$-Cl$_1$	2.18(1)	2.114(12)
Ge$_1$-Cl$_2$	2.19(1)	2.136(9)
Ge$_1$-Cl$_3$	2.18(1)	2.144(9)
Ge$_2$-Cl$_4$	2.17(1)	2.128(10)
Ge$_2$-Cl$_5$	2.20(1)	2.120(10)
Ge$_2$-Cl$_6$	2.22(1)	2.182(11)
Ge$_4$-Cl$_7$	2.19(1)	2.153(9)
Ge$_4$-Cl$_8$	2.19(1)	2.164(9)
Ge$_4$-Cl$_9$	2.19(1)	2.169(9)
Ge$_3$-Cl$_{10}$	2.18(1)	2.146(9)
Ge$_3$-Cl$_{11}$	2.19(1)	2.139(10)
Ge$_3$-Cl$_{12}$	2.17(1)	2.135(10)
Ru$_1$-C1	2.03(4)	1.99(4)
Ru$_1$-C2	2.04(4)	2.02(3)
Ru$_1$-C3	2.00(5)	1.96(4)
Ru$_1$-C4	1.99(4)	1.97(3)
Ru$_2$-C5	1.96(4)	1.93(3)
Ru$_2$-C6	1.96(4)	1.92(3)
Ru$_2$-C7	1.97(4)	1.95(3)
Ru$_2$-C8	1.97(4)	1.92(5)
C1-O1	not calculated	1.10(3)
C2-O2		1.07(3)
C3-O3		1.12(3)
C4-O4		1.17(3)
C5-O5		1.16(3)
C6-O6		1.16(3)
C7-O7		1.14(3)
C8-O8		1.13(4)

Table XXIV

Intramolecular Angles of Cis-$Ru(CO)_4(GeCl_3)_2$

Atoms	Angles(°)	Atoms	Angles(°)
$Ge_1-\hat{Ru}_1-Ge_2$	91.45(16)	$Ge_3-\hat{Ru}_2-Ge_4$	90.54(14)
$Ge_1-\hat{Ru}_1-C4$	177.9(9)	$Ge_3-\hat{Ru}_2-C7$	176.8(9)
$Ge_2-\hat{Ru}_1-C3$	177.5(1.1)	$Ge_4-\hat{Ru}_2-C8$	177.9(1.2)
$Ge_1-\hat{Ru}_1-C1$	87.2(1.0)	$Ge_3-\hat{Ru}_2-C5$	86.7(9)
$Ge_2-\hat{Ru}_1-C1$	89.7(1.2)	$Ge_4-\hat{Ru}_2-C5$	88.8(1.1)
$Ge_1-\hat{Ru}_1-C2$	87.3(8)	$Ge_3-\hat{Ru}_2-C6$	87.8(1.0)
$Ge_2-\hat{Ru}_1-C2$	85.5(9)	$Ge_4-\hat{Ru}_2-C6$	87.8(1.2)
$Ge_1-\hat{Ru}_1-C3$	86.7(1.1)	$Ge_3-\hat{Ru}_2-C8$	87.6(1.2)
$Ge_2-\hat{Ru}_1-C4$	86.8(1.0)	$Ge_4-\hat{Ru}_2-C7$	86.2(9)
$C1-\hat{Ru}_1-C2$	172.6(1.4)	$C5-\hat{Ru}_2-C6$	173.5(1.5)
$C1-\hat{Ru}_1-C3$	91.8(1.6)	$C6-\hat{Ru}_2-C8$	90.2(1.6)
$C1-\hat{Ru}_1-C4$	91.8(1.3)	$C5-\hat{Ru}_2-C7$	93.1(1.2)
$C2-\hat{Ru}_1-C3$	92.8(1.4)	$C6-\hat{Ru}_2-C8$	93.0(1.7)
$C2-\hat{Ru}_1-C4$	93.6(1.1)	$C6-\hat{Ru}_2-C7$	92.2(1.2)
$C3-\hat{Ru}_1-C4$	95.2(1.4)	$C7-\hat{Ru}_2-C8$	95.6(1.5)
$Ru_1-\hat{Ge}_1-Cl_1$	115.1(3)	$Ru_2-\hat{Ge}_3-Cl_{10}$	118.1(3)
$Ru_1-\hat{Ge}_1-Cl_2$	114.7(3)	$Ru_2-\hat{Ge}_3-Cl_{11}$	114.8(3)
$Ru_1-\hat{Ge}_1-Cl_3$	114.2(3)	$Ru_2-\hat{Ge}_3-Cl_{12}$	114.4(3)
$Ru_1-\hat{Ge}_2-Cl_4$	122.1(4)	$Ru_2-\hat{Ge}_4-Cl_9$	118.5(3)
$Ru_1-\hat{Ge}_2-Cl_5$	114.2(4)	$Ru_2-\hat{Ge}_4-Cl_7$	117.3(3)
$Ru_1-\hat{Ge}_2-Cl_6$	112.8(3)	$Ru_2-\hat{Ge}_4-Cl_8$	112.3(3)
$Cl_1-\hat{Ge}_1-Cl_2$	103.3(4)	$Cl_{10}-\hat{Ge}_3-Cl_{12}$	101.4(4)
$Cl_1-\hat{Ge}_1-Cl_3$	105.1(4)	$Cl_{10}-\hat{Ge}_3-Cl_{11}$	102.3(4)
$Cl_2-\hat{Ge}_1-Cl_3$	103.1(4)	$Cl_{12}-\hat{Ge}_3-Cl_{11}$	103.9(4)
$Cl_4-\hat{Ge}_2-Cl_5$	104.1(4)	$Cl_9-\hat{Ge}_4-Cl_7$	102.7(4)
$Cl_4-\hat{Ge}_2-Cl_6$	99.1(4)	$Cl_9-\hat{Ge}_4-Cl_8$	101.1(4)
$Cl_5-\hat{Ge}_2-Cl_6$	101.7(5)	$Cl_7-\hat{Ge}_4-Cl_8$	102.5(4)
$Ru_1-\hat{C}1-O1$	174(4)	$Ru_2-\hat{C}5-O5$	175(3)
$Ru_1-\hat{C}2-O2$	178(3)	$Ru_2-\hat{C}6-O6$	176(3)
$Ru_1-\hat{C}3-O3$	173(4)	$Ru_2-\hat{C}8-O8$	178(4)
$Ru_1-\hat{C}4-O4$	178(3)	$Ru_2-\hat{C}7-O7$	177(3)

Numbers in parentheses are estimated standard deviations occurring in the last digits listed.

Table XXV

Intramolecular Non-Bonded Contacts (<3.7Å) of Cis-Ru(CO)$_4$(GeCl$_3$)$_2$

Atoms	Distances (Å)	Atoms	Distances (Å)
Cl_1-C2	3.334	Cl_{10}-O6	3.586
Cl_1-Cl_2	3.356	Cl_{11}-C8	3.353
Cl_1-Cl_3	3.375	Cl_{11}-Cl_{12}	3.365
Cl_1-O2	3.496	Cl_{11}-O2	3.471
Cl_1-Cl_3	3.681	Cl_{11}-O8	3.556
Cl_2-Cl_3	3.333	Cl_{12}-O4	3.330
Cl_2-C2	3.533	Cl_{12}-O2	3.420
Cl_2-Cl_4	3.596	Cl_{12}-C4	3.534
Cl_4-Cl_6	3.279	Cl_{12}-C2	3.568
Cl_4-Cl_5	3.350	Cl_{12}-C5	3.611
Cl_5-Cl_6	3.336	Cl_3-O3	3.505
Cl_5-C1	3.422	C1-C3	2.838
Cl_5-O1	3.600	C1-C4	2.840
Cl_6-Cl_{12}	3.511	C1-O3	3.678
Cl_6-C2	3.563	C2-C1	2.883
Cl_6-C4	3.568	C2-C4	2.905
Cl_7-Cl_8	3.368	C4-C3	2.899
Cl_7-Cl_9	3.376	C5-C8	2.729
Cl_7-C5	3.410	C5-C7	2.812
Cl_7-O5	3.510	C5-C8	3.616
Cl_8-C7	3.259	C6-C7	2.790
Cl_8-Cl_9	3.346	C6-C8	2.791
Cl_8-O7	3.469	C6-O8	2.695
Cl_{10}-Cl_{12}	3.314	C7-C8	2.867
Cl_{10}-Cl_{11}	3.337	O5-C8	3.684
Cl_{10}-C6	3.427		

Table XXVI

Intermolecular Non-Bonded Contacts (<3.7Å) of Cis-Ru(CO)$_4$(GeCl$_3$)$_2$

Atoms	Distances	Symmetry Position of Second Molecule		
Cl_1-O7	3.375	x,	y,	1+z
Cl_1-O5	3.408	x,	y,	1+z
Cl_1-C5	3.530	x,	y,	1+z
Cl_1-C7	3.535	x,	y,	1+z
Cl_2-O7	3.363	1+x,	y,	1+z
Cl_2-O6	3.414	1+x,	y,	1+z
Cl_2-C7	3.569	1+x,	y,	1+z
Cl_2-C6	3.638	1+x,	y,	1+z
Cl_4-O8	3.516	-x,	½+y,	-z
Cl_4-O6	3.572	-x,	½+y,	-z
Cl_4-Cl_3	3.648	1-x,	½+y,	1-z
Cl_5-O5	3.431	1-x,	½+y,	-z
Cl_5-Cl_{11}	3.473	1-x,	½+y,	-z
Cl_5-Cl_{10}	3.677	1+x,	y,	z
Cl_6-O4	3.548	1-x,	½+y,	-z
Cl_6-O3	3.627	1-x,	½+y,	-z
Cl_6-C4	3.687	1-x,	½+y,	-z
Cl_7-O7	3.305	-x,	½+y,	-1-z
Cl_7-Cl_3	3.582	1-x,	½+y,	-z
Cl_8-O7	3.441	-x,	½+y,	-1-z
Cl_8-O8	3.485	-x,	½+y,	-1-z
Cl_8-C7	3.502	-x,	½+y,	-1-z
Cl_8-C8	3.522	-x,	½+y,	-1-z
Cl_9-O2	3.394	-x,	½+y,	-z
Cl_9-O3	3.562	-x,	½+y,	-z
Cl_9-C2	3.568	-x,	½+y,	-z
Cl_9-C3	3.595	-x,	½+y,	-z
Cl_{10}-O3	3.463	-x,	½+y,	-z
Cl_{10}-O4	3.482	x-1,	y,	z
Cl_{10}-O1	3.532	x-1,	y,	z
Cl_{10}-Cl	3.693	x-1,	y,	z
O1-O7	3.452	1+x,	y,	1+z
O4-O6	3.329	1+x,	y,	z
C2-O8	3.573	-x,	½+y,	-z
O6-O3	3.434	-x,	½+y,	-z

the individual standard deviations from ORFFE. The patterns do not appear to be the result of correlations between parameters of the independent molecules. The highest co-ordinate correlation between molecule one and molecule two is 0.12 in spite of the pseudo centering that was a problem in the Patterson solution. There is no detectable difference in Ru-C with the change of trans ligand from CO to $GeCl_3$.

In the ensuing discussion, comparisons of bond lengths in the two isomers are made both between the uncorrected interatomic distances and the interatomic distances with riding corrections applied. The second atom is assumed to "ride" on the first atom with account being taken of the thermal motion of the first atom. The method used for the riding correction calculations is that reported by Busing and Levy[61]. A comparison of the Ru-Ge bond lengths for the cis and trans isomers shows good agreement, the mean uncorrected distances being 2.473Å and 2.477Å, and the mean corrected distances having values of 2.481Å and 2.481Å respectively. Good agreement is also observed for the Ru-C distances, with mean values of 1.96Å and 1.978Å (uncorrected values), and 1.99Å and 1.980Å (corrected values) for the respective cis and trans isomers. These distances are somewhat longer than other reported values:

1.92Å for $Ru_3(CO)_{12}$[44,45],
1.93Å for $[(CO)_3RuBr_2]_2$[60],
1.89Å for $(SnCl_3)Ru_2Cl_3(CO)_5$[52], and
1.87Å for $[Me_3Sn(CO)_3RuSnMe_2]_2$[25].

There is no significant difference in the Ge-Cl distances in either the trans or the cis isomers, the mean uncorrected values being 2.154Å and 2.14Å with values of 2.172Å and 2.19Å for the mean corrected distances of the respective molecules. For the cis isomer a t-test indicates that the Ge-Cl distances may be treated as a single population, the calculated r.m.s. value of 0.01Å agreeing well with the individual standard deviations of .01Å calculated from ORFFE. No significant deviation from the mean value for the Ge-Cl distance was observed in the trans isomer.

The average value in the cis isomer of 92.9° for the C-Ru-C angle reflects the existence of stronger repulsive forces between the CO groups than between the CO and $GeCl_3$ ligands where the C-Ru-Ge angle is 87.6°. In the same isomer the mean Ge-Ru-Ge angle is 91.0° which indicates that there are weaker repulsion forces between the $GeCl_3$ groups than the CO moieties. The Ru-Ge-Cl angles are all somewhat greater than the value of ~109° expected for a perfect tetrahedron, and have average values of 115.7° and 115.2° for the cis and trans molecules respectively. The repulsive forces between the CO and Cl groups have led to increases in the Ru-Ge-Cl angles with concomitant reductions for the Cl-Ge-Cl angles which have mean values of 102.5° and 103.2° for the respective cis and trans isomers. A view down the Ge-Ru bond of the centrosymmetric trans isomer indicates that the Cl_1 atom comes closest to eclipsing a CO group. The repulsive interactions between these two groups is reflected in the $Ru-Ge-Cl_1$ angle of 117.00(5)° which is significantly larger than the mean value for the Ru-Ge-Cl of 115.20°. Projection diagrams down the Ru-Ge bonds of the two cis molecules also reveal the reason for the significant deviations from the mean value of 115.7°; for the $Cl_4-Ge_2-Ru_1$ and $Cl_9-Ge_4-Ru_2$ angles of 122.1(4)° and 118.5(3)° respectively. In each case the Cl's have positioned below and to each side of them two chlorines of the adjacent $GeCl_3$ (see Figures 7, 9). The increase in the Ru-Ge-Cl angle is a result of the mutual repulsions of the Cl atoms. Comparative views down the

Figure 7

A view down the Ge_1-Ru_1 axis of the cis-$Ru(CO)_4(GeCl_3)_2$ molecule showing the relative orientations of the $GeCl_3$ groups

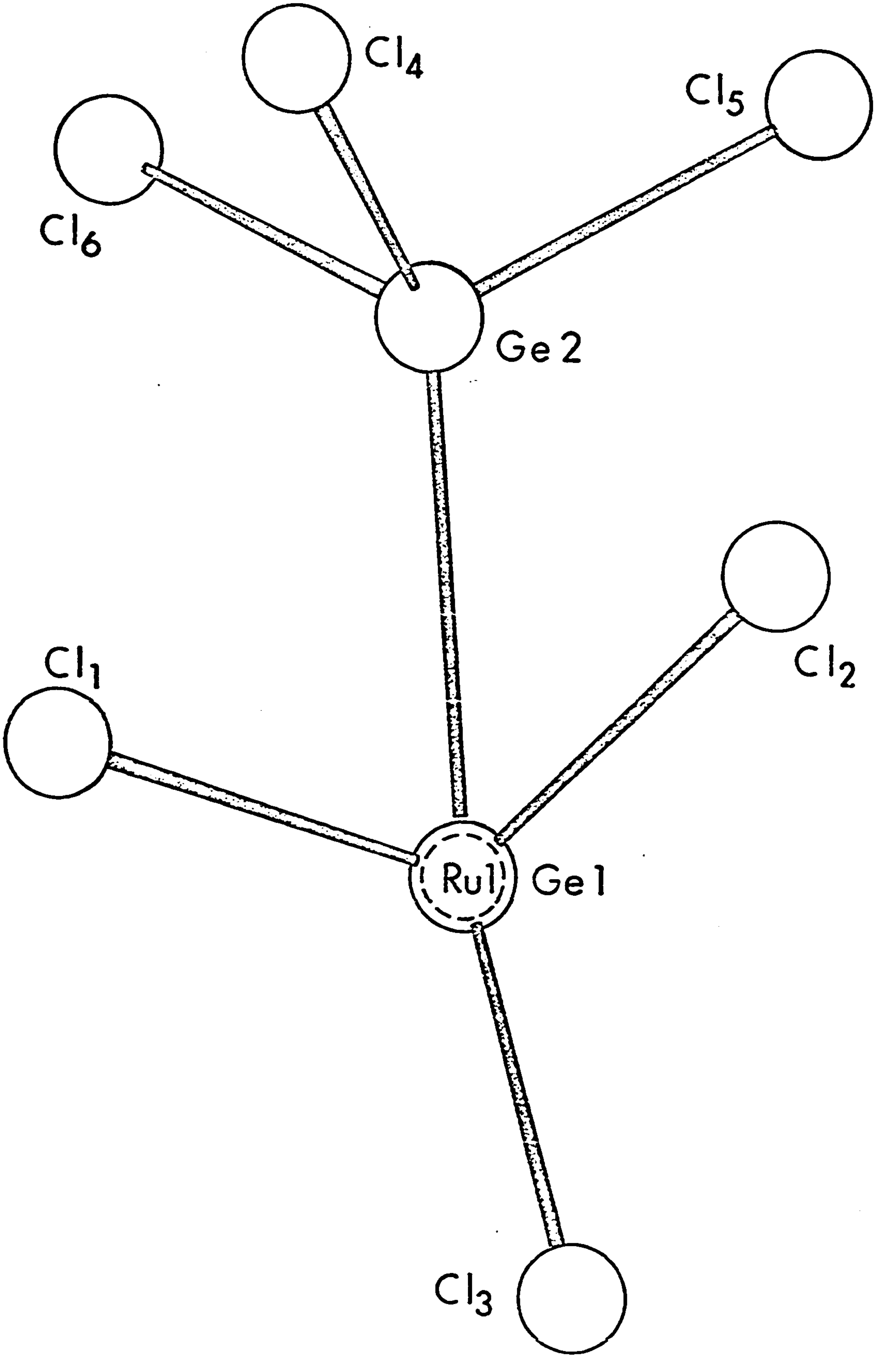

Cl4
Cl5
Cl6
Ge 2
Cl1
Cl2
Ru1
Ge 1
Cl3

Figure 8

A view down the Ge_2-Ru_1 axis of the

cis-$Ru(CO)_4(GeCl_3)_2$ molecule showing

the relative orientations of the $GeCl_3$ groups

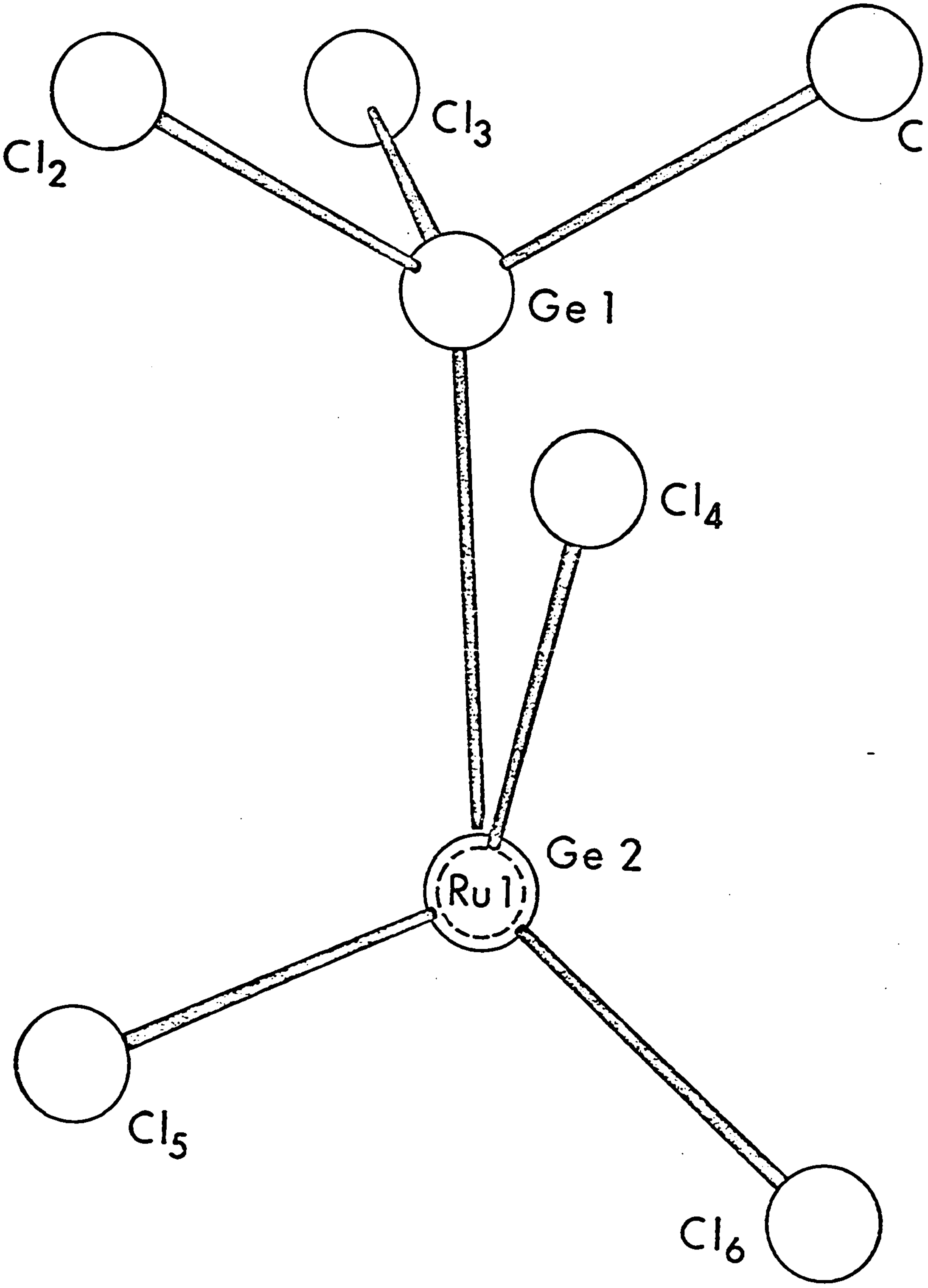

Cl2
Cl3
Cl1
Ge 1
Cl4
Ge 2
Ru 1
Cl5
Cl6

Figure 9

A view down the Ge_3-Ru_2 axis of the
cis-$Ru(CO)_4(GeCl_3)_2$ molecule showing
the relative orientations of the $GeCl_3$ groups

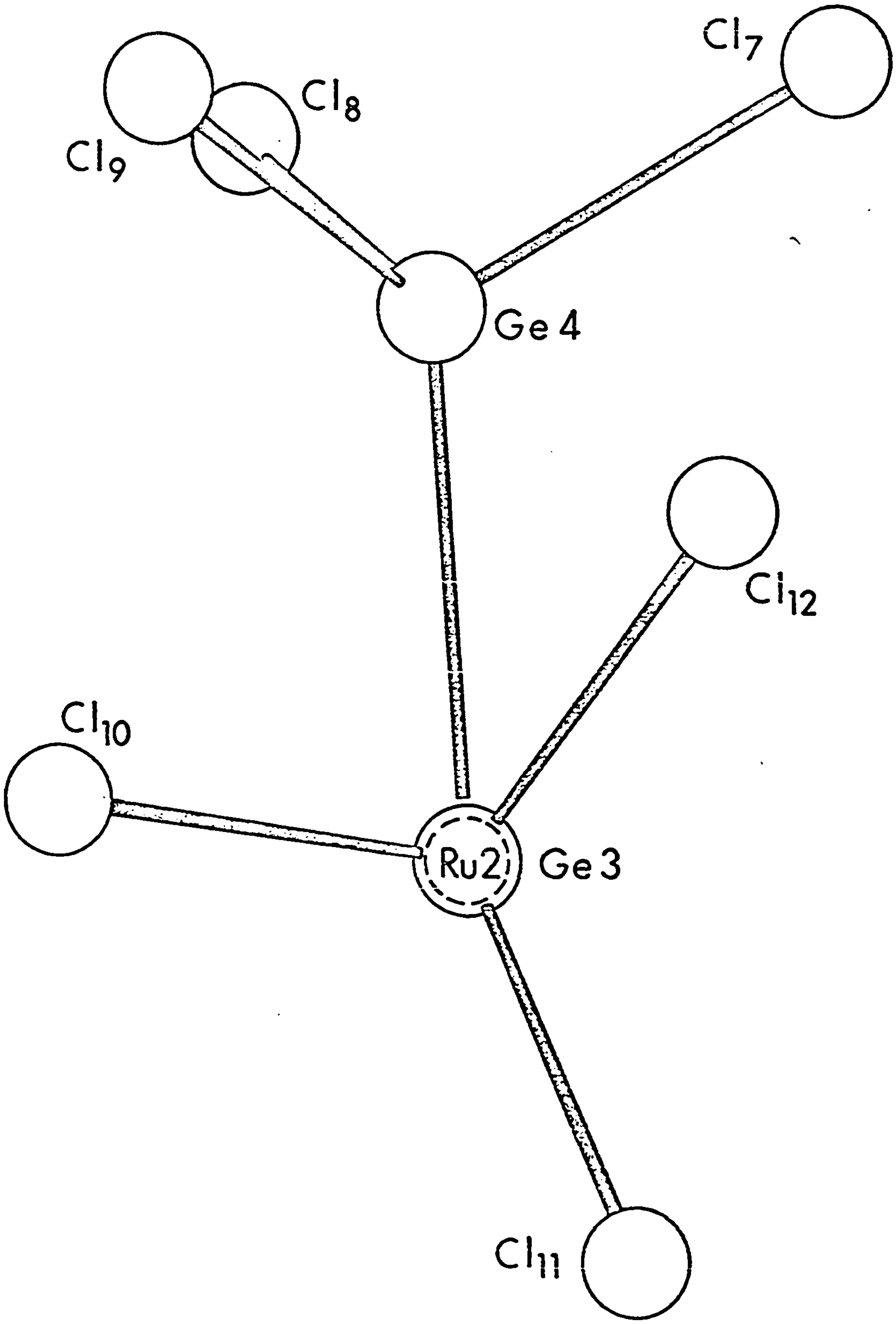
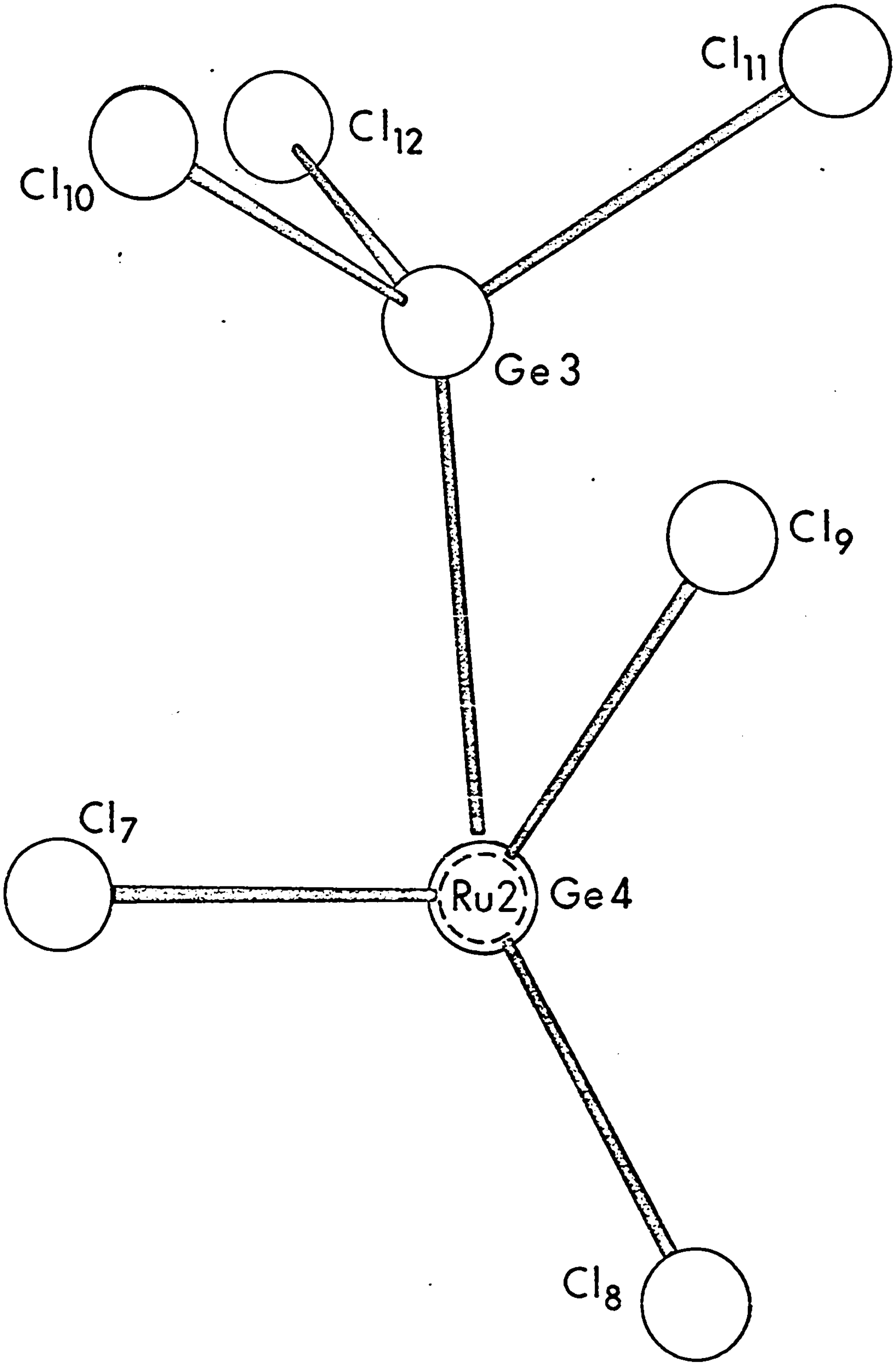

Cl7
Cl8
Cl9
Ge 4
Cl12
Cl10
Ru2
Ge 3
Cl11

Figure 10

A view down the Ge_4-Ru_2 axis of the

cis-$Ru(CO)_4(GeCl_3)_2$ molecule showing

the relative orientations of the $GeCl_3$ groups


Cl11
Cl12
Cl10
Ge 3
Cl9
Cl7
Ru2
Ge 4
Cl8

Ge-Ru bonds of the cis isomer show the equivalent $GeCl_3$ groups of each molecule to have significantly different orientations, and these are demonstrated in Figures 7, 8, 9 and 10.

Although there was no significant difference in the Ru-Ge or Ru-C bond lengths in either the cis or the trans isomers, which might indicate that the trans bond weakening effect for $GeCl_3$ and CO are much the same, the exchange of ^{13}CO is stereospecific. Recent work[62] has shown that the cis isomer exchanges ^{13}CO only in the position trans to the $GeCl_3$ groups, the exchange rate being considerably increased when the molecules are irradiated by ultra-violet light. The trans isomer only exchanges under ultra-violet light to isomerize. Assuming the reaction to be of the SN_1 type (which is most common), the type of reaction pathways shown in Figures 11 and 12. might be envisaged.

These pathways suggest the existence of a common reactive intermediate - a trigonal bipyramidal species with axial CO's. The existence of this activated species would explain the stereospecificity of the ^{13}CO exchange for both the isomers. Recent studies[62] of the molecule cis-$Fe(CO)_4(SiCl_3)_2$ have shown that the ^{13}CO exchange for this molecule is not stereo-

Figure 11

Proposed reaction pathways for carbonyl exchange of trans-Ru$(CO)_4(GeCl_3)_2$

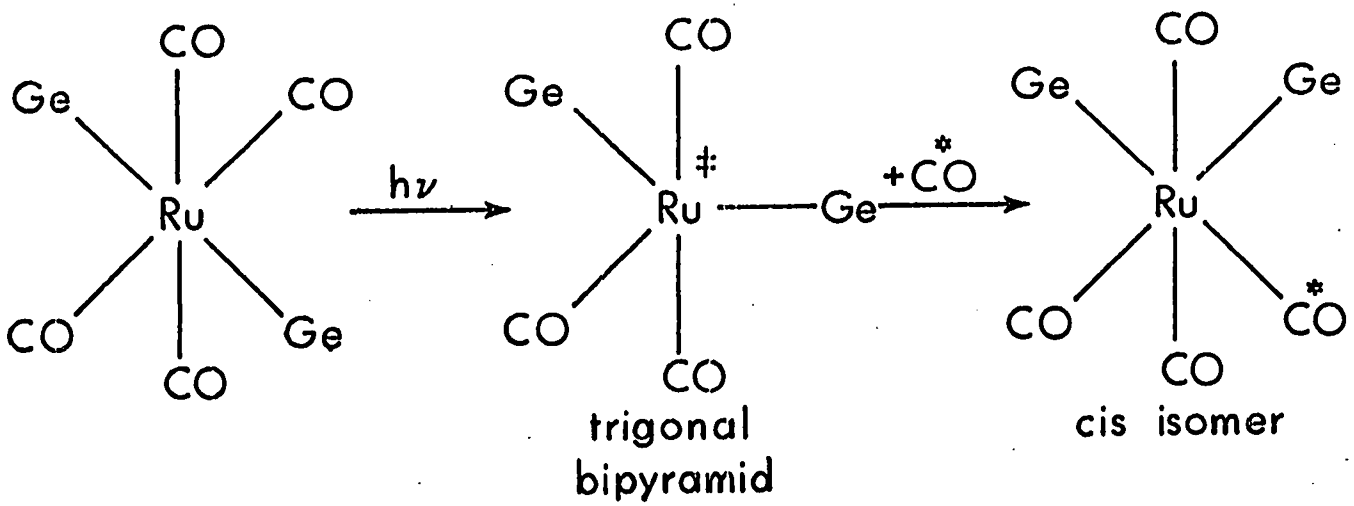
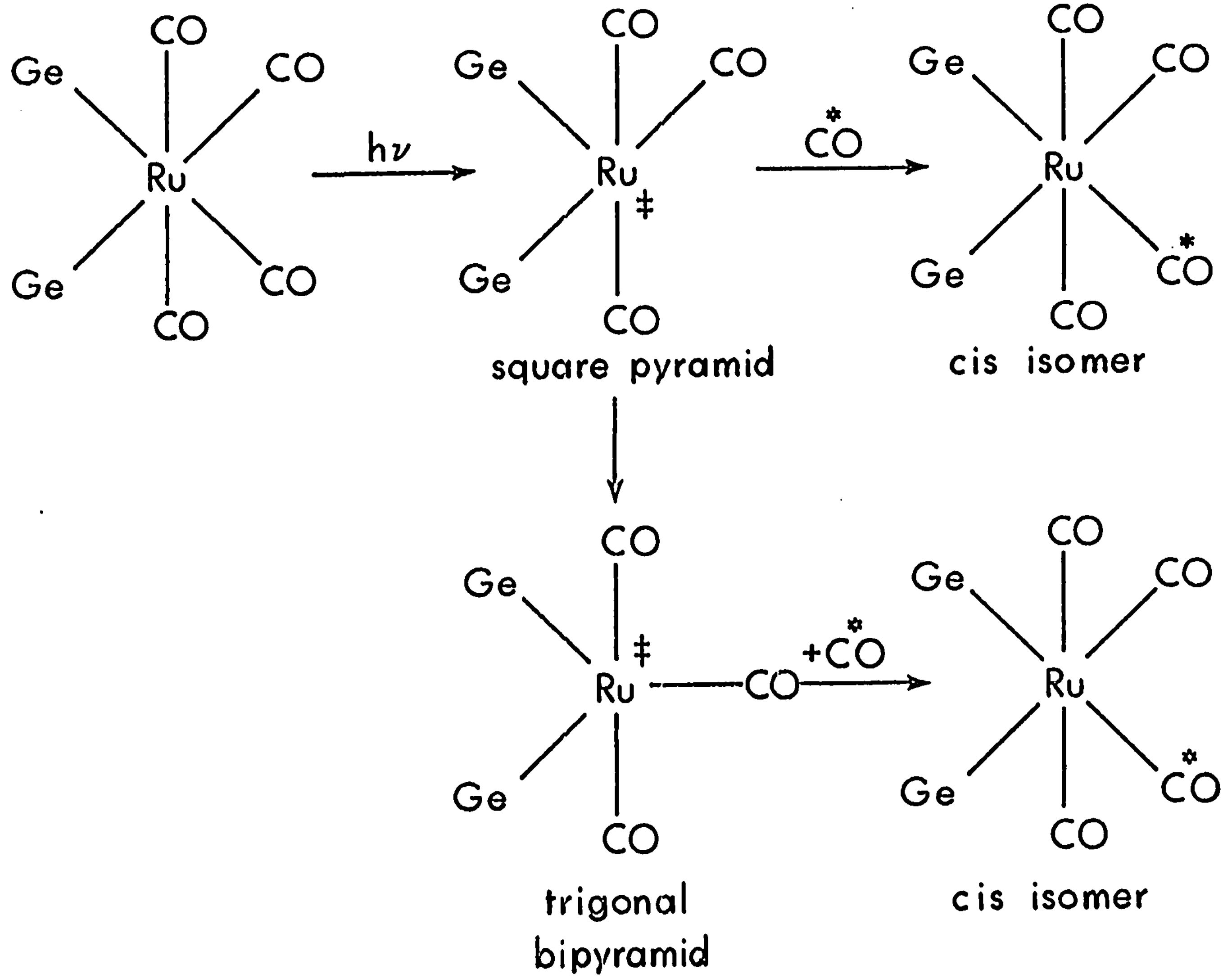

Ge
CO
CO
Ru
CO
CO
Ge
hν
Ge
CO
Ru
‡
Ge
+CO*
CO
CO
trigonal bipyramid
Ge
CO
Ge
Ru
CO
CO
CO*
cis isomer

Figure 12

Proposed reaction pathways for carbonyl exchange of cis-Ru$(CO)_4(GeCl_3)_2$



hν
square pyramid
*CO
cis isomer
+*CO
trigonal bipyramid
cis isomer

specific since exchange takes place in all possible positions.

An analysis of the force constants for the carbonyl stretches in the cis isomer was attempted using the method suggested by Graham[33]. The force constants of Gay[34] (k_1 for CO trans to X, k_2 for CO trans to CO) for the series $Ru(CO)_4X_2$ were used in a calculation where Δk_1 and Δk_2 were derived as $2\Delta\sigma + 3\Delta\pi$ and $2\Delta\sigma + 2\Delta\pi$ respectively. The Δ's are referenced to CH_3 and the results briefly listed as follows:

X	CH_3	Cl	Br	I	$GeCl_3$
k_1	16.70	17.79	17.64	17.49	18.09
k_2	17.48	18.79	18.70	18.37	18.21
Δk_1	0	1.09	0.94	0.79	1.39
Δk_2	0	1.31	1.22	0.89	0.73
$\Delta\sigma$	0	0.88	0.89	0.55	-0.30
$\Delta\pi$	0	-0.22	-0.28	-0.10	0.66

While the $\Delta\sigma$ value for the halogens appears reasonable, the value for $\Delta\sigma(GeCl_3)$ of -0.30 (i.e., electron donation) does not, unless the high value for the $\Delta\pi$ leads to electron donation in the sigma bond by a synergic mechanism. An assessment of the $\Delta\pi$ parameter is dubious in this situation and it would appear better to rely on the structural results of this determination.

The unusual solubility properties of the cis and trans isomers had raised the possibility of intra and intermolecular halogen to Ge bridge bonding respectively. The structures, however, have been shown to contain intra and intermolecular contacts which are consistent with a normal molecular crystal. Thus the unusual solubility properties cannot be explained simply in these terms.

The large difference in melting points between the cis (95°C.) and trans isomers (215°C.) leads to speculation as to the reason. When a crystal melts the crystal lattice forces (Van der Waals forces) holding a molecular crystal together must be broken. These binding forces consist of factors such as dipole-dipole and dipole-polarization interactions and the quantum mechanical dispersion forces. If any intermolecular bonding is present then the crystal lattice binding forces will be much stronger, and one might expect the crystal to melt at a higher temperature. However, these molecules contain no intermolecular bonding. The melting point of the crystal will also be higher if it is able to absorb heat into molecular rotational, vibrational and translational modes. Thus it was postulated that the higher melting point of the trans isomer might be due to an absorption of energy via a rotational mode such as freely rotating $GeCl_3$ groups. However, the heat capacity curve for this isomer fails to show the lambda point expected for a significant increase in the entropy due to a $GeCl_3$ rotational mode[74].

The cis/trans equilibrium for molecules of the type $M(CO)_4(M'X_3)$, (M = Fe, Ru, Os, Mn; M' = Ge, Sn; X = Cl, Br, I, alkyl or aryl groups) is not well understood. However, arguments based on steric hindrance, π-acceptance ability, and the electronegativity of the substituent groups have been variously invoked to explain the preference of a molecule for one or the other isomers. For the series $Fe(CO)_4(MX_3)_2$, (M = Ge, Sn; X = Cl, Br, I)[48], the cis isomer is the most usual compound formed. This was explained[48] by regarding the cis form as the electronically preferred isomer since it avoids as nearly as possible a condition in which the mutually trans carbonyl groups are competing for π-electron density of the iron. However, for the molecule $Fe(CO)_4(GeI_3)_2$ the trans isomer predominates and this was thought to be because of the steric requirements of the bulky GeI_3 groups. In the series $Ru(CO)_4(SnR_3)$, (R = Me, Et, Pr^n, Bu^n)[47,51], the cis/trans equilibrium strongly favours the trans form as the alkyl substituents become increasingly bulky. When R = C_6H_5 or $CH_2C_6H_5$, the complexes only exist as the trans isomer. Cotton *et al.*[51] speculate that this may be due to a combination of steric effects and Sn-Ru $d\pi$-$d\pi$ bonding. The more electronegative nature of the phenyl rings would contract the empty 5d orbitals of the Sn atom to a greater degree than the alkyl groups, and hence lead to a better overlap with filled d-orbitals of Ru. A linear Sn-Ru-Sn sequence would lead to better delocalization than that possible for the cis configuration. It is also possible that the $d\pi$-$d\pi$ overlap in the Ru-Sn system is more extensive than for the Fe-Sn system where the cis isomer predominates. However, the lack of trans isomers of the $Fe(CO)_4(SnR_3)_2$ species is possibly due to the decomposition of the cis complexes into $[R_2SnFe(CO)_2]_2$ in preference to isomerization. The trans isomer is also preferentially formed in the series $Ru(CO)_4(MCl_3)_2$, (M = Si, Ge, Sn). If, as was earlier shown in the discussion, the π-acceptance properties of the $GeCl_3$ group and the CO group are similar, then the $d\pi$-$d\pi$ overlap of the Ge-Ru system may well be the most important factor favouring the trans isomer. Since the π-acceptance properties of Cl_3Sn and Cl_3Si are not markedly different from those of Cl_3Ge, the same may also be true for the molecules containing these ligands. However, for the complexes $Os(CO)_4I_2$, $Ru(CO)_4I_2$ and $Fe(CO)_4I_2$ where I is a very weak π-acceptor ligand, the reaction equilibrium is displaced in favour of the cis forms for the Ru and Fe-complexes, and in favour of the trans form in the Os-complex (under pressure and CO). On exposure to light, however, trans-$Os(CO)_4I_2$ isomerizes. Hence one must be very careful when commenting on the relative stability of an isomer, since different experimental conditions have a considerable effect on the displacement of the equilibrium. None the less, it does indicate that for this molecule, where the $d\pi$-$d\pi$ overlap between Os and the very weak π-acceptor Br is minimal another effect is influencing the formation of the trans isomer.

The CO stretching frequency data for the series $Ru(CO)_4(MCl_3)_2$, (M = Ge, Sn, Si), are consistent with the MCl_3 groups being strong π-acceptor ligands, with $GeCl_3$ being the strongest. The strongest competition for π density on the Ru would be exerted by the $GeCl_3$ ligands, and in order to avoid direct competition these ligands would tend to favour a cis conformation rather more than molecules containing the $SiCl_3$ and $SnCl_3$ ligands. The cis isomer has only been observed for the $Ru(CO)_4(GeCl_3)_2$ molecule. The electronegativity of the ligands may also play an important role since the ligands where trans isomers form are very electronegative. Other transition metals also appear to give trans isomers when X is electronegative, e.g., HCF_2CF_2-$Mn(CO)_4PF_3$[63].

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