single step through the cuboctahedral pathway (Table VII). The one-step rotation of a pentagonal pyramid predicts the 9,10-meta isomer, while the rotation of a triangle in the icosahedron predicts the 5,9 isomer.

A second unique experimental result is that the initial ortho product from 9,12-Cl_2-*o*-$B_{10}H_8C_2(CH_3)_2$ is 8,9-Cl_2-*o*-$B_{10}H_8C_2(CH_3)_2$. This result does not arise from the simple cuboctahedral mechanism (Table VIII)[3] but is the unique product obtained by triangle rotation of a B_3 unit not attached to C *in the cuboctahedral intermediate.* This type of rotation was given preference in our earlier studies of ortho-ortho isomerizations of monohalocarboranes.[1] The one-step rotation of a pentagonal pyramid yields the 4,9-, the 8,9-, and the 8,10-ortho isomers in ratios of 2:2:1, respectively; and the triangle rotation in the icosahedron predicts the 8,9- and the 4,12-ortho isomers in a 2:1 ratio.

Rearrangement of 8,9-Cl_2-*o*-$B_{10}H_8C_2(CH_3)_2$, shown experimentally to yield the 9,12- and the 4,9-ortho derivatives, should also have yielded the 4,12-ortho product by the cuboctahedral mechanism (Table VIII). This and other more preliminary results suggest that the simple statistical application of these geometrical mechanisms will prove inadequate when detailed kinetic data are available. It has already been shown that there is an effect of substituent (Cl or F) on the final equilibrium of *m*- and *p*-carboranes. Other evidence for electronic effects, and also steric effects, is expected. Finally, we would not, at this stage, exclude minor contributions of other mechanisms than the cuboctahedral pathway, as modified by triangle rotation in this intermediate, in these interesting isomerization reactions.

Acknowledgment. We thank the Office of Naval Research and the National Institutes of Health for support of this research. We are also much indebted to Richard J. Wiersema of the University of California at Los Angeles for the ^{11}B nmr spectra.

Registry No. 9,10-Cl_2-*m*-$B_{10}H_8C_2(CH_3)_2$, 23810-46-0; 2,6-Cl_2-*m*-$B_{10}H_8C_2(CH_3)_2$, 41184-44-5; 2,4-Cl_2-*m*-$B_{10}H_8C_2(CH_3)_2$, 41184-45-6; 4,11-Cl_2-*m*-$B_{10}H_8C_2(CH_3)_2$, 41184-46-7; 5,12-Cl_2-*m*-$B_{10}H_8C_2(CH_3)_2$, 41267-46-3; 9,12-Cl_2-*o*-$B_{10}H_8C_2(CH_3)_2$, 41184-47-8; 4,9-Cl_2-*m*-$B_{10}H_8C_2(CH_3)_2$, 41184-48-9; 5,9-Cl_2-*m*-$B_{10}H_8C_2(CH_3)_2$, 41267-47-4; 4,8-Cl_2-*o*-$B_{10}H_8C_2(CH_3)_2$, 41184-49-0; 8,9-Cl_2-$B_{10}H_8C_2(CH_3)_2$, 41184-50-3; 4,9-Cl_2-*o*-$B_{10}H_8C_2(CH_3)_2$, 41184-51-4; boron-11, 14798-13-1.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-73-2644.

Contribution from the Department of Chemistry, Tulane University, New Orleans, Louisiana 70118

Crystal and Molecular Structure of Chloroaquobis(trimethylarsine)tetrakis(trifluoromethyl)rhodiacyclopentadiene, $RhCl(H_2O)(As(CH_3)_3)_2C_4(CF_3)_4$[1]

JOEL T. MAGUE

Received April 5, 1973

The structure of chloroaquobis(trimethylarsine)tetrakis(trifluoromethyl)rhodiacyclopentadiene, $RhCl(H_2O)As(CH_3)_3)_2C_4(CF_3)_4$, has been determined from three-dimensional X-ray data collected by counter methods. The final conventional and weighted R factors obtained from a block-diagonal least-squares refinement for 1689 reflections are 0.063 and 0.060, respectively. The material crystallizes in the orthorhombic system with space group $P2_12_12_1$ and a unit cell of dimensions $a = 11.580$ (1), $b = 20.034$ (1), and $c = 10.158$ (1) Å. There are four molecules in the unit cell and the crystal consists of the packing of these monomeric molecules with no unusual intermolecular contacts. The coordination about rhodium is in the form of a distorted octahedron with the Cl atom, the O atom of the water molecule, and the 1 and 4 C atoms of the $C_4(CF_3)_4$ moiety approximately defining a plane and the arsenic atoms disposed above and below it. Both the Rh-Cl (2.448 (5) Å) and Rh-O (2.241 (12) Å) distances are significantly longer than anticipated due to a strong trans influence exerted by the fluorocarbon moiety. The Rh-C distances of 2.047 (16) and 1.998 (16) Å are different to a marginally significant extent which is believed to be real while the C-C distances in the metallocyclopentadiene ring suggest the π bonding to be largely localized. Semiempirical molecular orbital calculations on a model for this complex suggest that the asymmetric ring geometry observed represents the geometry of minimum energy.

Introduction

In the course of our studies on the interaction of fluoroacetylenes with low-valent transition metal complexes, we investigated the decarbonylation of the six-coordinate metallocycle $Rh(CO)Cl(As(CH_3)_3)_2C_4(CF_3)_4$.[2] The material obtained was not the expected five-coordinate metallocycle $RhCl(As(CH_3)_3)_2C_4(CF_3)_4$, analogous to $RhCl(Sb(C_6H_5)_3)_2$-$C_4(CF_3)_4$ whose structure has been determined previously,[3] but initally appeared from infrared data to contain a molecule of formic acid. Since the production of formic acid from carbon monoxide in the coordination sphere of rhodium would be a novel process, the determination of the crystal structure of the material was undertaken to ascertain the nature of the sixth ligand. Unfortunately, the material did not prove to contain formic acid but rather is the aquo derivative of the five-coordinate metallocycle. Nevertheless, the com-

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[1] Supported by the National Science Foundation (Grant No. GP-8066) and the Gulf Research and Development Co.

[2] J. T. Mague, M. O. Nutt, and E. H. Gause, Abstracts, 161st National Meeting of the American Chemical Society, Los Angeles, Calif., April 1971, No. INOR 133.

[3] J. T. Mague, *Inorg. Chem.*, 9, 1610 (1970).

plex is of importance, it being the first completely structurally characterized complex containing both metal–carbon σ bonds and coordinated water. A preliminary account of the structure has appeared.[4]

Experimental Section

Preparation of $Rh(H_2O)Cl(As(CH_3)_3)_2C_4(CF_3)_4$. The title compound was prepared by refluxing $Rh(CO)Cl(As(CH_3)_3)_2C_4(CF_3)_4$[2] in benzene until a deep yellow solution was obtained (*ca.* 0.5 hr). This solution was evaporated to dryness at the water pump to give an off-white powder. Recrystallization from a diethyl ether–petroleum ether (bp 30–60°) mixture afforded very pale yellow, wedge-shaped columns which appear to be unaffected by the atmosphere.

Crystallographic Data. X-Ray diffraction data indicated that the crystals belonged to the orthorhombic system. Unit cell dimensions obtained by a least-squares analysis of the setting angles of 17 high-order reflections as previously described[3] are $a = 11.580$ (1), $b = 20.034$ (1), and $c = 10.158$ (1) Å. The unit cell volume is 2357 Å^3. No density was measured owing to the ready solubility of the complex in all suitable media. However, the calculated density of 2.03 g/cm^3 based on $Z = 4$ is a reasonable value based on previous experience. The systematic absences $h00$ for $h = 2n + 1$, $0k0$ for $k = 2n + 1$, and $00l$ for $l = 2n + 1$ uniquely define the space group as $P2_12_12_1$ ($D_2{}^4$, No. 19).[5]

The crystal used for the collection of the intensity data was a wedge-shaped column of dimensions 0.30 × 0.26 × 0.30 mm along *a*, *b*, and *c*, respectively. Using optical goniometry the developed faces were identified as $\{101\}$, $\{10\bar{1}\}$, $\{\bar{1}0\bar{1}\}$, $\{\bar{1}01\}$, $\{\bar{1}20\}$, $\{120\}$, and $\{0\bar{1}0\}$. The crystal was mounted such that the crystallographic *b* axis was coincident with the axis of the goniostat.

Intensity data were collected at room temperature, using a Picker four-circle, card-controlled, automated diffractometer, Zr-filtered Mo Kα radiation (λ 0.7107 Å), and a takeoff angle of 5.3°. Integrated intensities were measured with a scintillation counter employing a pulse height analyzer set to admit 90% of the Mo Kα pulse distribution. A θ–2θ scan of 2° in 2θ centered about $2\theta_{\text{calcd}}$ was used. The scan rate was 1°/min and backgrounds were counted for 20 sec at each limit. The nine reflections for which the maximum count rate was in excess of 10,000 cps were remeasured at reduced power to minimize coincidence losses and were scaled to the main data set using the three standard reflections which were used to monitor the stability of the system. These three reflections were scanned every 3–4 hr and although they showed no evidence for crystal decomposition, they appeared to be subject to an instability which caused a 5–8% variation ($\sim 2.3\sigma(I)$) in their intensities over the course of the data collection. We initially suspected that some lack of rigidity in the crystal mounting which would allow it to slip out of alignment from time to time was the cause but this did not appear to be the case. Subsequent exhaustive checks of the high voltage and counting circuits also failed to uncover any malfunctions which could cause the observed fluctuations. We therefore decided to place the data on a common scale using the successive values of the integrated intensities of the standards. The successful refinement of the structure to a low residual suggests that this treatment of the data did not introduce any serious error. The unique octant having h, k, and l all ≥ 0 and $\sin\theta/\lambda \leq 0.6$ was scanned to yield 2368 independent reflections. The derivation of the raw intensities (I) and their associated standard deviations ($\sigma(I)$) was accomplished as previously described.[3] The 777 reflections for which $I \leq 2\sigma(I)$ were rejected as statistically insignificant and were treated as unobserved. Each was assigned a threshold value given by $I_{\text{th}} = 2\sigma(I)$ and all reflections were corrected for Lorentz, polarization, and absorption effects. The linear absorption coefficient for the compound is 38.6 cm^{-1} for Mo Kα radiation which results in transmission factors ranging from 0.61 to 0.68.[6]

Solution and Refinement of the Structure. The structure was refined by a block-diagonal, least-squares process. Scattering factors for neutral Rh, As, Cl, C, F, and O were those tabulated by Cromer and Waber[7] while the values given by Stewart, *et al.*,[8] were used for hydrogen. The scattering factors for Rh, As, and Cl included both the real and imaginary parts of the correction for anomalous dispersion.[9] The function minimized was $w\Delta^2$ where $\Delta = K|F_o| - G|F_c|$; K and G are scale factors ($G = 1.0$) and $w = [\sigma(|F_o|)]^{-2}$. The standard deviation in $|F_o|$, $\sigma(|F_o|)$, was taken as $\sigma(|F_o|^2)/2|F_o|$. Unobserved reflections were included in the refinement if $|F_c|$ exceeded F_{th}.[10] In the final stages of the refinement, 98 reflections met this criterion but of these only five were greater than $1.5F_{\text{th}}$. The conventional and weighted residuals R_1 and R_2 are defined as $R_1 = \Sigma|\Delta|/\Sigma|F_o|$ and $R_2 = [\Sigma w\Delta^2/\Sigma wF_o{}^2]^{1/2}$.

A three-dimensional unsharpened Patterson function was calculated which provided coordinates for the rhodium and arsenic atoms. The initial model chosen was the configuration for which the coordinates of the rhodium atom are all positive. A difference Fourier synthesis calculated after two cycles of least-squares refinement of the positional parameters of the heavy atoms revealed the positions of the remaining nonhydrogen atoms although the presence of a degree of pseudosymmetry occasioned by the near-zero values for the x coordinates of the heavy atoms made it difficult to decide on the nature of the sixth ligand. After another two cycles of refinement which included all nonhydrogen atoms but those of this ligand, a second difference map clearly showed only one significant peak and it was concluded at this point that the sixth ligand was water rather than formic acid. Refinement was continued with inclusion of the oxygen atom of the water and anisotropic thermal parameters of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$ for the four heavy atoms and all twelve fluorine atoms. Several more cycles of refinement lowered R_1 to 0.91 and difference Fourier syntheses calculated in planes normal to the As–C bond directions showed peaks of heights 0.3–0.8 e/Å^3 in positions where the hydrogen atoms of the methyl groups were expected. As these peaks were rather diffuse and of comparable size to other peaks surrounding the methyl carbon atoms, it was decided to place the hydrogens using an idealized methyl group geometry with a C–H distance of 1.0 Å, a H–C–H angle of 109°, and the plane containing the hydrogens normal to the As–C bond direction. Utilizing these constraints, the best rotational orientation of each methyl group was obtained from the difference map calculated in the idealized plane of the three hydrogen atoms. The contribution of the hydrogen atoms, using isotropic thermal parameters equal to 1.1 times that of the carbon atom to which they were attached, was included in the subsequent calculations of structure factors but their positions were not refined. Instead they were reset manually after each cycle of refinement. A difference map at this point showed evidence for anisotropic thermal motion of the remaining nonhydrogen atoms and refinement was continued with anisotropic thermal parameters for these as well. With these changes, R_1 quickly dropped to 0.07 and the refinement process slowly converged at a value of 0.063 ($R_2 = 0.060$) for the 1689 reflections which were used.

The effect of change of configuration (accomplished by refining the molecule which was related to the original model by the transformation $(x, y, z) \rightarrow (\bar{x}, \bar{y}, \bar{z})$) was investigated with convergence being attained at essentially the same values of R_1 and R_2. Inspection of the calculated structure factors for the two models showed that no clear differentiation could be made between them so the original choice was retained.[11] A final difference Fourier synthesis showed no features greater than ±0.5 e/Å^3 except in the vicinities of the heavy atoms where slightly larger features (±1.0 e/Å^3) analogous to those observed previously[10] were present. We have not as yet been able satisfactorily to account for these. Attempts were made to locate the hydrogen atoms of the water molecule but these were unsuccessful. The error in an observation of unit weight is 1.95. The final atomic coordinates and anisotropic thermal parameters, together with their associated standard deviations as determined from the inverse matrix, are presented in Tables I and II. Table III presents the parameters assigned to the hydrogen atoms.

Results and Discussion

Description of the Structure. The crystal structure consists of the packing of discrete, monomeric units of $RhCl(H_2O)(As(CH_3)_3)_2C_4(CF_3)_4$ with no unusually short inter-

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(4) J. T. Mague, *J. Amer. Chem. Soc.*, **93**, 3550 (1971).

(5) "International Tables for X-Ray Crystallography," Vol 1, Kynoch Press, Birmingham, England, 1962.

(6) All computations were performed on an IBM 7044 computer at the Tulane University Computer Laboratory. Local programs were used except for those noted here: GSET-4, C. T. Prewitt (diffractometer settings); CELL, B. L. Trus (refinement of unit cell dimensions); BLSA-H (modification of the Gantzel–Sparks–Trueblood UCLALS-1 (ACA Program No. 317) for block-diagonal, least-squares refinement and distance–angle calculations), C. J. Fritchie, Jr.; ORABS, W. R. Busing (absorption corrections); ORTEP, C. K. Johnson (graphical illustrations).

(7) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).

(8) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

(9) D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).

(10) J. T. Mague, *Inorg. Chem.*, **8**, 1975 (1969).

(11) See paragraph at end of paper regarding supplementary material.

Table I. Final Atomic Coordinates[a]

Atom[b]	x	y	z
Rh	0.01728 (11)	0.18569 (6)	0.16543 (12)
As_1	0.01897 (18)	0.26319 (8)	0.35020 (16)
As_2	0.01623 (17)	0.11081 (8)	−0.02346 (16)
Cl	−0.07576 (41)	0.26983 (22)	0.02661 (50)
F_{51}	0.27221 (92)	0.12622 (64)	0.14863 (119)
F_{52}	0.27499 (109)	0.05140 (75)	0.29710 (130)
F_{53}	0.28655 (97)	0.16453 (70)	0.33829 (132)
F_{61}	0.11999 (124)	−0.02837 (56)	0.41782 (136)
F_{62}	−0.00134 (130)	0.02740 (58)	0.55806 (92)
F_{63}	0.17678 (110)	0.05872 (74)	0.51832 (123)
F_{71}	−0.10842 (118)	−0.02991 (60)	0.37396 (157)
F_{72}	−0.24663 (128)	0.01704 (76)	0.26455 (152)
F_{73}	−0.21827 (114)	0.03862 (68)	0.47221 (132)
F_{81}	−0.24802 (100)	0.022194 (57)	0.22547 (135)
F_{82}	−0.27738 (106)	0.13283 (67)	0.11124 (110)
F_{83}	−0.30751 (96)	0.13283 (58)	0.31450 (108)
O	0.16785 (105)	0.24311 (56)	0.08544 (110)
C_1	0.10758 (146)	0.11652 (83)	0.27224 (153)
C_2	0.04268 (164)	0.07472 (79)	0.33841 (154)
C_3	−0.07909 (148)	0.08594 (80)	0.32649 (163)
C_4	−0.11379 (145)	0.13523 (78)	0.24568 (156)
C_5	0.23495 (193)	0.11557 (119)	0.29187 (218)
C_6	0.08540 (216)	0.02912 (117)	0.27025 (202)
C_7	−0.15989 (205)	0.02946 (139)	0.45728 (194)
C_8	−0.24144 (156)	0.15395 (81)	0.36256 (163)
C_{11}	0.15415 (187)	0.31938 (121)	0.22209 (225)
C_{12}	−0.10843 (233)	0.32834 (109)	0.36188 (226)
C_{13}	0.00346 (204)	0.22761 (92)	0.34115 (163)
C_{21}	0.01496 (185)	0.01467 (69)	0.00819 (174)
C_{22}	−0.10952 (186)	0.12116 (87)	−0.14454 (182)
C_{23}	0.14576 (152)	0.12215 (143)	−0.14844 (192)

[a] Estimated standard deviations of the least significant figure(s) in parentheses. [b] Atom labeling is that of Figure 1.

Table II. Anisotropic Thermal Parameters (× 10^4)[a]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Rh	44 (1)	15 (1)	66 (1)	0 (1)	1 (2)	8 (1)
As_1	71 (2)	21 (1)	80 (2)	−3 (2)	−2 (4)	−11 (2)
As_2	63 (1)	17 (1)	78 (2)	−2 (2)	12 (4)	−7 (2)
Cl	72 (4)	19 (1)	130 (6)	7 (4)	−24 (9)	19 (5)
F_{51}	60 (9)	50 (4)	199 (17)	23 (11)	23 (23)	43 (16)
F_{52}	139 (12)	94 (6)	234 (18)	160 (14)	133 (28)	182 (17)
F_{53}	85 (10)	60 (5)	262 (20)	−42 (13)	−150 (26)	−56 (19)
F_{61}	229 (17)	25 (3)	280 (22)	111 (12)	76 (34)	98 (13)
F_{62}	200 (16)	52 (4)	114 (11)	−17 (20)	74 (31)	69 (11)
F_{63}	141 (13)	78 (6)	151 (15)	−7 (18)	−83 (29)	71 (19)
F_{71}	152 (15)	24 (4)	371 (26)	7 (13)	55 (37)	70 (17)
F_{72}	151 (13)	73 (6)	219 (20)	−140 (15)	−72 (29)	30 (19)
F_{73}	168 (15)	55 (5)	204 (16)	−16 (17)	151 (28)	96 (16)
F_{81}	86 (10)	29 (3)	284 (21)	34 (11)	31 (27)	−10 (17)
F_{82}	104 (12)	56 (5)	117 (13)	−21 (14)	−28 (22)	−21 (14)
F_{83}	83 (10)	40 (4)	168 (15)	−27 (11)	90 (23)	31 (14)
O	76 (11)	21 (3)	113 (14)	−39 (11)	48 (22)	16 (12)
C_1	56 (14)	15 (4)	69 (17)	8 (15)	−19 (29)	31 (16)
C_2	116 (20)	15 (4)	82 (17)	1 (16)	−78 (36)	34 (16)
C_3	64 (15)	15 (4)	91 (20)	−4 (15)	85 (33)	−18 (18)
C_4	48 (14)	12 (4)	87 (19)	−10 (14)	−34 (29)	−10 (16)
C_5	122 (22)	53 (8)	138 (27)	114 (22)	−21 (44)	33 (27)
C_6	178 (28)	49 (8)	130 (24)	−33 (29)	−139 (45)	94 (24)
C_7	136 (24)	77 (11)	116 (24)	17 (30)	146 (43)	107 (27)
C_8	83 (17)	17 (4)	68 (17)	−38 (16)	54 (31)	21 (16)
C_{11}	111 (22)	45 (8)	185 (33)	−54 (25)	−11 (49)	−38 (30)
C_{12}	252 (30)	39 (7)	162 (31)	155 (21)	−84 (60)	−49 (27)
C_{13}	164 (24)	38 (6)	93 (18)	70 (25)	121 (48)	16 (19)
C_{21}	146 (23)	10 (4)	139 (22)	22 (20)	79 (54)	8 (16)
C_{22}	130 (22)	11 (4)	117 (23)	−2 (18)	−28 (42)	−22 (19)
C_{23}	28 (14)	88 (12)	110 (25)	−14 (23)	43 (35)	−34 (33)

[a] Estimated standard deviation of the least significant figure(s) in parentheses.

Table III. Positional and Thermal Parameters Assigned to the Hydrogen Atoms

Atom[a]	x	y	z	B, Å^2
H_{111}	0.2082	0.3090	0.2919	6.9
H_{112}	0.1899	0.3130	0.4506	6.9
H_{113}	0.1352	0.3676	0.3525	6.9
H_{121}	−0.0964	0.3598	0.2801	8.5
H_{122}	−0.1063	0.3589	0.4222	8.5
H_{123}	−0.1859	0.3659	0.3359	8.5
H_{131}	−0.0160	0.2664	0.5886	6.8
H_{132}	0.0786	0.1799	0.5564	6.8
H_{133}	−0.0640	0.1927	0.5278	6.8
H_{211}	−0.0572	0.0011	0.0537	5.4
H_{212}	0.0807	0.0009	0.0626	5.4
H_{213}	0.0202	−0.0099	−0.0783	5.4
H_{221}	−0.1139	0.1677	−0.1860	6.2
H_{222}	−0.1899	0.1151	−0.0946	6.2
H_{223}	−0.1086	0.0866	−0.2160	6.2
H_{231}	0.1471	0.0836	−0.2131	5.8
H_{232}	0.2240	0.1220	−0.1001	5.8
H_{233}	0.1367	0.1653	−0.1960	5.8

[a] In the subscripts attached to these atoms, the carbon atom to which they are attached is given by the first two digits while the sequence number of the hydrogen atom is given by the third (*e.g.*, H_{111} is hydrogen atom 1 on C_{11}).

Table IV. Interatomic Distances (Å)[a]

Rh-As_1	2.436 (2)	C_6-F_{61}	1.284 (26)
Rh-As_2	2.436 (2)	C_6-F_{62}	1.435 (26)
Rh-Cl	2.448 (5)	C_6-F_{63}	1.362 (27)
Rh-O	2.241 (12)	C_7-F_{71}	1.335 (30)
Rh-C_1	2.047 (16)	C_7-F_{72}	1.436 (27)
Rh-C_4	1.998 (16)	C_7-F_{73}	1.316 (25)
C_1-C_2	1.311 (24)	C_8-F_{81}	1.364 (20)
C_2-C_3	1.433 (26)	C_8-F_{82}	1.273 (20)
C_3-C_4	1.346 (23)	C_8-F_{83}	1.283 (20)
C_1-C_5	1.475 (28)	As_1-C_{11}	1.932 (23)
C_2-C_6	1.593 (27)	As_1-C_{12}	1.972 (25)
C_3-C_7	1.513 (31)	As_1-C_{13}	1.937 (17)
C_4-C_8	1.544 (24)	As_2-C_{21}	1.953 (14)
C_5-F_{51}	1.326 (25)	As_2-C_{22}	1.917 (20)
C_5-F_{52}	1.394 (28)	As_2-C_{23}	1.978 (19)
C_5-F_{53}	1.340 (27)		

[a] Numbers in parentheses are the estimated standard deviations in the least significant figure(s).

molecular contacts. A perspective view of the molecule is given in Figure 1 while Figures 2 and 3 depict the molecular packing and the intramolecular F- - -F contacts, respectively. The interatomic distances are presented in Table IV, the interbond angles in Table V, and the weighted, least-squares planes through various parts of the molecule in Table VI. From Figure 1 and Table VI it is evident that the coordination about the rhodium atom is that of a distorted octahedron. The primary distortion is in the departure of the O-Rh-Cl and C_1-Rh-C_4 angles from 90° although it is also evident

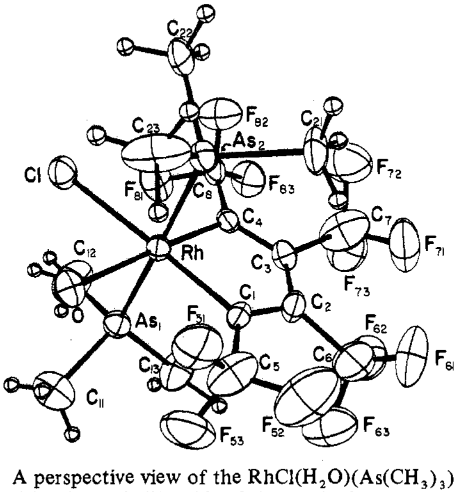

Figure 1. A perspective view of the $RhCl(H_2O)(As(CH_3)_3)_2C_4(CF_3)_4$ molecule. The thermal ellipsoids of the nonhydrogen atoms are represented by the 50% probability contours.

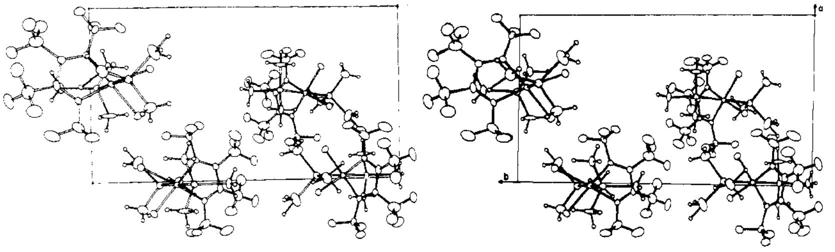

Figure 2. A stereoscopic view of the contents of the unit cell of $RhCl(H_2O)(As(CH_3)_3)_2C_4(CF_3)_4$ (*c*-axis projection).

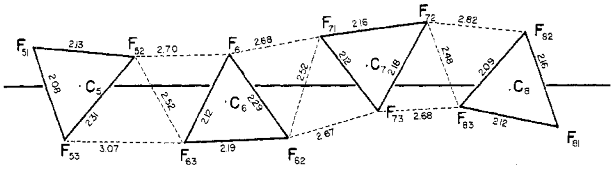

Figure 3. A schematic representation of the F- - -F contacts in the rhodiacyclopentadiene ring.

Table V. Interbond Angles (deg)[a]

As_1-Rh-As_2	178.41 (9)	F_{61}-C_6-F_{63}	106.9 (17)
As_1-Rh-Cl	90.5 (1)	F_{62}-C_6-F_{63}	103.3 (17)
As_1-Rh-O	86.9 (3)	C_2-C_3-C_7	118.1 (16)
As_1-Rh-C_1	91.1 (4)	C_4-C_3-C_7	120.8 (16)
As_1-Rh-C_4	90.8 (5)	C_3-C_7-F_{71}	114.3 (17)
As_2-Rh-O	92.0 (3)	C_3-C_7-F_{72}	113.2 (16)
As_2-Rh-Cl	88.2 (1)	C_3-C_7-F_{73}	114.7 (19)
As_2-Rh-C_1	90.2 (5)	F_{71}-C_7-F_{72}	102.6 (18)
As_2-Rh-C_4	90.3 (4)	F_{71}-C_7-F_{73}	106.3 (17)
Cl-Rh-O	77.3 (3)	F_{72}-C_7-F_{73}	104.6 (16)
Cl-Rh-C_4	104.4 (5)	C_3-C_4-C_8	124.0 (14)
O-Rh-C_1	98.2 (6)	Rh-C_4-C_8	122.8 (11)
C_1-Rh-C_4	80.2 (6)	C_4-C_8-F_{81}	107.0 (13)
Rh-C_1-C_2	114.3 (12)	C_4-C_8-F_{82}	111.7 (14)
C_1-C_2-C_3	114.9 (15)	C_4-C_8-F_{83}	112.2 (14)
C_2-C_3-C_4	117.4 (15)	F_{81}-C_8-F_{82}	109.6 (15)
C_3-C_4-Rh	113.2 (12)	F_{81}-C_8-F_{83}	106.1 (14)
Rh-C_1-C_5	120.8 (13)	F_{82}-C_8-F_{83}	110.0 (14)
C_5-C_1-C_2	124.9 (16)	Rh-As_1-C_{11}	115.2 (7)
C_1-C_5-F_{51}	109.6 (18)	Rh-As_1-C_{12}	112.3 (7)
C_1-C_5-F_{52}	110.0 (18)	Rh-As_1-C_{13}	118.5 (7)
C_1-C_5-F_{53}	115.4 (18)	C_{11}-As_1-C_{12}	102.9 (10)
F_{51}-C_5-F_{52}	102.8 (16)	C_{11}-As_1-C_{13}	102.6 (9)
F_{51}-C_5-F_{53}	102.6 (17)	C_{12}-As_1-C_{13}	103.5 (9)
F_{52}-C_5-F_{53}	115.2 (17)	Rh-As_2-C_{21}	118.5 (6)
C_1-C_2-C_6	125.2 (17)	Rh-As_2-C_{22}	116.3 (5)
C_3-C_2-C_6	117.4 (15)	Rh-As_2-C_{23}	115.5 (6)
C_2-C_6-F_{61}	112.0 (18)	C_{21}-As_2-C_{22}	101.9 (8)
C_2-C_6-F_{62}	109.7 (17)	C_{21}-As_2-C_{23}	98.7 (10)
C_2-C_6-F_{63}	109.7 (17)	C_{22}-As_2-C_{23}	103.0 (8)
F_{61}-C_6-F_{62}	114.8 (18)		

[a] Numbers in parentheses give the estimated standard deviations in the least significant figure(s).

Table VI. Weighted Least-Squares Planes in the $RhCl(H_2O)(As(CH_3)_3)_2C_4(CF_3)_4$ Molecule[a]

Atoms	Plane no.	*A*	*B*	*C*	*D*
Rh, Cl, O, C_1, C_4	1	0.029	−0.625	−0.780	−3.631
Rh, C_1, C_2, C_3, C_4	2	−0.014	−0.623	−0.781	−3.636
C_1, C_2, C_3, C_4	3	−0.016	−0.631	−0.775	−3.631

Distances of Atoms from Planes, Å

	Plane no.		
Atom	1	2[c]	3
Rh	0.000 (1)	−0.001 (1)	
Cl	0.015 (5)		
O	−0.035 (12)		
C_1	0.051 (16)	0.001 (16)	−0.007 (16)
C_2	0.028 (17)[b]	0.008 (17)	0.013 (17)
C_3	−0.059 (16)[b]	−0.017 (16)	−0.013 (16)
C_4	−0.048 (16)	0.014 (16)	0.007 (16)

[a] The equations of the planes are of the form $AX + BY + CZ - D = 0$ where *X*, *Y*, and *Z* are the orthogonal coordinates (in Å) which are related to the fractional coordinates (*x*, *y*, *z*) by the transformations $X = ax$, $Y = by$, and $Z = cz$. [b] These atoms not included in the calculation of plane 1. [c] Distances of other atoms of interest from plane 2 are as follows: C_5, 0.007 (23); C_6, −0.373 (23); C_7, 0.416 (24); C_8, −0.011 (17) Å.

that the four equatorial light atoms deviate significantly from coplanarity with the rhodium atom. These latter deviations are primarily the result of rather short intramolecular contacts involving these atoms, *viz.*, Cl- - -O = 2.93 Å, Cl- - -F_{81} = 3.00 Å, and O- - -F_{51} = 2.71 Å.

The two Rh-As distances are both 2.436 (2) Å. These may be compared with distances of 2.404 (1) and 2.410 (1) Å in $[Rh(CO)Cl((C_6H_5)_2AsCH_2As(C_6H_5)_2)]_2$,[10] of 2.492 (2) and 2.494 (2) Å in π-$C_4H_7RhCl_2((C_6H_5)_3As)_2$,[12] and of 2.333 (5) and 2.354 (6) Å in $RhCl_3(o\text{-}CH_3OC_6H_4As(C_6H_5)_2)_2$.[13] In the last named compound the arsenic atoms are mutually cis and the shortness of the bonds has been attributed to π bonding. By contrast, the Rh-As distances in the π-methylallyl complex are considered to be appropriate for normal single bonds, despite the cis arrangement of the arsenic atoms, presumably because most of the π bonding capability of the rhodium is utilized in bonding the π-methylallyl group. We conclude that the Rh-As distance found here is that which should be expected for a trans As-Rh-As moiety in six-coordinate Rh(III) complexes, where the π bonding is evened out (*vide infra*).[14,15]

Of considerably greater interest are the other metal-ligand distances. The Rh-Cl bond length of 2.448 (5) Å is significantly longer than that found in $RhCl(Sb(C_6H_5)_3)_2C_4(CF_3)_4 \cdot CH_2Cl_2$ (2.318 (3) Å; $\Delta/\sigma = 13$).[3] This is undoubtedly due primarily to a strong trans effect exerted by the organic ligand, an interpretation which is further supported by the observation that the chlorine is almost immediately precipitated by silver nitrate in methanol. By contrast the chlorine in the five-coordinate triphenylstibine complex is removed only with difficulty.[16] A similar structural trans effect has been demonstrated in $[Rh(C_2H_5)(NH_3)_5]Br_2$.[17] Further

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(12) T. G. Hewitt, J. J. DeBoer, and K. Anzenhofer, *Acta Crystallogr., Sect. B*, 26, 1244 (1970).

(13) R. Graziani, G. Bombieri, L. Volponi, C. Panattoni, and R. J. H. Clark, *J. Chem. Soc. A*, 1236 (1969).

(14) In the complex *mer*-$RhCl_3(nas)_2$ (nas = *o*-dimethylaminophenyldimethylarsine), where a trans As-Rh-As moiety is also present, the Rh-As distances are 2.529 (5) and 2.342 (4) Å.[15] However in this case one of the nas ligands chelates, the other remaining monodentate. The shortness of the Rh-As bond to the chelate ligand is attributed to $d\pi$-$d\pi$ bonding, probably accentuated by the geometrical constraints of the chelate ring. Presumably if both ligands were monodentate, any π bonding would be evened out between them and a Rh-As distance of ~2.44 Å would be anticipated.

(15) G. Bombieri, R. Graziani, C. Panattoni, L. Volponi, R. J. H. Clark, and G. Natile, *J. Chem. Soc. A*, 14 (1970).

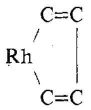
(16) J. T. Mague and E. H. Gause, unpublished observation.

(17) A. C. Skapski and P. G. H. Troughton, *Chem. Commun.*, 666 (1969).

evidence for a strong trans effect exerted by the *cis*-1,2,3,4-tetrakis(trifluoromethyl)-1,3-butadienylene moiety is the Rh-O distance of 2.241 (12) Å which compares very favorably with the Rh-N distance of 2.254 (8) Å observed for the ammonia trans to the ethyl group in $[Rh(C_2H_5)(NH_3)_5]Br_2$[17] (all other Rh-N distances are 2.072 (6) Å). Although not strictly comparable, an $Rh-OH_2$ distance of 2.310 (3) Å has been found in $Rh_2(OOCCH_3)_4(H_2O)_2$[18] and characterized as being indicative of a weakly bound water molecule. Further evidence that the observed Rh-O distance should be considered unusually long and that the water molecule is therefore weakly coordinated comes from the observation that the water readily dissociates in solution.[2]

The $Rh-C_1$ and $Rh-C_4$ distances of 2.047 (16) and 1.998 (16) Å, respectively, are different by an amount which is of marginal significance ($\Delta/\sigma = 3.1$). In a previous paper we had dismissed a similar difference as being either an artifact of the structure determination or a result of packing forces.[3] Despite the optimistic assessment of error inherent in the block-diagonal refinement procedure, the fact that the same pattern has now been found in a second compound in which the rhodium has different ligands and for which there is an entirely different crystal structure leads us to believe that it is real even though the structural data do not provide a clear proof. The molecular orbital calculations discussed below provide a further argument for the reality of the difference. These values can be compared with Rh-C distances of 2.048 (16) Å in $[Rh(C_2H_5)(NH_3)_5]Br_2$,[17] 2.083 (7) Å, in $RhI_2(CH_3)(P(C_6H_5)_3)_2 \cdot C_6H_6$,[19] and 2.08 Å in $RhI_2(S(CH_3)_2)_3)(CH_3)_4$.[20]

An inspection of the C-C bonds in the ring indicates that there is an increased *localization* of the π interactions within the rhodiacyclopentadiene ring as compared with the molecule studied previously.[3] Thus the C_1-C_2 and C_3-C_4 distances are essentially equal and are of a length expected for an olefinic double bond while the C_2-C_3 distance is significantly longer than either of these. The bonding within the ring therefore most closely resembles



Once again the ring is planar within experimental error ($\sigma_{plane} = 0.017$) while the carbon atoms of the trifluoromethyl groups (particularly C_6 and C_7) are displaced out of the mean plane presumably to minimize F- - -F contacts between adjacent groups (see Figure 3).

The C(ring)-C(trifluoromethyl) distances show considerable variation which we ascribe primarily to the difficulty of accurately locating the trifluoromethyl groups due to their considerable thermal motion and the probable inadequacy of the individual anisotropic model employed in the refinement. However, we have not been able to devise a significantly improved model for the thermal motion. Similar difficulties in handling this problem have been noted previously.[3,21]

Molecular Orbital Calculations. We have carried out a series of semiempirical molecular orbital calculations on models for the five- and six-coordinated rhodiacycles in order to learn more about the origins of the asymmetry in the Rh-C bond lengths and to gain information on the π bonding within the rhodiacyclopentadiene ring. Details of these calculations are presented elsewhere[22] and only the results will be summarized here. Since the complete molecules would have required prohibitively large amounts of computing time, the axial ligands were approximated by AsH_3 in these model compounds. This simplification has been previously shown not seriously to prejudice the computational results.[23,24] For the six-coordinate model, $Rh(H_2O)Cl(AsH_3)_2C_4(CF_3)_4$, the geometry used was that determined in the present study. The five-coordinate model, $RhCl(AsH_3)_2C_4(CF_3)_4$, utilized the molecular dimensions found for $RhCl(Sb(C_6H_5)_3)_2C_4(CF_3)_4$ with the exception that the Rh-As distances were the same as in the six-coordinate case.

Table VII. Overlap Populations of Selected Bonds in Five- and Six-Coordinate Rhodiacyclopentadienes

	$Rh(H_2O)ClL_2C_4(CF_3)_4$		$RhClL_2C_4(CF_3)_4$	
Bond	OP(σ)	OP(π)	OP(σ)	OP(π)
$Rh-As_1$	0.2602	0.2678	0.2886	0.2414
$Rh-As_2$	0.2699	0.2709	0.2884	0.2500
Rh–Cl	0.1042	−0.0986	0.3381	−0.0867
Rh–O	−0.1159	−0.0869		
Rh–Cl	0.0707	0.1214	0.0465	0.1034
$Rh-C_4$	0.1232	0.1211	0.0394	0.1215
C_1-C_2	0.6374	0.3834	0.6475	0.3774
C_2-C_3	0.7442	0.1537	0.7207	0.2142
C_3-C_4	0.6550	0.3642	0.6475	0.3518

Table VII lists pertinent overlap populations derived from a Mulliken population analysis for the interatomic interactions of interest. Of particular note is the considerable decrease in Rh-Cl overlap population on going from the five-coordinate to the six-coordinate complex and the lack of covalent contribution to the Rh-O interaction in the latter. Both of these results are in accord with the structural data discussed above and with the observed lability of these ligands in the latter complex.[25] Further consideration of Table VII shows that for the carbon-carbon interactions C_1-C_2 and C_3-C_4 there is a small increase in π-overlap population in going from the five- to the six-coordinate species. This is accompanied by a marked decrease in that for the C_2-C_3 interaction, all of which agrees with our contention (*vide supra*) that the π interactions in the rhodiacyclopentadiene ring are more localized in the six-coordinate derivative. The interpretation of the calculated overlap populations for the rhodium-carbon interactions is not nearly so straightforward. It is apparent that the percentage π character decreases in going to the six-coordinate complex which might be expected on the basis of the increased localization of π interactions within the organic portion of the ring. However, the decrease is more for $Rh-C_1$ than for $Rh-C_4$ and the overall overlap population ($\sigma + \pi$) in fact increases. Evidently the decreased covalent interaction between rhodium and chlorine in the six-coordinate species coupled with the addition of the antibonding interaction with the water molecule in positions directly trans to the Rh-C bonds forces electron density into these regions.

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(22) H. S. Aldrich, J. T. Mague, and L. C. Cusachs, *Int. J. Quantum Chem.*, in press.

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(25) It might be noted that the experiment demonstrating the ready removal of the chloride was suggested by the results of the calculations.

Table VIII. Valence Energies of Rhodiacyclopentadiene Model Complexes

	Valence energy, eV	
Geometry[a]	$Rh(H_2O)ClL_2C_4(CF_3)_4$	$RhClL_2C_4(CF_3)_4$
Opposite equilibrium distortion		−11,157.330
Symmetric	−11,738.170	−11,162.606
Equilibrium	−11,738.169	−11,171.992
Distortion	−11,738.957	−11,159.426
Extreme distortion	−11,735.925	

[a] For a more detailed description of these geometries see ref 21.

A second objective of these calculations was to see if the apparent nonequivalence of the Rh-C bonds was electronic in origin rather than the result of packing forces in the solid state. To that end, the valence energies were calculated for a series of models of the five- and six-coordinate complexes incorporating varying degrees of distortion of the rhodiacyclopentadiene ring from the observed geometry. The various geometries used ranged from that in which both Rh-C distances were made equal and C_1-C_2 was the same as C_3-C_4 ("symmetrized" configuration) to one in which the differences between Rh-C_1 and Rh-C_4 and C_1-C_2 and C_3-C_4 were considerably greater than observed ("extreme distortion").[21] The results of these calculations are presented in Table VIII and it is apparent that the experimental geometry of the ring represents the configuration of minimum energy in each case. These minima are rather shallow however.

In summary, the structural and computational results appear to form a consistent body of data although it would be very desirable to have structural data on larger numbers of derivatives of the tetrakis(trifluoromethyl)rhodiacyclopentadiene moiety which incorporate a variety of ligands in the sixth position in the equatorial plane in order to check further the validity of our computational results. Such complexes are in hand and structural studies are planned in the near future.

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Registry No. $Rh(H_2O)Cl(As(CH_3)_3)_2C_4(CF_3)_4$, 41184-52-5.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy of $2.00 for microfiche, referring to code number INORG-73-2649.

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Crystal and Molecular Structure of Trinitrato-1,2-bis(pyridine-2-aldimino)ethanegadolinium(III)[1]

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The crystal and molecular structure of trinitrato-1,2-bis(pyridine-2-aldimino)ethanegadolinium(III), $[Gd(NO_3)_3(C_{14}H_{14}N_4)]$, has been determined by X-ray analysis. The crystals are orthorhombic, space group *Pbca* with $a = 14.774$ (3), $b = 16.072$ (5), $c = 16.198$ (3) Å, and $Z = 8$. The structure was solved from Patterson and three-dimensional electron-density syntheses and refined by least squares to $R = 0.033$ using 1478 observed reflections. Gadolinium is ten-coordinated. The coordination polyhedron approximates a distorted pentagonal bipyramid, where four of the five equatorial positions are occupied by the nitrogen atoms of the tetradentate amine ligand, the remaining three positions being occupied by the three bidentate nitrate groups.

Introduction

There has been a recent increase of interest in structural aspects of lanthanide complexes. Among other factors this can be ascribed to the tendency of these compounds to adopt high coordination numbers and novel coordination polyhedra,[2] to their possibilities in laser technology,[3] to the study of the Stark-split fluorescence spectra of Eu(III) complexes in relation to the symmetry of the coordination sphere,[4] and particularly to the use of certain lanthanide complexes as nmr shift reagents.[5] We here report and discuss the structure of $[Gd(NO_3)_3(dpae)]$, where dpae = 1,2-bis(pyridine-2-aldimino)ethane, $C_5H_4N\cdot CH{:}NCH_2CH_2N{:}CH\cdot C_5H_4N$.

The compounds $[MX_3(dpae)]$ ($X = NO_3$, Cl, NCS; M = Y, La–Lu except Pm) have been previously reported.[6] Their properties were described and on the basis of chemical evidence and infrared spectra, it was suggested[6a] that the nitrates probably had an irregular pentagonal-bipyramidal structure, in which one equatorial and two axial positions would be occupied by the three bidentate nitrate groups. A detailed knowledge of this ten-coordinate polyhedron should be of interest, for comparatively few examples of this coordination number are known. Also, it was desirable firmly to establish the mode or modes of coordination of the nitrate groups. Finally, a comparison with the structures of the rather analogous but less sterically constrained bipyridine complexes

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