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The Crystal and Molecular Structure of Di- μ -bis(diphenylarsino)methane-bis(*trans*-chlorocarbonylrhodium(I)), Rh(CO)Cl((C₆H₅)₂AsCH₂As(C₆H₅)₂)₂Rh(CO)Cl

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The structure of di- μ -bis(diphenylarsino)methane-bis(*trans*-chlorocarbonylrhodium(I)), Rh(CO)Cl((C₆H₅)₂AsCH₂As(C₆-H₅)₂)₂Rh(CO)Cl, has been determined from three-dimensional X-ray data collected by counter methods. The final *R* factor obtained from a block-diagonal least-squares refinement for 2544 reflections is 0.068. The material crystallizes in the triclinic system with space group PI and a unit cell of dimensions a = 11.371 (2), b = 10.413 (2), c = 12.753 (3) Å and $\alpha = 100.35$ (3), $\beta = 103.60$ (2), $\gamma = 118.42$ (2)°. The calculated density for two empirical formula units, Rh(CO)Cl(C₆H₅)₂-AsCH₂As(C₆H₅)₂, is 1.747 g/cm³ which agrees with the experimental value of 1.71 g/cm³ determined by the flotation method. The crystal consists of discrete dimeric molecules of \overline{I} symmetry held together by bridging diarsine molecules. The Rh–Rh distance within the dimer is 3.396 (1) Å and appears to be more the result of the steric requirements of the diarsine molecules than any significant metal–metal interaction. The approach is sufficiently close, however, that the coordination about each rhodium atom is best described as approximately square pyramidal. The centrosymmetrically related rhodium atom occupies the apical position while the "basal plane" consists of a terminal chlorine atom, a terminal carbonyl group, and two arsenic atoms, one from each of the two bridging diarsine molecules, in a *trans* configuration.

Introduction

Until recently, there have been only scattered reports of rhodium(I) complexes of chelating ditertiary phosphines and arsines.¹⁻⁸ Our discovery that bis(cis-1,2bis(diphenylarsino)ethylene)rhodium(I) chloride, [Rh- $(cis-(C_6H_5)_2AsCH=CHAs(C_6H_5)_2)_2$]Cl, would reversibly activate molecular hydrogen and undergo a variety of facile oxidative addition reactions4 prompted a search for similar Rh(I) complexes which might behave in an analogous manner. In the course of this work, we prepared complexes of bis(diphenylarsino)methane and its phosphorus analog which were found to possess the empirical formula Rh(CO)Cl(L-L) (L-L = diphosphine or diarsine).⁵ The two complexes are isomorphous from powder data but molecular weight studies produced conflicting results which, although indicating a dimer, prevented an unequivocal determination of the molecular formula. The similarity of their infrared spectra to that of $trans-Rh(CO)Cl(P(C_6H_5)_3)_2$ and related complexes⁶ suggested a similar geometry about the metal and the likelihood of ligand bridges if the molecule were indeed dimeric. Such a formulation would be similar to the dimeric carboxylate complexes of Rh,⁷ Ru,⁸ Mo,⁹ Re,¹⁰ and Cu¹¹ where significant metal-metal interaction occurs in that in both cases a three-atom moiety links the two metals.

While this work was in progress, the preparation of a

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- (7) M. A. Porai-Koshits and A. S. Antsyshkina, Proc. Acad. Sci. USSR, Chem. Sect., 146, 902 (1962).
- (8) M. J. Bennett, K. G. Caulton, and F. A. Cotton, Inorg. Chem., 8, 1 (1969).
- (9) D. Lawton and R. Mason, J. Am. Chem. Soc., 87, 921 (1965).

(10) M. J. Bennett, W. K. Bratton, F. A. Cotton, and W. R. Robinson, *Inorg. Chem.*, 7, 1570 (1968).

complex, also of empirical formula $Rh(CO)Cl(C_6H_5)_2$ -PCH₂P(C₆H₅)₂, was reported with a *polymeric* formulation being postulated.³ We have shown this product to be identical with the phosphine complex which we have prepared and for which we had data indicating a dimeric formulation.⁵ We therefore felt it necessary to know the exact structure of the complexes in order to determine unequivocally the molecular formula and to investigate the possibility of metal-metal interaction. We report here the results of that study of the diarsine complex.

Experimental Section¹²

Unit Cell Data and Collection of Intensities .- Bright orange crystals of $Rh(CO)Cl((C_6H_5)_2AsCH_2As(C_6H_5)_2)_2Rh(CO)Cl^5$ were grown by slow diffusion of diethyl ether into a dichloromethane solution of the complex. Equiinclination Weissenberg photographs taken with Ni-filtered, Cu Ka radiation indicated that the crystal belonged to the triclinic system and inspection of the 0kl-2kl and hk0-hk2 zones did not reveal any systematic absences. A least-squares refinement of the setting angles of 34 high-order reflections which had been carefully centered on a Picker fourcircle diffractometer (Zr-filtered, Mo $K\alpha$ radiation $(\lambda~0.7107~{\rm \AA}))$ gave the following unit cell parameters: a = 11.371 (2), b =10.413 (2), c = 12.753 (2) Å and $\alpha = 100.35$ (3), $\beta = 103.60$ (2), $\gamma = 118.42$ (2)°. The experimental density of 1.71 g/cm³ as measured by flotation in aqueous zinc chloride is in agreement with the value of 1.747 g/cm³ calculated on the basis of two empirical formula units $(Rh(CO)Cl(C_{6}H_{5})_{2}AsCH_{2}As(C_{6}H_{5})_{2})$ per unit cell. With Z = 2 and an indication from the molecular weight measurements that the molecule was probably dimeric⁵ the most likely space group was $\mathrm{P}\overline{1}$ (C_i^1, no. 2^{13}). The subsequent successful refinement of the structure confirms this choice.

⁽¹⁾ A. Sacco and R. Ugo, J. Chem. Soc., 3274 (1964).

⁽²⁾ R. J. Mawby and L. M. Venanzi, *Experientia*, Suppl., No. 9, 240 (1964).

⁽³⁾ W. Hieber and H. Lagally, Chem. Ber., 100, 148 (1967).

⁽¹¹⁾ J. N. van Niekerk and F. R. L. Schoenig, Acta Cryst., 5, 227 (1953).

⁽¹²⁾ 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); LPIN (Lorentz and polarization corrections), FOUR (Fourier synthesis), BLSA (modification of the Gantzel-Sparks-Trueblood UCLALS-1, ACA Program No. 317 for block-diagonal least-squares refinement and distance-angle calculation), LSPL (least-squares planes), all by C. J. Fritchie, Jr.; ORABS, W. L. Busing (absorption corrections); ORTEP, C. K. Johnson (graphical illustrations); CELL, B. L. Trus (refinement of unit cell dimensions).

^{(13) &}quot;International Tables for X-Ray Crystallography," Vol. I, The Kynoch Press, Birmingham, England, 1962.

The crystal used for the collection of the intensity data was a plate with parallelogram faces measuring $0.1 \times 0.3 \times 0.5$ mm, the largest face being identified as $\{001\}$. It was mounted on one end such that the crystallographic a axis was coincident with the ϕ axis of the goniostat. The latter was in turn approximately parallel to the minor diagonal of the {001} face. The data were collected at room temperature on a card-controlled, Picker fourcircle diffractometer using Zr-filtered, Mo K α radiation (λ 0.7107 Å) and a takeoff angle of 5.3° . The integrated intensities were measured with a scintillation counter employing a pulse-height analyzer set to admit about 90% of the Mo K α pulse distribution. Preliminary inspection of the stronger reflections showed noticeable tailing to higher 2θ . As this continued essentially undiminished for at least 3° in 2θ beyond the peak maximum, it did not appear feasible to employ an asymmetric scan range, particularly since the tailing did not produce more than a 2% error in the measured intensities. The moving-crystal, moving-counter scan technique¹⁴ was employed in which the 2θ scan was from $2\theta_{calcd} - 1.25^{\circ}$ to $2\theta_{calcd} + 1.25^{\circ}$. The scan rate was $1^{\circ}/\text{min}$ and background counts were made for 20 sec at each scan limit. Two standard reflections were monitored approximately every 4 hr throughout the course of the data collection and no significant variation in their intensities was noted. Coincidence losses were found to affect only the most intense reflections. Reflections for which the counting rate exceeded 10,000 cps were remeasured at reduced power and were scaled to the remaining data using the same standard reflections.

The unique hemisphere having $h \ge 0$ and $(\sin \theta)/\lambda \le 0.55$ was scanned to yield 3589 independent reflections. Raw intensities, I, were obtained from the diffractometer output according to the formula $I = CT - 0.5(t_c/t_b)(B_1 + B_2)$ where CT is the total integrated count obtained in time t_c and B_1 and B_2 are the background counts, each obtained in time t_b . The standard deviation of the raw intensity, $\sigma(I),$ was estimated as $\sigma(I)$ = (CT + $0.25(t_c/t_b)^2(B_1 + B_2) + (pI)^2)^{1/2}$ with p^{15} taken as 0.02. Using the criterion $I < 2\sigma(I)$, 602 reflections were rejected as statistically insignificant and were treated as unobserved. Each of these reflections was assigned a threshold value given by $I_{\rm th}$ = $2\sigma(I)$. Owing to program limitations and the fact that many of these unobserved reflections occurred at high values of $(\sin \theta)/\lambda$, a smaller data set was chosen having $(\sin \theta)/\lambda \leq 0.525$. The resulting 2941 reflections of which 419 were unobserved were then corrected for Lorentz, polarization, and absorption effects. The linear absorption coefficient for the compound is 37.9 cm^{-1} for Mo K α radiation.

Solution and Refinement of the Structure.—The structure was refined by a block-diagonal least-squares process. Scattering factors for neutral Rh, As, Cl, O, and C were obtained from ref 16, and those for Rh, As, and Cl included both the real and imaginary parts of the correction for the effects of anomalous dispersion.¹⁷ The function minimized was $\Sigma w(K|F_o| - G|F_o|)^2$ where F_o and F_c are, respectively, the observed and calculated structure factors, K and G are scale factors (G = 1.0), and w is $1/\sigma^2$ (F_o). The standard deviation in F_o , $\sigma(F_o)$, was taken as $\sigma(F_o^2)/2F_o$. Unobserved reflections were included in the refinement if $|F_c|$ exceeded $F_{\rm th}$ where $F_{\rm th}$ is the threshold value for F_o obtained by correcting $I_{\rm th}$ for Lorentz, polarization, and absorption effects. In the final stages of refinement only 49 of the unobserved reflections met this criterion. The conventional residual, R, is defined as $R = \Sigma(||F_o| - |F_e||)/\Sigma|F_o|$.

A three-dimensional, unsharpened Patterson function which clearly showed the heavy-atom vectors was readily interpretable in terms of a centrosymmetric dimer thus further indicating $P\overline{1}$ as the correct space group. The remaining nonhydrogen atoms were found from successive cycles of least-squares refinement followed by a difference Fourier synthesis. After all 31 nonhy-

drogen atoms had been located and their positional and isotropic thermal parameters refined, a difference Fourier map was calculated which indicated anisotropic thermal motion about the heavy atoms. Refinement was therefore continued with anisotropic temperature factors of the form $\exp[-(B_{11}h^2 + B_{22}k^2 +$ $B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl$ for these atoms, leading to an R of 0.071 and to an improvement in the appearance of the difference map in the immediate vicinity of these atoms. (However, see below.) Inspection of the list of observed and calculated structure factors showed some rather large discrepancies between $|F_{o}|$ and $|F_{c}|$ among the strongest and the weakest reflections. Since the latter receive relatively large weights but make only small contributions to the total electron density, it was thought that the large errors here might be impeding the refinement and 146 were omitted. Also omitted were the strong reflections 001 and 002 which appeared to be severely affected by either extinction or by overlap with the "tail" of the direct beam. Other than this, the effects of extinction were neglected. Three more cycles reduced R to 0.063 and improved the agreement among the strong reflections. The agreement among the weaker reflections was not noticeably affected so the 146 omitted data were returned and three more cycles of refinement were performed leading to a final R of 0.068. At this point no parameter was shifted by more than 0.1 of its estimated standard deviation and there were no significant changes in the molecular dimensions from those determined prior to the temporary removal of the 146 reflections. The final difference map indicated reasonable positions for most of the phenyl hydrogens but the peaks were very diffuse ($<0.5 \text{ e}^{-}/\text{Å}^3$). In addition each heavy atom was surrounded by a pair of peaks $(\sim 1.6 \text{ e}^{-\text{Å}3})$ and a pair of holes $(\sim -2.0 \text{ e}^{-/\text{Å}3})$ which resembled uncorrected anisotropic thermal motion but which occurred about 1.1 Å from the atoms. These anomalies were smaller here than on a map calculated after convergence had been reached on the data set which included no absorption corrections. The directions of the peaks and holes were, respectively, in the approximate directions of the minimum and maximum dimensions of the crystal. These observations, together with the fact that similar anomalies in another case¹⁸ could not be removed by manual changes in the size and orientation of the thermal ellipsoid of the atom with which they were associated, suggest that they may be connected in some way with the absorption correction. Although there may be a somewhat larger uncertainty than desirable in the angular dimensions of the crystal since good reflections from the faces could not be obtained on an optical goniometer, all linear dimensions were accurately measured on a microscope fitted with a micrometer eyepiece. Thus it does not appear that any serious error has been made in applying the absorption correction. Another contributing factor may be the white radiation problem inherent with Mo K α radiation¹⁹ although, as mentioned earlier, this did not appear to be an appreciable effect either. The final standard deviation of an observation of unit weight is 2.98. This high value probably results from the anomalies noted above and to the neglect of the contributions of the hydrogen atoms to the scattering. It may possibly also indicate an underestimation of the value of p. Despite this, the molecular features of chemical interest are quite adequately established and further refinements in the treatment of the data such as inclusion of the hydrogens and a detailed analysis of the noise features in the final map do not appear to be economically feasible.

The final values of $|F_o|$ and F_c are presented in Table I. The positional and thermal parameters obtained from the last cycle of least-squares refinement are listed in Table II together with the associated standard deviations as estimated from the inverse least-squares matrix.

Description of the Structure

The structure consists of discrete dimeric molecules having $\overline{1}$ symmetry with the centers located at (1/2, 0, 1/2). A perspective view of the dimer in given in Figure

⁽¹⁴⁾ T. C. Furnas, "Single Crystal Orienter Instruction Manual," General Electric Co., Milwaukee, Wis., 1957.

⁽¹⁵⁾ W. R. Busing and H. A. Levy, J. Chem. Phys., 26, 563 (1957).

^{(16) &}quot;International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, p 200 ff.

⁽¹⁷⁾ Reference 16, Table 3.3.2C.

⁽¹⁸⁾ C. J. Fritchie, Jr. and J. L. Wells, private communication.

⁽¹⁹⁾ R. Eisenberg and J. A. Ibers, Inorg. Chem., 4, 773 (1965).



Figure 1.—A perspective view of the centrosymmetric dimeric molecule with pertinent dimensions. Additional angles which could not conveniently be included in the figure are: Cl-Rh-As₁, 93.73 (7)°; Cl-Rh-C₁₀, 171.4 (3)°; Rh-C₁₀–O, 177.1 (9)°; As₁-Rh-C₁₀, 88.3 (3)°; Cl-Rh-As₂', 87.22 (7)°; As₂'-Rh-C₁₀, 91.2 (3)°; C₅'-As₁-C₇', 99.4 (4)°; C₅'-As₁'-Rh', 119.3 (2)°; C₆'-As₂'-Rh, 120.8 (2)°.

1, together with selected interatomic distances and angles, while the molecular packing is depicted in Figure 2. The halves of the molecule are held together by bridging diarsine molecules. The coordination about each rhodium atom is effectively that of a square pyramid with the basal atoms consisting of an arsenic atom from each of the diarsine molecules, a terminal chlorine atom, and the carbon atom of a terminal carbonyl group. The arrangement of these four atoms is *trans*, and in this respect each half of the molecule is analogous to the known complexes *trans*-Rh(CO)ClL₂ (L = monotertiary phosphine or arsine).²⁰ The coordination about the rhodium is completed by the second rhodium which occupies the apical position at a distance of 3.396 (1) Å. This distance is significantly greater than the intramolecular Rh–Rh distances found in [Rh-(CH₃COO)₂(H₂O)]₂ (2.45 Å)⁷ and [Rh(CO)₂Cl]₂ (3.21 Å)²¹ where metal-metal bonding has been postulated (in rhodium metal theRh –Rh distance is 2.690 (12) Å²²). On the other hand it has been suggested that weak

(20) L. Vallarino, J. Chem. Soc., 2473 (1957).

(21) L. F. Dahl, C. Martell, and D. S. Wampler, J. Am. Chem. Soc., 83, 1761 (1961).

(22) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, Table 11-2.

TABLE I

Observed and Calculated Structure Amplitudes ($\times 10,$ in electrons) for

 $Rh(CO)Cl((C_6H_5)_2AsCH_2As(C_6H_5)_2)_2Rh(CO)Cl^{\alpha}$

3 80 4 -54 5 -56 6 298 7 501 8 328 9 246 10 264 10 264 10 264 10 264	0 -40 -20 -330 -552 -332 -212 -212 -330 -556	U 8 -10 723 - -9 374 - -8 -81 - -7 100 -6 90 -5 80 -5	-10 400 396 -11 184 -174 -13 -135 -152 400 -13 -83 -12 -74 1 124 1 -80 -12 117 -101 1124 1 -80 -12 117 -101 113 -11 -79 116 329 -10 23 266 33 -9 1015 -1054 -12 -59 7 1019	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	-2 87 -81 -1 57 -50 0 122 127 1 749 -744 2 691 697 3 315 -326 4 158 167 5 178 -191 6 608 623 7 680 -598 8 316 330 9 -78 -35	6 -75 -14 5 73 86 4 -71 49 3 163 -137 2 281 276 1 91 -57 0 298 -285 -1 452 -456 1 452 -456 1 452 113 -3 1367 -1358 -4 601 608	-/ -50 14 -/ 982 -960 0 1854 1867 1 1843 -1532 3 350 312 4 214 -208 5 155 -148 6 149 161 7 201 170 8 254 -228	-6 212 191 -5 -77 -46 -4 127 -127 -3 -74 -38 -2 592 582 -1 548 848 0 603 608 1 111 -96 2 210 -206 3 146 132 4 298 -290 5 709 6/3	-7 109 -8 193 -9 433 -10 122 -11 100 -12 106 -13 131 -12 552 -11 678	90 122 216 -3 146 216 -2 154 13 -1 662 95 0 662 95 1 300 5 36 3 -15 573 2 207 573 1 562	-113 149 137 -685 677 -394 4 -37 212 -570	3 62H -651 4 355 366 5 85 -7 6 -78 -10 7 127 -125 8 -40 42 4 48 477 10 535 -537 5 -4 10 314 -300	-4 623 608 -3 622 -681 -4 247 281 -4 369 162 0 337 -144 9 5 -91 3 505 467 4 228 -195 5 142 -144 6 184 -10 7 -48 -10 7 -48 -10
0 11 424 10 234 9 145 8 -49 7 -65 5 521 5 934 4 1152 3 1118 2 276 1 132 0 1009	1 377 -219 135 -11 -36 551 -L080 1259 -1176 -225 108 971	1 421 - 2 605 3 377 - 0 9 0 203 -1 -78 -2 -78 -3 80 -4 123 - -5 518 -6 526 - -7 182	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	2 3 8 -77 24 7 432 -445 6 800 788 5 624 -600 4 153 141 3 102 93 2 95 61 1 82 56 0 841 -835 -1 936 938 -2 109 -75 -3 368 -300	-6 203 -207 -7 -66 -13 -8 340 -281 -9 748 753 -10 455 -427 -11 455 -427 -12 147 142 -3 3 -13 353 361 -12 153 -169 -11 -77 -35 -10 269 -240	10 -80 -20 11 397 377 3 -4 11 96 -98 10 112 122 9 441 456 8 870 -873 6 392 -385 5 406 -381 4 123 83 3 178 -142 2 762 711	6 794 -732 7 277 260 8 97 90 9 94 31 10 309 -313 4 -7 10 721 -763 4 503 456 8 233 -210 7 118 96 0 384 -361 5 103 -50	-10 460 - -9 -72 -8 -69 -7 99 -5 1362 -1 -4 1011 -3 662 -2 99 -1 261 - 0 763 1 785 - 2 412 3 126 - 13 - 2 - 2 125 - 2 125	465 0 671 -2 249 35 -1 289 357 -5 101 -70 -4 484 337 -5 365 671 -4 484 337 -5 365 903 -7 -73 -69 -8 -77 -504 -8 -9 -76 712 -10 147 254 -9 -76 712 -11 328 424 134 -12 409 -12 409 134	-254 -258 -258 -258 -258 -258 -258 -128 -129 -129 -124 -129 -124 -447 	y -83 601 y -82 246 y -82 246 y -82 447 y -17 704 y -82 447 y -17 704 y -82 -238 y -17 704 y -10 -10 y -10 -10	6 -7 9 376 363 8 450 -449 7 473 493 6 238 -226 5 87 -55 4 -82 27 3 102 76 2 491 432 1 901 -861 0 425 45 -1 106 43
-1 1170 -2 94 -3 241 -4 82 -5 1022 -6 456 -7 1252 -8 1110 -9 339	-996 -87 228 106 136 -431 1333 -1171 350	-8 195 1 9 -6 541 -5 177 - -4 -81 -3 -80	245 7 174 -150 8 -72 -22 9 32H -309 10 376 358 577 11 334 -293 -159 -52 1 0 01 11 745 -711	- 300 -331 - 226 -254 3 -7 - 4 -76 -78 -6 -91 -42 -5 -244 -276 -5 -166 -152 -7 -464469 -4 -126 -115 - 8 -847 -3 -149 -121 -9 -1010 -1026 -2 -26 -59 -10 -545 -557 -1 -227 -226 -11 -95 -121	-4 187 -243 -5 669 650 -6 1205 -1153 -7 750 705 -8 143 -132 -9 -73 33 -10 -77 72 -11 319 -307 -12 499 469	-8 382 3/4 -7 885 -863 -6 365 302 -5 133 113 -4 127 -73 -3 768 -685 -2 1438 1395 -1 900 -867 0 317 313	1 847 - 807 0 515 515 -1 137 -126 -2 275 -259 -3 78 -60 -4 935 882 -5 411 -417 -6 288 265 -7 -70 42	3 530 -506 2 108 117 1 251 240 0 115 106 -1 824 +816 -2 1084 1076 -3 451 +450 -4 225 190 -5 111 20	5 122 6 434 - 7 831 8 497 - 9 - 81 4 1	476 -L2 -81 476 -L1 195 885 -L0 378 474 -9 346 22 -8 99 -7 139 -6 210 54 -5 772	54 -104 -306 -335 -22 120 198 -745	-5 446 531 -7 541 -578 -8 244 251 -9 111 -103 -10 104 99 -11 93 -117 5 -5	-2 309 -115 -3 194 -198 -4 584 567 -5 460 -459 -6 113 111 -7 108 -152 -8 171 102 6 -6
-10 77 -11 -74 -12 200 0 -12 127 -11 113 +10 198	-62 35 -160 2 113 126 -198	1 676 0 665 - -1 225 -2 -75 -3 161 -4 257 - -5 -77 -6	10 636 617 9 255 - 224 705 8 148 - 147 707 7 - 56 - 65 206 6 184 191 45 5 182 189 146 4 267 - 293 269 3 59 - 63 51 2 78 - 75 20 1 537 - 54	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	-13 481 -501 2 4 -13 534 -594 -12 255 242 -11 -79 73 -10 -78 30 -9 323 +275	1 - 59 7 2 62 60 3 226 212 4 574 - 546 5 802 814 6 506 - 484 7 126 99 3 2	-8 -74 -60 -9 108 75 +10 329 -329 3 -5 -9 331 -342 -8 128 107 -7 -73 -42	-6 -75 28 -7 119 105 -8 340 -333 4 -6 -9 562 544 -8 321 -304 -7 -74 -50	7 139 6 -73 5 309 - 4 175 3 220 2 102 1 753 - 0 554 -1 1071 -1	125 -4 1009 40 -3 599 303 -1 234 151 0 74 266 1 174 -66 2 385 897 4 79 897 6 76	-545 -63 -23 -58 [83 -384 4[3 -102 -249	-10 -83 4 -9 101 -38 -8 133 140 -7 844 -641 -6 1008 1022 -5 763 -776 -4 142 134 +3 434 458 -2 167 -166	-9 175 -156 -6 -78 40 -7 339 342 -5 555 -553 -5 241 247 -4 61 -32 -3 223 211 -2 -66 -39 -1 624 -591
-9 366 -8 816 -7 6 63 -5 77 -4 821 -3 243 -2 1665 -1 220	-863 601 51 -67 -731 273 -1462 -208	-7 150 - -8 86 -9 -82 1 7 -11 403 - -10 428 -9 158 -	126 C 1050 -1102 89 -2 1229 -1268 28 -3 188 184 -4 226 260 -5 79 93 -6 123 -131 440 -7 257 -256 452 -8 580 601 169 -9 120 -76	9 329 -302 7 -71 2 10 167 151 6 77 70 11 99 105 5 122 -151 4 -59 46 1 -8 3 568 491 2 1764 -1661 10 427 453 1 1911 1853 9 724 -757 0 1169 -1125 8 476 450 -1 626 641 7 149 -133 -2 761 -136	-8 592 560 -7 94 32 -6 396 -391 -5 273 256 -4 141 128 -3 7D3 647 -2 1352 -1297 -1 1316 1298 0 391 -396 1 549 -513	6 -77 41 6 925 -847 5 699 705 4 271 -268 3 75 55 2 213 169 1 398 429 0 620 -603 -1 306	+5 206 -202 -4 768 765 -3 924 -910 -2 370 374 -1 141 125 0 57 -58 1 106 125 2 205 -165 3 602 542	-6 102 100 -5 122 97 -4 280 -256 -3 113 -93 -2 370 353 -1 269 -279 0 277 297 1 497 -478 2 1130 1045 3 1313 -1216	-2 407 -3 -56 -4 -56 -5 313 - -6 303 - -7 453 -8 -70 -9 120 - -10 123	356 235 42 55 290 6 113 254 413 254 413 4647 109 3724 147 2341 147 1129	2 132 264 -628 728 -331 -107	0 237 -252 1 947 428 2 289 -289 3 105 -79 4 -73 89 5 588 590 6 103 -1003 7 425 404 8 -84 18	0 1000 984 1 1050 -1054 2 381 323 3 187 179 4 128 94 5 407 -341 6 282 288 7 189 -169 8 123 -128
0 105 1 476 2 88 3 1134 4 942 5 63 6 234 7 326 8 341 9 410	104 446 111 -1141 988 -56 -244 335 354	-8 170 -7 218 - -6 126 - -5 707 -4 936 - -3 781 -2 152 - 152 - 0 168 - 0 168 -	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	2 190 185 3 78 74 4 172 -156 5 -72 -85 6 96 103 7 80 38 2 5	-1 213 243 -2 339 304 -3 -54 36 -4 52 -55 -5 755 -706 -6 1386 -1288 -7 1268 -1193 -8 268 249 -9 233 264 -10 140 -122	4 385 - 351 5 228 - 185 5 258 254 7 257 247 8 805 - 790 9 762 751 10 255 - 249 11 - 84 - 35	4 581 546 5 378 323 6 421 -364 7 -81 19 8 133 100 9 232 217 10 255 -284 11 -87 10	-12 608 - -13 496 -13 236 -12 276 - -11 100 - -10 179	C -63 518 -1 355 -3 -63 -3 -63 -4 244 228 -5 119 297 -7 226 109 -8 948 109 -8 948	42 346 -285 -218 115 -326 -202 959 -913	9 -86 -146 1C -88 26 5 -6 1C -87 12 9 192 -205 8 134 143 7 168 203 1 168 203	9 148 142 0 -5 9 -89 80 8 108 -91 7 -86 -32 6 507 504 5 1080 -1049 6 923 978
10 306 11 -81 0 10 257 9 45C 8 565 7 430	300 -56 3 236 -443 589 -437	2 131 - 3 -76 1 6 5 168 - 4 646 3 585 - 2 195	-10 -7 401 425 -10 -7 401 425 -6 775 -987 -5 561 610 -4 755 793 -507 -3 1422 -1632 650 -2 370 -365 196 -1 754 786	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	6 -78 -15 5 127 115 4 559 -536 3 769 761 2 383 -404 1 153 -134 0 253 257 -1 168 138 -2 470 -449 -3 324 330	-LL 1/9 -229 -L2 141 122 -L3 -84 1Co 3 L -13 L66 -L57 -L2 400 413 -L1 770 -794	11 262 -265 10 125 101 9 159 133 8 133 104 7 309 -278 6 170 139 5 602 551 4 1288 -1180	11 91 -15 10 142 -127 9 -53 16 8 681 663 7 850 -833 5 447 416 5 298 295 4 101 -95	-9 391 -8 1078 -1 -7 1089 - -6 149 - -5 344 - -4 265 -3 114 -2 90 -1 319	402 -10 568 1018 -11 163 144 -13 87 252 5 73 -13 506 -300 -12 251	553 -163 -41 -59 1 -524 202	5 174 -141 4 317 506 3 532 472 2 1316 -1243 1 1173 1172 0 587 -607 -1 74 -23 -2 147 166 -3 92 55	$\begin{array}{cccccccccccccccccccccccccccccccccccc$
6 216 5 338 4 -56 3 77 2 527 1 601 0 214 -1 937 -2 -48	-209 330 -3 -71 -520 563 -192 -893 18	1 151 0 214 - -1 167 -2 563 - -3 984 -4 603 - -5 115 -6 163 -7 121	131 0 1236 -1152 209 1 796 724 162 2 575 576 576 3 166 188 977 4 107 -131 598 5 293 -301 -91 6 909 966 131 7 916 -964 108 8 343 366	3 752 - 278 - 5 / 75 - 882 4 553 - 588 - 4 197 - 204 5 539 - 586 - 3 94 142 5 132 112 - 42 410 - 392 7 247 265 - 1 704 708 8 177 - 205 0 565 - 614 9 226 - 242 1 1846 1812 2 400 - 435 1 0 3 553 - 334 4 187 1/7	-5 80 324 -5 80 34 -6 219 -201 -7 116 -111 -8 803 813 -9 890 -382 -10 530 539 -11 111 -111 -12 87 -55	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	3 874 833 2 132 d8 1 115 -68 0 184 -173 -1 201 235 -2 376 -364 -3 167 -157 -4 -68 68 -5 186 173	3 331 -293 2 1057 961 1 708 -642 0 173 159 -1 369 -382 -2 138 105 -3 325 296 -4 842 -846 -5 835 844	L 192 2 330 - 3 137 - 4 637 5 800 - 6 327 7 -78	207 -11 -79 314 -0 -77 -134 -9 444 628 -7 435 624 -5 138 26 -4 229 -3 479	71 -33 -413 680 -432 2 132 -222 447	-4 318 302 -5 414 -389 -6 219 202 -7 -76 81 -8 59 -73 -9 159 -127 5 -7	-6 650 -668 -7 849 865 -8 421 -390 -9 155 124 -10 -83 47 6 -4 -11 -83 22
-3 1655 -4 1514 -5 507 -6 219 -7 -63 -8 170 -9 135 -10 458 -11 230	1485 -1363 454 177 -40 -176 -111 486 -241	-8 440 - -9 404 -10 115 -11 -83 -12 -84 1 5 -12 -83	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2 6 -12 -86 61 -11 217 -226 -10 277 286 -9 286 -298 -8 97 -87 -7 196 188	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	-7 282 -267 -8 594 565 3 -7 -7 334 -316 -6 125 131 -5 129 116 -4 129 -169	-6 562 -550 -7 -73 62 -8 -75 -59 -9 143 145 -10 224 -213 -4 -4 -11 227 -220	6 97 - 5 279 - 4 558 3 341 - 2 90 1 - 65 0 150 - +1 365	-1 1051 2200 0 787 250 1 118 -352 2 238 -352 3 109 65 4 229 11 5 98 -155 6 134 -373 7 -77	1305 -779 -140 218 63 -248 63 -248 63 167 -26	-8 40 130 -7 -77 40 -6 90 71 -5 -73 16 -4 275 -271 -3 657 652 -2 510 -510 -1 -68 -62 0 118 109 1 297 278	-9 91 85 -8 324 -343 -7 333 354 -6 79 -111 -5 136 -173 -4 471 -474 -3 1184 1190 -7 1016 -976 -1 376 371
-12 107 -13 153 0 -12 491 -11 798 -10 500 -9 249	554 -795 510 -246	-10 95 -9 495 -8 1012 - -7 741 -6 196 - -5 149 -4 -62 -3 229 -2 -59	83 9 135 -137 441 8 614 632 966 7 880 -704 699 6 496 477 167 5 124 109 150 4 678 ~609 64 3 ~55 36 213 2 853 799 71 1 1385 -1314	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	-5 447 -558 -4 964 990 -3 409 -375 -2 135 119 -1 97 -73 0 177 153 0 177 153 1 266 253 2 488 -475	3 0 10 227 207 9 618 ->90 8 647 670 7 107 -108 6 219 -239 5 96 -7%	-3 285 215 -2 709 -711 -1 1116 1107 0 810 -815 1 128 113 2 310 295 3 310 -278 4 319 -306 5 405 370	-9 235 237 -8 171 -171 -7 369 377 -5 588 -613 -5 619 655 -4 145 -153 -3 629 -625 -2 70 46 -1 67 687	-2 1225 : -4 575 : -5 -65 -6 328 -7 -65 -8 401 - -9 491 -10 84 -11 -80	-47 524 -47 7 524 321 6 /21 -14 8 93 510 5 520 -47 3 65 -47 3 65	0 -547 738 14 -541 120 -65	2 966 -917 3 723 667 4 182 -206 5 121 -125 6 148 -106 7 271 -252 8 614 595 9 646 -684 10 510 539	0 160 137 1 -69 -67 2 378 337 3 520 -534 4 780 868 5 441 -455 6 95 113 7 98 43 8 103 50
-7 131 -6 370 -5 102 -4 158 -3 286 -2 823 -1 94 0 763 1 1255	-123 329 85 -164 -278 741 -67 -778 1271	-1 390 - 0'151 1 300 2 241 - 3 306 - 4 866 - 6 258 7 -77	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	4 -77 57 2 7 2 143 129 1 271 -279 0 445 462 -1 348 -360 -2 171 -171 -3 100 -173	4 -59 -26 3 311 322 2 703 -745 1 376 375 0 205 246 -1 783 -704 -2 68 -78 -3 1379 1244 -4 1432 -1405	7 -82 -44 8 91 -53 9 -84 24 10 306 314 11 596 -615 3 -8 10 98 -99	0 1316 -1250 1 952 827 2 207 -139 3 127 -183 4 158 -156 5 282 -267 6 705 687 7 717 -741 8 217 284	-12 179 - -13 +85 -12 121 -11 499 -9 277	-101 2 122 35 0 855 -1 1086 -2 59 86 -3 246 537 -5 576 513 -5 576 514 -7 5624	221 -860 1087 -31 231 -263 541 -858 520	5 -8 9 453 -486 8 150 120 7 214 225 6 -86 45 4 578 448 3 43 71 2 -74 -63	6 -3 9 549 -575 2 467 -575 2 467 -459 7 175 -145 6 171 - 82 5 256 -309 4 99 -136
2 974 3 391 4 131 5 109 6 -68 7 195 8 109 9 -78	-958 391 -110 103 -204 121 -77	1 4 8 - 76 7 156 6 102 5 92 4 122 3 137 7 108	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	-5 344 -343 -8 479 512 -7 715 736 -9 125 -114 -3 377 -335 -10 84 -70 -2 139 -148 -11 180 -158 -1 196 -148 -11 180 -158 -1 196 -148 -12 129 -91 0 111 84 1 420 -448 2 0 2 327 328 75 -58 -12 167 166 76 -59 -12 167 166	-3 100 127 -4 447 457 -5 771 -797 -6 367 379 -7 122 118 -8 177 -170 -9 -79 28 -10 127 -108	-5 694 673 -6 153 -168 -7 212 235 -8 102 -49 -9 219 -232 -10 425 424 -11 406 -379 -12 -81 43 -13 152 169	9 116 -44 6 451 434 7 893 -668 6 780 777 5 416 -397 4 85 56 3 132 -157 2 241 -229 1 729 734	4 -3 10 530 538 9 -81 12 8 140 -122 7 -78 -3	-3 295 - -6 77 -5 534 -4 933 -3 687 -2 92 -1 176 - 0 132 - 1 519	199 -8 -72 -306 -9 -74 -73 -10 99 -869 -11 340 -84 -13 526 -183 -13 52	-18 50 -364 501 -552 -1	1 308 -311 0 76 74 -1 432 424 -2 869 -879 -3 596 581 -4 96 -57 -5 220 -224 -6 -79 ~37	3 423 471 2 632 -747 1 346 373 0 372 398 -1 229 -213 -2 320 -340 -3 1056 1225 -4 860 -1039 -5 417 476
8 117 7 116 6 685 5 753 4 200 3 213 2 100	5 -86 119 -661 754 -194 -203 74 -09	1 536 - 0 1353 1 -1 1207 -1 -2 500 -3 244 -4 392 - -5 435 - -6 77 -7 282	-537 -6 236 235 1307 -5 236 235 1307 -5 421 410 132 -4 186 -165 452 -3 467 -440 216 -2 530 545 -210 -1 111 -110 55 2 1923 1768	4 181 -12 -14 16 5 120 -39 -10 174 -160 6 133 -123 -9 377 345 7 467 417 -8 199 -211 8 631 -706 -7 94 128 9 317 334 -8 80 -52 10 168 204 -5 205 199 -4 442 395 -1212 -1206 2 -7 -3 1212 -1206 -7 -3 1212 -12106	-8 205 -265 -7 194 203 -6 107 -124 -5 110 -65 -4 116 -1C5 -3 135 126 -2 273 294 -1 727 -794	3 -1 -12 -82 -20 -11 -78 15 -10 -77 -49 -9 438 433 -8 657 -697 -7 546 609 -8 -62 -51	0 789 - 190 -1 398 400 -2 74 34 -3 -74 -52 -4 279 - 268 -5 468 465 3 -9 -3 336 337	6 195 -105 5 355 390 4 717 -706 3 150 148 2 401 329 1 97 79 0 1448 -1232 -1 1043 993 -2 464 -459	2 446 - 3 201 4 -75 5 77 4 ! 3 -76 2 397 -	+12 -83 203 -11 68 -27 -9 -77 74 -8 180 -7 99 -6 686 -24 -5 1143 -5 1143	32 45 -170 -43 183 110 -588 1144 -759	5 -9 -5 -81 24 -4 216 217 -3 187 -213 -2 78 -61 -1 92 50 0 106 86 1 113 -99	-6 212 -226 -7 296 331 -8 85 -9 418 -409 -10 528 521 -11 506 -499 e -2
-1 0070 -1 585 -2 434 -3 203 -4 200 -5 610 -6 1062 -7 1052	-749 564 418 170 200 -593 1014 -1033 394	-8 269 -9 232 -10 160 -11 361 -12 611 -13 594 1	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	3 7 -9 -80 -9 -0 93 -00 -7 415 451 -6 556 -061 -5 224 219 -4 225 253 -3 78 -10	-5 225 - 140 -4 935 - 1052 -3 1087 1209 -2 998 - 979 -1 116 111 0 206 204 1 -55 - 135 2 196 212 3 822 - 1003	-2 91 -23 -1 -76 -22 0 -76 -39 1 186 -181 2 416 403 3 496 -498 4 240 198 5 -80 102 5 438 419	-3 180 176 -4 250 255 -5 81 115 -6 97 94 -7 407 -428 -8 524 578 -9 151 -156 -10 227 -222 -11 131 115	1 736 0 755 -1 320 -2 74 -3 121 -4 96 -5 17C -6 254 -7 37C	733 -3 287 753 -2 172 298 -1 -52 33 - 75 -99 2 477 -99 2 477 -170 4 134 -364 5 159	283 177 9 -101 -219 513 -80 -108 -189 512	2 153 -135 3 161 144 4 416 403 5 783 -775 6 607 632 7 136 -84 8 99 -135 5 -10	-12 410 395 -11 578 -580 -10 523 508 -9 169 ~159 -8 146 -112 -7 76 98 -6 365 363 -5 328 -336 -3 195 196
-9 206 -10 316 -11 -80 -12 98 -12 98 -12 100 -11 89	178 -305 -15 94 6 -113 L03	-13 207 -12 406 -11 584 -10 225 -9 117 -8 223 -7 128 -6 1169 -5 1611 -1	183 12 10 11 -618 596 1 -4 596 1 -4 211 -211 12 -83 72 209 11 422 426 -158 10 963 -883 1086 9 577 575 1086 8 142 -136 1086 7 172 161	2 392 383 8 -74 -78 1 682 -710 9 672 635 0 916 936 9 672 635 -1 551 -537 10 723 -948 -2 88 -63 11 399 348 -3 -73 -25 -4 160 186 2 1 -5 80 -29 -6 310 -307 9 30 351 -237 -6 310 -307 9 30 335	-3 77 -284 -1 418 426 0 286 -230 3 6 3 -77 72 2 235 231 1 408 -397	4 999 1155 5 533 -589 6 86 -38 7 384 362 8 143 138 9 555 -558 10 399 393 3 +2	7 794 -805 8 602 620 9 260 -262 3 -10 7 -86 -35 6 131 -122 5 121 60	4 -2 -12 L23 -LD1 -11 -79 58 -10 239 225 -9 773 -787 -8 678 913 -7 265 -275	-10 -17 -10 -110 -11 726 - -11 726 - -1010 -1010 -1010 -1010	47 7 765 91 8 462 29 8 462 783 9 -82 5 5 5 -57 9 122 58 8 100 58 7 80	-766 447 -55 -2 131 88 -101	7 115 -59 6 194 180 5 111 -60 4 147 -194 3 175 210 2 283 293 1 672 -694 0 554 694 -1 279 -281	-2 265 -212 -1 67 -57 0 641 -679 1 982 1058 2 737 -856 3 73 19 4 209 223 5 109 -32 6 220 -205
-10 147 -9 -79 -8 703 -7 761 -6 417 -5 119 -3 816 -3 816 -2 865	-154 -58 608 -765 414 122 -57 -807 845	-4 1409 1 -3 805 - -2 940 - 1 124 0 333 1 530 - 2 -53 3 -56 4 -59	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2 -6 8 121 -101 7 6 -56 -8 509 -510 5 -62 29 -7 503 509 5 -62 29 -5 388 -369 3 1181 -1258 -6 388 -369 3 1181 -1258 -4 289 280 2 1855 1952 -3 -68 -20 1 761 -#20 -2 87 77 0 188 -213	0 212 143 -1 88 -104 -2 107 100 -3 119 19 -4 188 -161 -5 808 793 -6 747 -751 -7 292 298 -6 168 207	11 296 299 10 188 -159 9 162 184 8 223 -218 7 119 105 5 591 640 5 1118 -1269 4 1100 1231 3 236 -277	4 467 511 3 659 -765 2 547 559 1 110 -81 0 88 -83 -1 81 -55 4 -10 -1 107 -138	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	-7 768 - -6 547 -5 359 -4 -75 -3 110 -2 181 - -1 254 0 365 - 1 314	613 6 100 677 5 79 -353 3 1072 -24 2 1170 109 1 442 -164 0 648 264 -1 332 -405 -2 83 311 -2 83	-106 70 334 -1261 1353 -534 -753 313 93	-2 177 188 6 -10 -3 173 152 -2 288 -298 -1 680 709 0 640 -675 1 98 65	7 257 284 8 -83 24 6 -1 8 -82 28 7 437 427 6 762 -751 5 567 600
-1 33 0 100 1 80 2 -60 3 284 4 783 5 771 6 24	-350 -81 -95 -38 302 -763 783 -229	5 141 6 412 - 7 755 8 355 - 9 - 78 1 2 10 - 79	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	-9 140 77 -10 371 -375 -11 382 393 3 5 -12 168 -173 -11 605 624 -10 892 -920	2 489 460 1 560 -547 0 641 754 -1 386 -331 -2 231 -215 -3 -54 -14 -4 375 403 -5 166 -171 -6 758 -793	-1 107 -128 0 -79 -46 1 415 461 2 555 -617 3 262 274 4 135 129 5 146 -157 6 101 -59 7 225 253	3 1234 1495 4 1349 -1496 5 423 437 6 80 59 7 108 -143 8 -77 -86 9 -80 -85 10 252 215 4 -1	4 -3 257 -4 -80 -5 203 -6 112 -7 487 -8 532	-3 174 -4 422 -5 198 -260 -7 203 -78 -7 203 -78 -7 203 -78 -7 203 -78 -7 203 -78 -7 203 -79 -07 -31 -9 607 -510 -55 -510 -510 -55 -510 -55	211 -468 203 78 -259 82 618 +651 329	2 126 155 3 -82 -60 4 233 -273 5 243 249 6 -91 -96 6 -9 8 127 154	+ 181 - 185 3 203 - 141 2 190 238 1 200 310 0 115 - 122 -1 143 - 118 -2 135 123 -3 -61 - 37 -4 119 - 103 -5 107 101
0 5 12 4 8 3 8 2 9 1 9 1 24 -1 24	-49 -49 58 27 -52 -745 829	- 224 8 544 - 7 268 6 194 5 109 4 652 - 3 911 2 1267 -1 1 620 0 60	537 263 -8 142 103 176 -7 287 -/87 -66 -6 690 677 -644 -5 72 48 927 -4 125 -149 307 -3 361 -364 626 -2 1020 1011 65 -1 1188 -1171	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	-v 675 680 -8 100 67 -7 147 -166 -6 188 -224 -5 74 45 -4 313 320 -3 346 -337 -2 -67 33 -1 140 108	-7 985 1103 +8 866 - 887 -9 207 281 -10 -77 -31 -11 -80 -38 -12 -84 -78 3 -3	4 -9 4 -40 -46 8 265 -275 7 648 696 6 752 -770 5 260 235 4 237 213 3 117 -116	10 83 -43 4 429 429 8 630 -631 7 352 330 6 166 142 5 104 -87 4 376 -631 3 1165 1328	5 -2 -79 -3 86 -4 -79 -5 -79 -6 300 -7 603	-12 88 52 -17 181 79 -11 -82 -28 -10 269 -48 -10 269 -48 -9 471 570 -8 319 570 -8 319	-3 -3 -282 -328 -328	/ 209 -226 6 -90 -29 5 487 472 4 689 -700 3 615 589 2 125 -84 1 81 27 D 189 -190 -1 225 747	
-3 L13 -4 60 -5 30 -6 11 -7 9 -8 -7 -9 23 -10 31 -11 10	7 - 1140 617 5 -307 5 -134 7 -134 7 -136 7 -136 7 -136 7 -136 124	-1 659 -2 905 -3 650 - -6 1336 1 -5 1167 -1 -6 337 -7 271 -8 323 -9 737 -	568 0 489 562 721 1 -56 -59 601 2 60 -59 222 3 369 -301 117 4 1128 -1065 320 5 1198 1150 237 6 1006 -966 336 7 353 321 142 8 208 188	IU 710 725 -11 194 186 9 718 -738 -16 227 -200 8 204 220 -9 95 -73 1 191 173 -8 333 327 6 192 172 -7 -64 96 5 1111 -652 -6 1190 -1105 4 944 885 -5 1600 1483 3 504 -460 -4 1256 -1122 2 158 -131 -3 691 628	cic 199 1 735 -734 2 795 764 3 476 -477 4 -74 14 5 136 113 3 4	-11 352 307 -10 173 189 -9 222 -227 -8 97 -96 -7 425 439 -6 465 -492 -5 270 287 -4 265 +251 -3 230 237	2 -76 -66 1 145 128 0 93 -104 -1 -76 3 -2 254 -273 -3 209 220 -4 163 159 4 -8	2 571 -630 1 217 228 0 219 -214 -1 263 245 -2 553 474 -3 1080 -1000 -4 1012 1688 -5 1226 -1307 -6 81 -35	-a /90 - 5 - -10 120 -9 -78 -6 232 - -7 354 -6 324 - 5 219		141 -106 253 -917 -840 -380 437 423	-3 191 -200 -4 84 -34 -5 191 207 6 -8 -7 115 -98 -5 107 -99 -5 101 -144	-12 94 -123 -11 108 -82 -10 -78 50 -9 -78 2 -8 88 72 -7 504 -495 -6 317 299 -5 153 107

TABLE I (Continued)

^a The data are separated into groups having the common values of h and k listed above each one. Within each group the three columns list l, $|F_o|$, and F_o . Unobserved reflections are indicated by a negative F_o .

	Final H	OSITIONAL	AND THERM	al Para	METERSa	FOR Rh(CC	$O)Cl((C_6H_5)_2A_5)$	CH ₂ As(C	$(\mathbf{G}_{6}\mathbf{H}_{5})_{2})_{2}\mathbf{Rh}(\mathbf{G}_{6})_{2}$	CO)Cl	
$Atom^b$	x		У	z		B_{11}^c	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Rh	0.5278	39 (7) (0.86905 (8)	0.5442	8 (6)	5.85(7)	5.64(8)	4.32(5)	5.0(1)	3.8(1)	5.1(1)
As_1	0.3197	7 (9)	0.66271 (9)	0.3802	4 (8)	4.89 (9)	3,96 (9)	3.93(7)	4.1(1)	3.4(1)	4.3(1)
As_2	0.2711	8 (9)	0.91780 (9)	0.2917	6 (8)	4.97 (9)	4.69(9)	3.38(7)	4.5(1)	2.4(1)	4.6(1)
C1	0.6722	2 (3)	0.9569 (3)	0.4340) (2)	9.8(2)	9,6(3)	7.6(2)	9.7 (4)	8.5 (4)	9, 2(4)
Atom	×x	У		z	B, Å ²	Atom	x		У	z	B, Ų
C5	0.3467 (9)	0.5667 (10) 0.25	02 (8)	2.4(2)	C19	0.3263 (12) 0.4	7599 (14)	-0.0535(11)	5.1(3)
Ce	0.2942 (9)	0.8577 (10) 0.14	88 (8)	2.1(2)	C ₂₀	0.1877 (10) 0.1	7315 (13)	-0.0587 (11)	4.9(3)
C7	0.1952 (8)	0.4781 (9) 0.40	98 (8)	2.0(2)	C_{21}	0.1756(10) 0.1	7841 (11)	0.0443(9)	3.2(2)
C_8	0.1089 (9)	0.9376 (10) 0.24	25 (8)	2, 3(2)	C22	0.2586(11)) 0.3	3999 (11)	0.4492 (9)	3.2(2)
C9	0.1818 (9)	0.7205 (10) 0.31	88 (8)	2.2(2)	C23	0,1736(10) 0,1	2664 (12)	0.4761 (10)	3.8(3)
C_{10}	0.4335 (10)	0.7896 (12) 0.63	43 (9)	3.5(2)	C24	0,0310(10) 0.1	2134 (11)	0.4601 (9)	3, 4(2)
0	0.3741 (8)	0,7352 (9) 0.68	67 (7)	4.9(2)	C25	-0.0330 (9)	0.3	2891 (11)	0.4187 (9)	3,3(2)
C_{12}	0.4679(11)	0.5627 (12) 0.27	08 (10)	3.9(3)	C26	0.0523 (9)	0.4	4240 (10)	0.3942 (8)	2.5(2)
C18	0.4845 (13)	0.4779 (15) 0.17	86 (12)	5.4(3)	C27	0.1221 (10) 1.0	0469 (11)	0.1880 (9)	3.4(2)
C_{14}	0.3789(13)	0.4037 (14) 0.07	17 (11)	5.2(3)	C 28	0.0128 (12) 1.6	0711 (14)	0.1517(11)	5.0(3)
C15	0.2532 (12)	0.4093 (13) 0.04	83 (11)	4.8(3)	C29	-0.1171 (12) 0.9	821 (13)	0.1758(11)	4.8(3)
C_{16}	0.2362 (11)	0.4886 (12) 0.13	94 (9)	3.6(2)	C 80	-0.1308 (11) 0.8	8758 (12)	0.2317 (10)	3.9(3)
C17	0.4254(10)	0.8815 (11) 0.15	08 (9)	3.4(2)	C ₈₁	-0.0186(10) 0.8	8513 (11)	0.2651 (9)	3.2(2)
C18	0.4396 (12)	0.8301 (13) 0.04	69 (11)	4.6(3)						

TABLE II

^a The standard deviations of the least significant figure(s) are given in parentheses here, in other tables and figures, and in the text. ^b The atom labeling conforms to that shown in Figure 1. ^c Anisotropic thermal parameters ($\times 10^3$). The form of the ellipsoid is that given in the text.

intermolecular metal-metal interactions occur in [Rh-(CO)₂Cl]₂ (Rh-Rh = 3.31 Å),²¹ Rh(CO)₂(CH₃CO)₂-CH (Rh-Rh = 3.27 (1), 3.26 (1) Å),²³ and Rh(CO)₂-(CF₃CO)₂CH (Rh-Rh = 3.34 (1) Å).²³ This last value is only marginally shorter than that found in this work so, while it is unlikely that there is significant metal-metal interaction here, it cannot be completely ruled

out. Thus each rhodium atom should best be considered to be effectively five-coordinate. In view of the As₁-Rh-As₂' angle of 176.88 (4)° and particularly the As₁-C₉-As₂ angle of 113.5 (4)°, it appears that the relatively short "bite" of the diarsine ligand is the major factor responsible for the close approach of the rhodium atoms.

(23) N. A. Bailey, E. Coates, G. B. Robertson, F. Bonati, and R. Ugo, Chem. Commun., 1041 (1967).

The Rh–Cl distance of 2.372 (3) Å is comparable to those found in similar complexes of elements in the



Figure 2.---A projection of four neighboring dimers upon {100} showing the molecular packing.

infra).

latter part of the second transition series, viz, Rh–Cl (2.386 (3) Å) in Rh(CS)Cl(P(C₆H₅)₃)₂,²⁴ Pd–Cl (2.33 (4) Å) in [Pd(TPAS)Cl]ClO₄ (TPAS = *o*-phenylenebis(*o*-dimethylarsinophenylmethylarsine)),²⁵ and Ru– Cl (2.388 (8) Å) in RuCl₂(P(C₆H₅)₃)₃.²⁶ The two independent Rh–As distances (Figure 1) are different to an extent which is only barely significant and therefore probably not meaningful. They can be compared to those found in similar instances, viz., Pd–As (2.408 (7), 2.375 (7) Å) in [Pd(TPAS)Cl]ClO₄²⁵ and Ru–As (2.308 (5), 2.398 (5), 2.468 (5) Å) in Ru(QAS)Br₂ (QAS = tris(*o*-diphenylarsinophenylarsine)).²⁷ The As₁-C₉ and (24) J. L. DeBoer, D. Rogers, A. C. Skapski, and P. G. H. Troughton,

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 As_2-C_9 distances (Figure 1) are also different to a barely

significant extent $(\Delta/\sigma \sim 3)$ but since C₉ lies in the vicin-

ity of some of the anomalies about the arsenic atoms, its

position may be somewhat affected by this so we do not

attach any significance to this difference in bond

lengths. Finally, the $Rh-C_{10}$ and $C_{10}-O$ distances

(Figure 1) are in the ranges found previously for a variety of terminal carbonyl groups bound to transition

metals.^{23,24,28-30} The slight distortion of the Rh- C_{10} -O

moiety from linearity is not significant but is in the di-

rection expected from the intramolecular contacts (vide

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W BIGHTED ISBNST	by come by the second by the second s	mocon me bimen	•			
Plane no.	A	В	С	D		
1	-0.346	0.932	-0.109	2.954		
2	-0.492	-0.288	-0.821	-7.996		
3	0.845	-0.140	-0.516	-1.665		
	Distances of	Atoms from Planes, Å-				
1		2 2		3		
0.011(1)		0.009(1)	0.	0.022(1)		
		-0.001 (1)	-0.	022 (1)		
0.074(1)			-0.	015 (1)		
			0.	015 (1)		
			0.	015 (1)		
0.077(1)			-0.	015(1)		
-0.166(3)	-	-0.010 (3)				
-0.122(14)		-0.022 (14)				
-0.235(12)		-0.009 (12)				
	$\begin{array}{c} \text{Plane} \\ \text{no.} \\ 1 \\ 2 \\ 3 \end{array}$	$\begin{array}{c} \begin{array}{c} \text{Plane} \\ \text{no.} & A \\ 1 & -0.346 \\ 2 & -0.492 \\ 3 & 0.845 \end{array}$ $\begin{array}{c} \hline \\ 1 \\ 0.011 (1) \\ 0.077 (1) \\ -0.166 (3) \\ -0.122 (14) \\ -0.235 (12) \end{array}$	$\begin{array}{c cccccc} Plane & & & & & & & & & \\ & no. & & & & & & & & \\ & 1 & & -0.346 & & 0.932 \\ & 2 & & -0.492 & & -0.288 \\ & 3 & & 0.845 & & -0.140 \end{array}$ $\begin{array}{c} \hline & & & & & \\ \hline & & & & & \\ \hline & & & & &$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		

Table III Weighted Least-Souares Planes Through the Dimer^a

^a The equations of the planes are of the form AX + BY + CZ - D = 0 where X, Y, and Z are orthogonal coordinates (in Å). The transformations from the fractional triclinic coordinates (x, y, z) are: $X = ax \sin \gamma + cz (\cos \beta - \cos \alpha \cos \gamma)/\sin \gamma$; $Y = ax \cos \gamma + by + cz \cos \alpha$; $Z = cz (1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2 \cos \alpha \cos \beta \cos \gamma)^{1/2}$.

The C-C distances within the phenyl rings range from 1.465 (16) (C₂₇-C₂₈) to 1.350 (17) Å (C₁₈-C₁₉) with the average value being 1.404 (15) Å. The root-mean-square deviation of an individual value from the mean is 0.026 Å indicating a slight underestimation of the standard deviations by the least-squares refinement process. The average C-C-C angle is 120.0 (9)° with the individual values ranging from 117.3 to 122.0°. In addition the rings are planar within experimental error ($\sigma_{\text{plane}} = 0.02$ Å) no atom being more than 0.02 Å from the best plane through the ring.

Although there are no unusually short nonbonded contacts in this structure, there are sufficient interactions of the phenyl rings containing C_{δ} and C_{6} with each other and with the adjacent chlorine atom and carbonyl group to render the major portion of the molecule quite rigid. Using the calculated positions of the hydrogen atoms on C_{17} and C_{12} (hereafter called H_{17} and H_{12}) assuming a C-H distance of 1.08 Å, the following intramolecular contacts are found: H_{17} --Cl, 2.7 Å; H_{17} --Cl₁₀', 2.8 Å; H_{17} --O', 2.9 Å. In addition, the C_{16} --Cl₁₇ contact is 3.57 Å and that for H_{12} --Cl is 3.5 Å. The only intermolecular contacts of possible significance are those between C_{24} and the atoms C_{29} and C_{30} in the adjacent molecule at (1 - x, 2 - y, -z) which are found to be 3.4 Å.

An examination of the data in Table III shows that the coordination about the rhodium (excluding the apical metal atom) is not rigorously planar. The rhodium atom is approximately in the "basal plane" (no. 1) while the arsenic atoms are ~ 0.07 Å from this plane toward the center of the molecule and the chlorine atom and the carbonyl group are considerably bent away. A similar distortion of the coordinated atoms alternately above and below the best plane has been found in Rh(CS)Cl- $(P(C_6H_5)_3)_2$ but in the latter it is not nearly as pronounced. The displacement of the arsenic atoms toward the center of the molecule provides further evidence for the short "bite" of the ligand being mainly responsible for the close approach of the rhodium atoms, while the marked bending back of the chlorine atom and the carbonyl groups is largely due to the close contacts with H17. The heavy-atom skeleton is very nearly planar (plane 3) with the small displacements of the atoms (~ 0.02 Å) from this plane being in the direction of a "chair" conformation. This slight buckling is probably to relieve the strain occasioned by the abovementioned contacts as well as the As₂---Cl contact of 3.3 Å. Finally, C_9 is ~ 0.6 Å from the plane of the heavy atoms as expected from the approximately tetrahedral coordination about the arsenic atoms.

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