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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(C₆H₅)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 P $\bar{1}$ 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)₂AsCH₂As(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 $\bar{1}$ 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.^{1–3} Our discovery that bis(*cis*-1,2-bis(diphenylarsino)ethylene)rhodium(I) chloride, [Rh(*cis*-(C₆H₅)₂AsCH=CHAs(C₆H₅)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(C₆H₅)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

complex, also of empirical formula Rh(CO)Cl(C₆H₅)₂PCH₂P(C₆H₅)₂, was reported with a *polymeric* formulation being postulated.⁸ 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((C₆H₅)₂AsCH₂As(C₆H₅)₂)₂Rh(CO)Cl⁵ were grown by slow diffusion of diethyl ether into a dichloromethane solution of the complex. Equiinclination Weissenberg photographs taken with Ni-filtered, Cu K α 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 four-circle diffractometer (Zr-filtered, Mo K α radiation (λ 0.7107 Å)) 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(C₆H₅)₂AsCH₂As(C₆H₅)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 P $\bar{1}$ (C₁¹, no. 2¹³). The subsequent successful refinement of the structure confirms this choice.

(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).

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(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).

(4) J. T. Mague and J. P. Mitchener, *Chem. Commun.*, 911 (1968).

(5) J. T. Mague and J. P. Mitchener, *Inorg. Chem.*, **8**, 119 (1969).

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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).

(11) J. N. van Niekerk and F. R. L. Schoenig, *Acta Cryst.*, **6**, 227 (1953).

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 four-circle diffractometer using Zr-filtered, Mo $K\alpha$ 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 $K\alpha$ 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 $2\theta_{\text{calcd}} - 1.25^\circ$ to $2\theta_{\text{calcd}} + 1.25^\circ$. 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 re-measured at reduced power and were scaled to the remaining data using the same standard reflections.

The unique hemisphere having $h \geq 0$ and $(\sin \theta)/\lambda \leq 0.55$ was scanned to yield 3589 independent reflections. Raw intensities, I , were obtained from the diffractometer output according to the formula $I = \text{CT} - 0.5(t_o/t_b)(B_1 + B_2)$ where CT is the total integrated count obtained in time t_o 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 $\sigma(I) = (\text{CT} + 0.25(t_o/t_b)^2(B_1 + B_2) + (pI)^2)^{1/2}$ 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 $I_{\text{th}} = 2\sigma(I)$. 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 $K\alpha$ 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 $\sum w(K|F_o| - G|F_c|)^2$ 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_{th} where F_{th} is the threshold value for F_o obtained by correcting I_{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 $R = \sum(|F_o| - |F_c|)/\sum|F_o|$.

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 $P\bar{1}$ 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 $K\alpha$ 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 $\bar{1}$ symmetry with the centers located at $(1/2, 0, 1/2)$. A perspective view of the dimer is 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) "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).

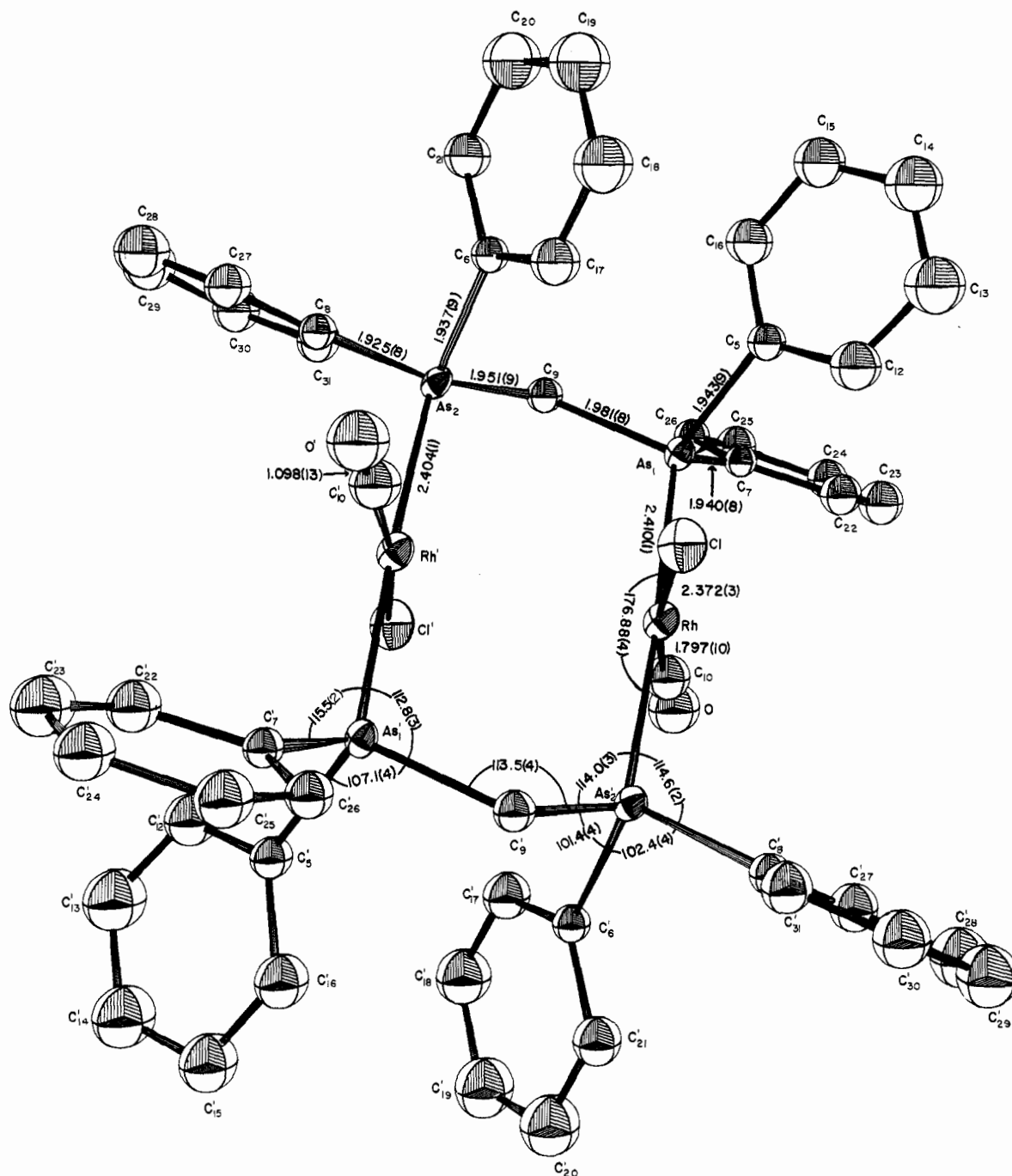


Figure 1.—A perspective view of the centrosymmetric dimeric molecule with pertinent dimensions. Additional angles which could not conveniently be included in the figure are: Cl-Rh-As₁, 93.73 (7)°; Cl-Rh-C₁₀, 171.4 (3)°; Rh-C₁₀-O, 177.1 (9)°; As₁-Rh-C₁₀, 88.3 (3)°; Cl-Rh-As₂', 87.22 (7)°; As₂'-Rh-C₁₀,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

dination 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 the Rh-Rh distance is 2.690 (12) Å²²). On the other hand it has been suggested that weak

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(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 (X 10, IN ELECTRONS) FOR
Rh(CO)Cl((C6H5)2AsCH2As(C6H5)2)Rh(CO)Cl^2

Table with multiple columns of numerical data representing structure amplitudes. The table is organized into rows and columns, with some cells containing symbols like 'h', 'k', 'l' and others representing indices or specific values. The data is presented in a grid-like format, typical of a scientific data table.

TABLE I (Continued)

Table of diffraction data including reflections (hkl) and structure factor amplitudes |F_o| and phases F_e. Includes sub-tables for atoms Rh, As1, As2, and Cl.

^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_e. Unobserved reflections are indicated by a negative F_e.

TABLE II

FINAL POSITIONAL AND THERMAL PARAMETERS^a FOR Rh(CO)Cl((C6H5)2AsCH2As(C6H5)2)2Rh(CO)Cl

Table of positional and thermal parameters for atoms Rh, As1, As2, and Cl, including x, y, z coordinates and B values in Angstrom squared.

^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 (x 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)2CH (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 remains possible.

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) degrees and particularly the As1-C9-As2 angle of 113.5 (4) degrees, 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

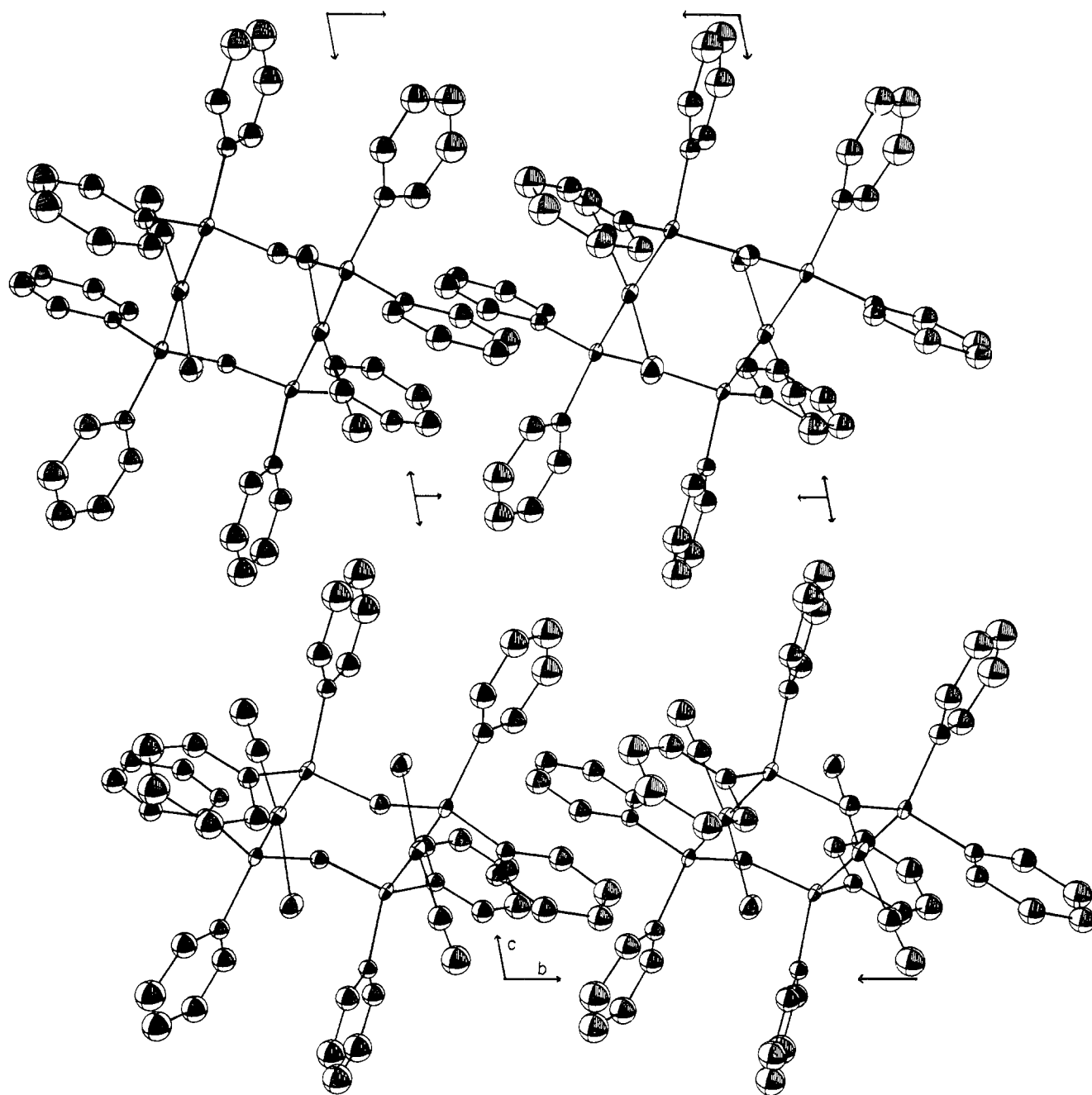


Figure 2.—A projection of four neighboring dimers upon $\{100\}$ showing the molecular packing.

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

As₂-C₉ distances (Figure 1) are also different to a barely significant extent ($\Delta/\sigma \sim 3$) but since C₉ lies in the vicinity 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-C₁₀ and C₁₀-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-C₁₀-O moiety from linearity is not significant but is in the direction expected from the intramolecular contacts (*vide infra*).

(24) J. L. DeBoer, D. Rogers, A. C. Skapski, and P. G. H. Troughton, *Chem. Commun.*, 756 (1966).

(25) T. L. Blundell and H. M. Powell, *J. Chem. Soc., A*, 1650 (1967).

(26) S. J. La Placa and J. A. Ibers, *Inorg. Chem.*, **4**, 778 (1965).

(27) R. H. B. Mais and H. M. Powell, *J. Chem. Soc.*, 7471 (1965).

(28) F. Calderazzo, R. Ercoli, and G. Natta in "Organic Syntheses via Metal Carbonyls," Vol. 1, I. Wender and P. Pino Ed., Interscience Publishers, New York, N. Y., 1968, p 47.

(29) S. J. La Placa and J. A. Ibers, *Acta Cryst.*, **18**, 511 (1965).

(30) R. Mason and A. I. M. Rae, *J. Chem. Soc., A*, 778 (1968).

TABLE III
 WEIGHTED LEAST-SQUARES PLANES THROUGH THE DIMER^a

Atoms	Plane no.	A	B	C	D
Rh, As ₁ , As ₂ , Cl, C ₁₀ , O	1	-0.346	0.932	-0.109	2.954
Rh, Rh', Cl, C ₁₀ , O	2	-0.492	-0.288	-0.821	-7.996
Rh, Rh', As ₁ , As ₁ ', As ₂ , As ₂ '	3	0.845	-0.140	-0.516	-1.665

Atom	Distances of Atoms from Planes, Å		
	Plane no. 1	Plane no. 2	Plane no. 3
Rh	0.011 (1)	0.009 (1)	0.022 (1)
Rh'		-0.001 (1)	-0.022 (1)
As ₁	0.074 (1)		-0.015 (1)
As ₁ '			0.015 (1)
As ₂			0.015 (1)
As ₂ '	0.077 (1)		-0.015 (1)
Cl	-0.166 (3)	-0.010 (3)	
C ₁₀	-0.122 (14)	-0.022 (14)	
O	-0.235 (12)	-0.009 (12)	

^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 C₅ and C₆ 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 C₁₇ and C₁₂ (hereafter called H₁₇ and H₁₂) assuming a C-H distance of 1.08 Å, the following intramolecular contacts are found: H₁₇---Cl, 2.7 Å; H₁₇---C₁₀', 2.8 Å; H₁₇---O', 2.9 Å. In addition, the C₁₆---C₁₇ contact is 3.57 Å and that for H₁₂---Cl is 3.5 Å. The only intermolecular contacts of possible significance are those between C₂₄ and the atoms C₂₉ and C₃₀ 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(C₆H₅)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 above-mentioned contacts as well as the As₂---Cl contact of 3.3 Å. Finally, C₉ is ~ 0.6 Å from the plane of the heavy atoms as expected from the approximately tetrahedral coordination about the arsenic atoms.

Acknowledgments.—We are indebted to the donors of the Petroleum Research Fund administered by the American Chemical Society for support of this research. The assistance of the Tulane University Computer Laboratory is gratefully acknowledged. We are also particularly indebted to Dr. C. J. Fritchie, Jr., of this department for the use of his equipment and programs and for much helpful advice.