CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
THE PENNSYLVANIA STATE UNIVERSITY, UNIVERSITY PARK, PENNSYLVANIA 16802

The Crystal Structure of Tetra-*n*-butylammonium *cis*-Dichlorodicarbonylrhodate(I)

BY CHARLES K. THOMAS AND JOSEPH A. STANKO*

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The crystal structure of tetra-*n*-butylammonium *cis*-dichlorodicarbonylrhodate(I) has been determined by X-ray diffraction using counter techniques. The complex crystallizes in the monoclinic system with $a = 15.07$ (6) Å, $b = 8.774$ (8) Å, $c = 20.39$ (8) Å, and $\beta = 118.1$ (0.4)°. The space group is C_{2h}^5-$P2_1/c$. The measured density of 1.27 ± 0.03 g cm^{-3} agrees with that calculated for four formula units in the unit cell, 1.32 ± 0.01 g cm^{-3}. A total of 1545 independent reflections was used in solving the structure, which was refined to a conventional R factor of 0.083 and a weighted R factor of 0.086. The alkylammonium cation shows no unusual features. The anionic rhodium complex is square planar, with one of the carbonyl groups and the chloride ligand trans to it disordered. The unusually short Rh–C distance of 1.72 ± 0.02 Å is rationalized in terms of extensive Rh–CO π bonding.

Introduction

We have been interested in the structures and reactions of platinum metal complexes of small covalent molecules.[1-3] Recently we reported,[1] simultaneously with others,[4,5] the preparation and isolation of the pentachlorocarbonylrhodate(III) anion, $RhCl_5CO^{2-}$, as a reaction intermediate in the carbonylation of $RhCl_3$ solutions to form the dichlorodicarbonylrhodate(I) ion, $RhCl_2(CO)_2^-$,[6] first isolated and characterized by Vallarino.[7] We also observed that the $RhCl_2(CO)_2^-$ complex undergoes a novel oxidative addition reaction with molecular oxygen to produce the initial $RhCl_5CO^{2-}$ complex and CO_2. This cyclic process provides a catalytic pathway for the oxidation of carbon monoxide to carbon dioxide at atmospheric pressure and moderate temperatures.

In order to determine whether the ease of oxidation of coordinated carbon monoxide in the rhodium(I) complex might be related in some way to the geometry of the complex, we have solved the crystal structure of the salt tetra-*n*-butylammonium *cis*-dichlorodicarbonylrhodate(I). In addition, except for the structural determination of the parent rhodium(I) dimer, $[RhCl(CO)_2]_2$,[8] this, to our knowledge, is the first structure of a rhodium carbonyl complex where the other ligands are not strong π acceptors; we thought it would be of interest to see if this might have a significant effect on the Rh–C bond lengths.

Experimental Section

Preparation of the Crystals.—The compound $[(n\text{-}C_4H_9)_4N][RhCl_2(CO)_2]$ was prepared in a manner similar to that of ref 1. CO was bubbled at 70° through a solution of $RhCl_3$ in methanol acidified with concentrated HCl until the solution had turned from the original red to a pale yellow color. The stoichiometric amount of $(n\text{-}C_4H_9)_4NCl$ dissolved in a minimum volume of methanol was then added and the solution was evaporated in a desiccator containing H_2SO_4 and a CO atmosphere until crystals had formed. The solution was filtered and the yellow crystals were washed with dilute HCl and allowed to dry in air. The infrared spectrum in the region of the carbonyl stretching frequencies agreed with that reported by Vallarino.[7]

Collection of X-Ray Data.—A preliminary optical and X-ray examination of a crystal of the compound indicated a lattice of monoclinic symmetry. Weissenberg photographs of the zones *h*0*l* and *h*1*l* and precession photographs of the zones *hk*0 and 0*kl* showed extinction of the reflections *h*0*l* for *l* odd and 0*k*0 for *k* odd. These absences uniquely identify the space group as C_{2h}^5-$P2_1/c$ (no. 14).[9]

Intensity data were collected on a Syntex four-circle diffractometer. A prismatic shaped crystal of approximate dimensions 0.1 × 0.2 × 0.1 mm along the *a*, *b*, and *c* crystal axes, respectively, was mounted with its *b* axis coincident with the ϕ axis of the goniostat. The unit cell dimensions, determined from a least-squares refinement of the setting angles of ten reflections measured using Mo K$\bar{\alpha}$ radiation (λ 0.7107 Å) at 20 ± 1°, are $a = 15.07$ (6) Å, $b = 8.774$ (8) Å, $c = 20.39$ (8) Å, and $\beta = 118.1$ (0.4)°. A density of 1.27 ± 0.03 g cm^{-3}, measured by flotation in aqueous $ZnCl_2$ solution, agrees satisfactorily with a density of 1.32 ± 0.01 g cm^{-3}, calculated for four formula units in the unit cell. No crystallographic symmetry conditions need be imposed on the molecule.

The data were collected using Mo K$\bar{\alpha}$ radiation (λ 0.7107 Å) filtered on the incident beam side through zirconium foil. A 1-mm diameter collimator was used on the incident beam side of the crystal and a 2-mm diameter circular aperture on the diffracted beam side. A takeoff angle of 4°, which gave an approximately square focal spot, was used. The crystal-to-source and crystal-to-counter distances were both 13.5 cm. A θ–2θ scan mode was used with the scan ranging from -1.0 to $+1.0°$ from the calculated 2θ position. The scan rate was 1.0°/min and the background was counted for 10 sec at each end of the scan range. A check reflection, 212, was counted after every 25 reflections; its intensity remained constant, with an rms deviation of 0.8%, throughout the data collection.

Of a total of 3398 independent reflections collected within the sphere defined by $\theta(\text{Mo K}\bar{\alpha}) < 22.5°$, 1545 had $I > 3\sigma(I)$ and were used in the solution and refinement of the structure. The standard deviation of the intensity, $\sigma(I)$, was computed as $[S + (B_1 + B_2)\alpha^2 + (pS)^2]^{1/2}$,[10] where S is the scan count, B_1 and B_2 are the fixed-time background counts, α is half the scan width divided by the scan rate, and p is a constant, here set equal to 0.02, which incorporates uncertainties in the measurements other than counter statistics. The linear absorption coefficient, μ, for the crystal was calculated to be 9.29 cm^{-1}; with this value of μ and assuming minimum and maximum path lengths of 0.010 and

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(1) J. A. Stanko, G. Petrov, and C. K. Thomas, *Chem. Commun.*, 1100 (1969).

(2) J. A. Stanko and T. W. Starinshak, *Inorg. Chem.*, **8**, 2156 (1969).

(3) J. A. Stanko and S. Chaipayungpundhu, *J. Amer. Chem. Soc.*, **92**, 5580 (1970).

(4) D. Forster, *Inorg. Chem.*, **8**, 2556 (1969).

(5) M. J. Cleare and W. P. Griffith, *J. Chem. Soc. A*, 372 (1969).

(6) B. R. James and G. L. Rempel, *ibid.*, *A*, 78 (1969).

(7) L. M. Vallarino, *Inorg. Chem.*, **4**, 161 (1965).

(8) L. F. Dahl, C. Martell, and D. L. Wampler, *J. Amer. Chem. Soc.*, **83**, 1762 (1961).

(9) "International Tables for X-Ray Crystallography," Vol. I, Kynoch Press, Birmingham, England, 1962, p 99.

(10) S. W. Peterson and H. A. Levy, *Acta Crystallogr.*, **10**, 70 (1957).

0.014 cm through the crystal, the error introduced into F_o by absorption should not be more than about 2%. Therefore no absorption corrections were applied to the data.

Solution and Refinement of the Structure

The structure was solved using conventional heavy-atom methods. A three-dimensional Patterson function,[11] computed initially, clearly showed the intermolecular Rh–Rh vectors and one of the intramolecular Rh–Cl vectors near the origin. A second more diffuse peak near the origin and of appropriate length was assigned to the second independent Rh–Cl intramolecular vector. A trial structure based on the rhodium and two chlorine atoms gave values of R_1 and R_2 of 0.409 and 0.457, respectively. R_1 and R_2 are the unweighted and weighted R factors defined, respectively, as $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o^2)]^{1/2}$, where F_o and F_c are the observed and calculated structure factors and w is the weight. The weight w was defined as $1/\sigma^2(F_o)$, where $\sigma(F_o)$ is the standard deviation of the observed structure factor and is related to the standard deviation of the measured intensities, $\sigma(I)$, through the formula $\sigma(F_o) = 0.5\sigma(I)[LpI]^{-1/2}$.[12] Atomic scattering factors for this and later structure factor calculations were taken from the following sources: Rh^+, from Cromer and Waber;[13] Cl^-, C^0, O^0, and N^0, from the compilation by Ibers.[14] The real part of the anomalous dispersion correction given by Cromer[15] was subtracted from the Rh^+ scattering curve.

A Fourier summation phased on the Rh and what we had assumed were the two bonded Cl ligands showed most of the remaining atoms clearly but indicated the probable existence of disorder in the rhodium complex. Only one of the carbonyl ligands was clearly resolved; both peaks cis to this carbonyl had approximately equal electron density, about one-half that of the peak trans to the resolved carbonyl. The coordinates of this latter peak coincided with those obtained for the chloride ligand which gave the well-resolved Rh–Cl vector in the Patterson function. The disorder of the second chloride with the carbonyl group trans to it accounts for the lesser intensity of its Rh–Cl vector in the Patterson function. Disorder in halocarbonyl complexes of the platinum metals has been observed previously,[16–18] and we decided to treat the disorder according to the method of La Placa and Ibers.[16] Since there was no resolution of the C, O, and Cl half-atoms at the disordered ligand sites, the two ligands cis to the well-resolved carbonyl were assigned Cl^- scattering curves and occupancy factors of 1.0. A structure factor calculation which included all the atoms of the anion, within the previous approximation for the disordered Cl–CO ligand, and the N and 16 C atoms of the cation led to values of R_1 and R_2 of 0.20 and 0.19. Two cycles of full-matrix least-squares refinement[19] of 92 positional and isotropic thermal parameters and an overall scale factor reduced R_1 and R_2 to 0.099 and 0.105. The function minimized was $\Sigma w(|F_o - F_c|)^2$ and the weighting scheme was that described above based on counter statistics.

From a "difference" Fourier synthesis computed at this stage it appeared that the disorder was being treated satisfactorily but that the thermal motion of rhodium was anisotropic. The F_o, F_c list was also examined and we noticed that the reflection $\bar{2}00$, the most intense reflection from the crystal, was apparently suffering from extinction; we therefore removed it from the refinement. Four subsequent cycles of refinement, during which the rhodium was allowed to vibrate anisotropically, converged to $R_1 = 0.083$ and $R_2 = 0.086$. The largest change in any coordinate or thermal parameter at this stage was less than $^1/_{20}$th of its standard deviation, and most of the parameter changes were less than $^1/_{200}$th of their standard deviation. We did not attempt to refine the cation atoms anisotropically nor to introduce hydrogen atoms on the alkyl chains because of the large amount of computer time which would have been necessary for the refinement, and because we suspected their addition to the model would not have improved significantly the uncertainty in the positional and thermal parameters of the anion. The observed and calculated structure factors are listed in Table I and the final atomic positional and thermal parameters in Table II. Selected interatomic bond distances and angles are listed in Table III.

Results and Discussion

A stereoscopic view of the alkylammonium cation and the anionic rhodium(I) complex which comprise the asymmetric unit of the cell, drawn with the program ORTEP,[20] is shown in Figure 1. The overall coordination geometry about the rhodium atom is closely square planar, with the two carbonyl ligands arranged in a cis configuration as had been previously predicted on the basis of the infrared spectrum of the complex.[7] However, in the crystal one of the CO ligands is fully disordered in position with the chloride ligand trans to it. The details of the anion geometry are depicted in Figure 2, with the disordered CO–Cl ligands designated as X_1 and X_2. The equation for the least-squares plane through the Rh, C, Cl, X_1, and X_2 ligands and the distances of these ligands from the plane are given in Table IV.

The Rh(I)–Cl distance of 2.345 (6) Å in the complex is very close to the Rh(I)–bridging Cl distances of 2.33

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[11] Fourier calculations were performed using Program B-149 (Argonne National Laboratory), a version of Shoemaker, Sly, and Van den Hende's ERFR-2, written by J. Gvildys.

[12] G. H. Stout and L. H. Jensen, "X-Ray Structure Determination," Macmillan, New York, N. Y., 1968, p 457.

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

[14] J. A. Ibers in "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, pp 201–207.

[15] D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).

[16] S. J. La Placa and J. A. Ibers, *J. Amer. Chem. Soc.*, **87**, 2581 (1965).

[17] J. A. McGinnety, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 2243 (1967).

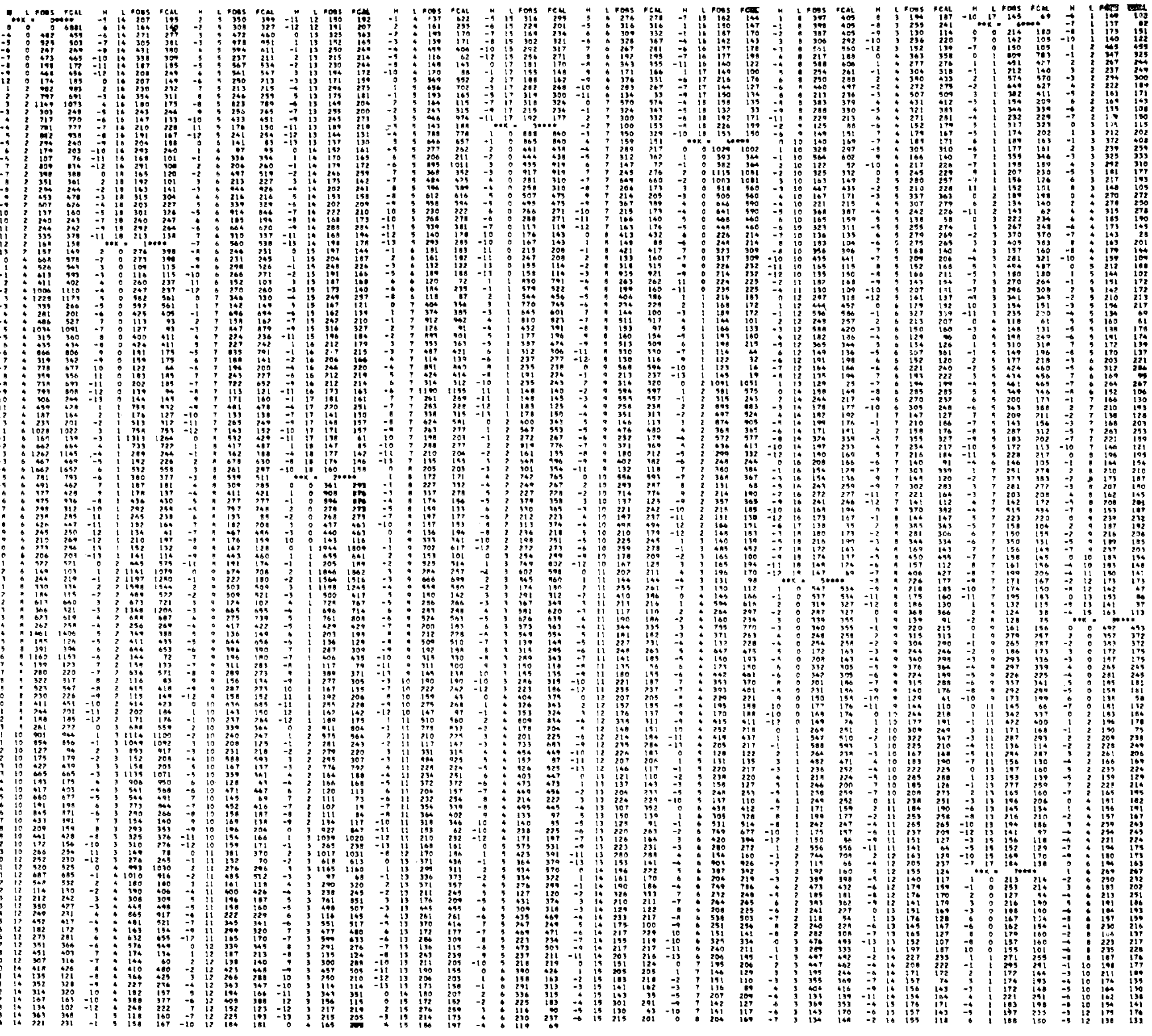
[18] N. C. Payne and J. A. Ibers, *ibid.*, **8**, 2714 (1969).

[19] Least-squares and structure factor calculations were performed using the program ANL-FLS-14E, J. Gvildys' version of W. Busing, K. Martin, and H. A. Levy's program OR-FLS: a Fortran crystallographic least-squares program, Report ORNL-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.

[20] Crystallographic illustrations were produced using C. K. Johnson's program ORTEP: a Fortran thermal ellipsoid plot program, Report ORNL-3794, Revised, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1966.

TABLE I

OBSERVED AND CALCULATED STRUCTURE FACTOR AMPLITUDES (×10) FOR TETRA-*n*-BUTYLAMMONIUM *cis*-DICHLORODICARBONYLRHODATE(I)



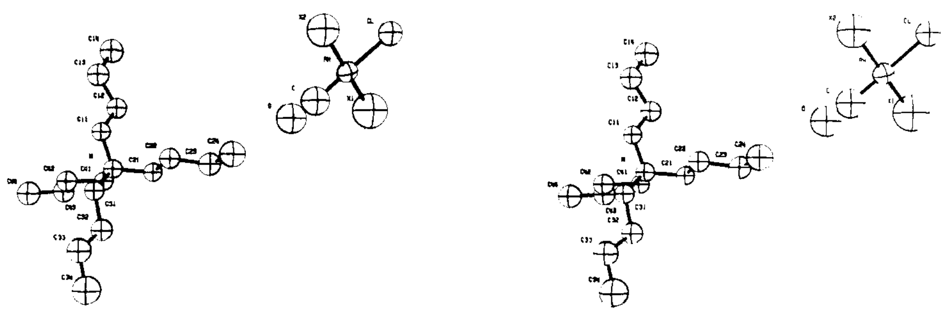


Figure 1.—Stereoscopic view of the crystal structure of tetra-*n*-butylammonium dichlorodicarbonylrhodate(I), drawn with the program ORTEP, viewed down the *b* crystal axis. Only one asymmetric unit is shown; 50% thermal ellipsoids are plotted. The disordered Cl–CO ligands are designated as X_1 and X_2. The *a* crystal axis runs horizontally in the figure from left to right, and the *c* axis runs obliquely to it (118.1°) from top to bottom. The origin is at the upper left-hand corner of the drawing.

and 2.38 Å observed in the parent $[RhCl(CO)_2]_2$ dimer.[8] When the available data on Rh(I)–Cl distances for bridging *vs.* nonbridging chloride ligands are compared, however, it appears that those bonds involving bridging chlorides are, on the average, longer (2.355 (2) Å in $RhCl(CO)SO_2(P(C_6H_5)_3)_2$,[21a] 2.372 (3) Å in Rh(CO)-

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[21] (a) K. W. Muir and J. A. Ibers, *Inorg. Chem.*, **8**, 1921 (1969); (b) J. T. Mague, *ibid.*, **8**, 1975 (1969).

TABLE II

FINAL ATOMIC COORDINATES[a] AND ANISOTROPIC THERMAL PARAMETERS[b] FROM LEAST-SQUARES REFINEMENT

Atom	*X*	*Y*	*Z*	*B*, Å^2
Rh	0.7176 (1)	0.1265 (2)	0.2238 (1)	...
C	0.6752 (18)	0.1339 (32)	0.2886 (15)	10.5 (7)
O	0.6369 (12)	0.1339 (22)	0.3280 (10)	11.8 (5)
Cl	0.7788 (4)	0.1118 (7)	0.1374 (3)	7.4 (1)
X_1	0.8511 (7)	−0.0425 (12)	0.3051 (6)	17.2 (3)
X_2	0.5861 (6)	0.3032 (9)	0.1434 (5)	12.8 (3)
N	0.2439 (9)	0.1259 (18)	0.4428 (7)	4.4 (3)
C_{11}[c]	0.1603 (11)	0.1528 (19)	0.3607 (9)	4.3 (4)
C_{12}	0.1621 (13)	0.0289 (20)	0.3049 (10)	5.3 (5)
C_{13}	0.0655 (14)	0.0611 (22)	0.2320 (11)	6.3 (5)
C_{14}	0.0597 (15)	−0.0548 (23)	0.1727 (11)	7.3 (6)
C_{21}	0.3526 (11)	0.1219 (21)	0.4501 (8)	4.3 (4)
C_{22}	0.3759 (12)	0.2669 (21)	0.4193 (10)	5.1 (4)
C_{23}	0.4857 (13)	0.2378 (23)	0.4310 (10)	6.2 (5)
C_{24}	0.5251 (14)	0.3805 (27)	0.4099 (11)	7.9 (5)
C_{31}	0.2302 (12)	0.2530 (21)	0.4892 (9)	4.5 (4)
C_{32}	0.3037 (13)	0.2434 (22)	0.5728 (11)	5.4 (4)
C_{33}	0.2764 (14)	0.3781 (24)	0.6118 (11)	6.7 (5)
C_{34}	0.3491 (16)	0.3666 (28)	0.6961 (13)	9.4 (6)
C_{41}	0.2341 (13)	−0.0386 (20)	0.4714 (9)	4.6 (4)
C_{42}	0.1340 (14)	−0.0586 (21)	0.4720 (10)	5.6 (5)
C_{43}	0.1344 (14)	−0.2282 (23)	0.4974 (11)	6.3 (5)
C_{44}	0.0388 (15)	−0.2554 (25)	0.5038 (11)	7.7 (6)

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Rh	804 (12)	1462 (25)	431 (7)	−169 (21)	234 (7)	−53 (16)

[a] Coordinates in fractions of the unit cell edge. Estimated standard deviations (×10^4) in parentheses. [b] β's and standard deviations (in parentheses) ×10^5. The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [c] Carbon atom C_{ij} is *j*th atom from nitrogen in the *i*th butyl group.

TABLE III

SELECTED INTRAMOLECULAR BOND DISTANCES AND BOND ANGLES[a]

Bond	Bond length, Å	Bonds	Bond angle, deg
Rh–C	1.72 (3)	Rh–C–O	173.4 (23)
Rh–O	2.90 (2)	C–Rh–Cl	178.4 (9)
C–O	1.19 (3)	C–Rh–X_1	89.2 (10)
Rh–Cl	2.345 (0.6)	C–Rh–X_2	90.8 (9)
Rh–X_1	2.42 (1)	Cl–Rh–X_1	89.2 (3)
Rh–X_2	2.44 (1)	Cl–Rh–X_2	90.7 (3)
		X_1–Rh–X_2	178.4 (3)
N–C_{11}[b]	1.57 (2)		
N–C_{21}	1.58 (2)	C_{11}–N–C_{21}	112.3 (9)
N–C_{31}	1.54 (2)	C_{11}–N–C_{31}	105.9 (10)
N–C_{41}	1.59 (2)	C_{11}–N–C_{41}	111.1 (12)
		C_{21}–N–C_{31}	113.2 (9)
C_{11}–C_{12}	1.58 (3)	C_{21}–N–C_{41}	102.6 (12)
C_{12}–C_{13}	1.54 (3)	C_{31}–N–C_{41}	111.9 (11)
C_{13}–C_{14}	1.55 (3)		
C_{21}–C_{22}	1.53 (3)	N–C_{11}–C_{12}	112.8 (9)
C_{22}–C_{23}	1.58 (3)	C_{11}–C_{12}–C_{13}	103.8 (17)
C_{23}–C_{24}	1.53 (3)	C_{12}–C_{13}–C_{14}	108.2 (14)
C_{31}–C_{32}	1.54 (3)	N–C_{21}–C_{22}	111.8 (11)
C_{32}–C_{33}	1.58 (3)	C_{21}–C_{22}–C_{23}	103.2 (16)
C_{33}–C_{34}	1.54 (3)	C_{22}–C_{23}–C_{24}	110.0 (18)
C_{41}–C_{42}	1.53 (3)	N–C_{31}–C_{32}	114.0 (11)
C_{42}–C_{43}	1.58 (3)	C_{31}–C_{32}–C_{33}	107.2 (11)
C_{43}–C_{44}	1.53 (3)	C_{32}–C_{33}–C_{34}	107.2 (12)
		N–C_{41}–C_{42}	111.7 (12)
		C_{41}–C_{42}–C_{43}	105.0 (15)
		C_{42}–C_{43}–C_{44}	108.5 (16)

[a] Estimated standard deviations of bond lengths (×10^2) and bond angles (×10) in parentheses. [b] Carbon atom C_{ij} is the *j*th atom from nitrogen in the *i*th *n*-butyl group.

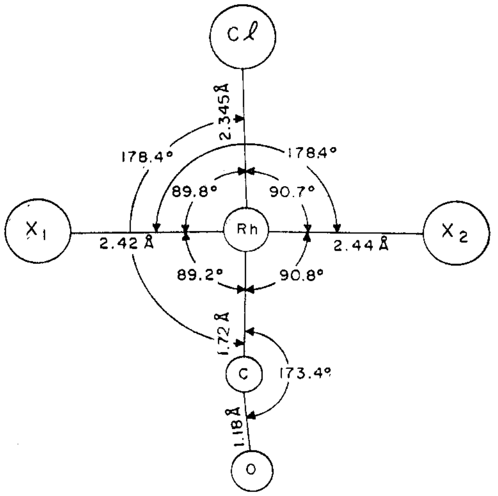

Figure 2.—Bond angles and distances within the square-planar dichlorodicarbonylrhodate(I) anion. The disordered Cl–CO ligands are designated as X_1 and X_2.

$Cl((C_6H_5)_2AsCH_2As(C_6H_5)_2)_2Rh(CO)Cl$,[21b] and 2.386 (3) Å in $Rh(CS)Cl(P(C_6H_5)_3)_2$,[22] all of which have terminal Cl's compared with mean Rh(I)–Cl lengths of 2.38 (1) Å in $[RhCl(C_8H_{12})_2]_2$,[23] 2.40 Å in $[RhCl(C_2H_4)_2]_2$, referred to in ref 24, and 2.416 (6) Å in $[Rh_2Cl_2(CO)(C_2H_5C_2C_2H_5)_2]_2$,[24] in which chloride bridges are present).

The (resolved) carbonyl group is bonded to the rhodium atom of the complex in an essentially linear fashion with the Rh–C–O angle equal to 173 ± 2°. The Rh–C distance of 1.72 (3) Å found here is close to that observed for the Rh–carbonyl C bond distance of 1.75 (2) Å in

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[22] J. L. Deboer, D. Rogers, A. C. Skapski, and P. G. H. Troughton, *Chem. Commun.*, 756 (1966).

[23] J. A. Ibers and R. G. Snyder, *Acta Crystallogr.*, **15**, 923 (1962).

[24] L. R. Bateman, P. M. Maitlis, and L. F. Dahl, *J. Amer. Chem. Soc.*, **91**, 7292 (1969).

TABLE IV

LEAST-SQUARES PLANES FOR TETRA-*n*-BUTYLAMMONIUM *cis*-DICHLORODICARBONYLRHODATE(I)[a]

1. Plane Containing Rh, Cl, X_1, X_2, C

Equation of Plane:[b,c] $0.4471X + 0.7798Y + 0.1761Z = 6.5190$

Distances of Atoms to Plane, Å

Rh	−0.013	X_1	0.021	C	−0.016
Cl	−0.012	X_2	0.021	O[d]	−0.133

2. Plane Containing N, C_{12}, C_{14}, C_{22}, C_{24}, C_{32}, C_{34}, C_{42}, C_{44}

Equation of Plane:[b] $-0.5727X + 0.7477Y - 0.0269Z = -1.5841$

Distances of Atoms to Plane, Å

N	0.063	C_{22}	−0.137	C_{34}	0.597
C_{12}	0.207	C_{24}	−0.675	C_{42}	−0.214
C_{14}	0.614	C_{32}	0.247	C_{44}	−0.703

[a] Unit weights were employed in the calculation of all planes. [b] The equations of the planes are expressed with respect to the crystallographic axes. [c] For the anion atoms related to those in the asymmetric unit by the twofold screw axis the equation of the plane is $-0.4471X + 0.7798Y - 0.1761Z = 1.4084$. [d] Oxygen atom not used in calculation of plane.

2,4-pentanedionatodicarbonylrhodium(I)[25] and of 1.75 (1) Å for the terminal Rh–CO bond in the cyclopentadienylcarbonylrhodium(I) trimer, $[Rh(C_5H_5)CO]_3$,[26] but is considerably shorter than those distances reported for Rh–CO bonds in the parent dimer $[RhCl(CO)_2]_2$,[8] 1.77 and 1.85 Å, in $Rh(CO)Cl((C_6H_5)_2AsCH_2As(C_6H_5)_2)_2Rh(CO)Cl$,[21] 1.80 (1) Å, in $RhH(CO)(P(C_6H_5)_3)_3$,[27] 1.83 (3) Å, in $RhCl(CO)(SO_2)(P(C_6H_5)_3)_2$,[20] 1.85 (1) Å, in $Rh_6(CO)_{16}$,[28] 1.86 (2) Å, in $Rh_2(C_5H_5)_2(CO)_3$,[29] 1.87 (2) Å, or in $RhI(C_5H_5)(C_2F_5)(CO)$,[30] 1.97 (3) Å. The C–O distance of 1.18 (3) Å in the $RhCl_2(CO)_2^-$ complex is not significantly different from those reported for the above rhodium carbonyls or for most other metal complexes of carbon monoxide. These findings are in accord with the results of Cotton and Wing,[31] who showed that the C–O bond length in metal carbonyls is relatively insensitive to bond order in the range 2–3 but that the metal–carbon bond distance is very sensitive to bond order. The unusually short Rh–C bond we find in the dichlorodicarbonylrhodate(I) may therefore imply a greater Rh–C bond order in this than in several of the other rhodium carbonyls. The complexes whose structures are reported in ref 21a and 27–30 all contain, besides carbon monoxide, other good π-acceptor ligands which should compete with CO for metal π-electron density; and that reported in ref 8 for the parent chlorodicarbonylrhodium dimer is postulated to contain an Rh–Rh bond.[32] In contrast, since Cl^- is a reasonable π donor and poor acceptor, the carbonyl groups in the $RhCl_2(CO)_2^-$ complex should be able to accept rather more π-electron density, thereby increasing the Rh–C bond order and shortening the bond length.

The Rh–X (disordered Cl–CO) distances of 2.42 (1) and 2.44 (1) Å are approximately the same as 2.38 (2) and 2.42 (2) Å, found by La Placa and Ibers[16] for Ir–X in the oxygen adduct of bis(triphenylphosphine)chlorocarbonyliridium(I). The high temperature factors, *B*, of the X groups used to represent the disordered ligands are undoubtedly due, as La Placa and Ibers suggest, to the facts that the composite CO peak is very broad and that the center of this peak is not necessarily coincident with that of the Cl^- peak. To treat the disorder differently we would have had to assign Rh–C and Rh–Cl distances arbitrarily and Rh, C, and O thermal parameters in advance; since our main purpose in pursuing this work was to investigate the Rh–carbonyl linkage, such an approach would have been self-defeating.[33]

There are no unusual aspects to the geometry of the alkylammonium cation. The average N–C distance is 1.57 (2) Å, the average C–C distance is 1.55 (2) Å, the average C–N–C bond angle is 109.5 (4.2)°, and the average C–C–C bond angle is 108.6 (3.5)°. These observed N–C and C–C distances are slightly greater than those of 1.52 and 1.51 Å, respectively, reported for the tetra-*n*-butylammonium cation in three previous determinations.[34] The agreement with the previous values for these bond lengths may have been improved had anisotropic thermal parameters for the atoms of the cation been employed. The four butyl chains of the cation are all in their most extended form, giving it a very flat appearance (see Figure 1). The chains are all very nearly trans; Table V lists the dihedral angles between planes defined by the nitrogen and carbon atoms of each of the four chains.

TABLE V

THE DIHEDRAL ANGLES FOR THE FOUR BUTYL CHAINS IN THE TETRA-*n*-BUTYLAMMONIUM ION

Plane 1 defined by atoms			Plane 2 defined by atoms			Dihedral angle, deg
N	C_{11}	C_{12}	C_{11}	C_{12}	C_{13}	8.8
C_{11}	C_{12}	C_{13}	C_{12}	C_{13}	C_{14}	0.2
N	C_{21}	C_{22}	C_{21}	C_{22}	C_{23}	0.7
C_{21}	C_{22}	C_{23}	C_{22}	C_{23}	C_{24}	5.5
N	C_{31}	C_{32}	C_{31}	C_{32}	C_{33}	1.2
C_{31}	C_{32}	C_{33}	C_{32}	C_{33}	C_{34}	1.1
N	C_{41}	C_{42}	C_{41}	C_{42}	C_{43}	2.7
C_{41}	C_{42}	C_{43}	C_{42}	C_{43}	C_{44}	3.2

There are no intermolecular contacts in the crystal less than the sum of van der Waals radii, though with regard to the observed disorder in the crystal, it seems worth mentioning that the anion–cation contacts involving the disordered X_1 and X_2 groups are fewer and longer than those for the ordered CO and Cl^- ligands.

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(32) The compound $[Rh(C_5H_5)CO]_3$ from ref 26, which also contains an acceptor other than CO, does not fit this pattern. The short Rh–C bond length indicates that the Rh–CO bond is unusually strong, as in the $RhCl_2(CO)_2^-$ complex.

(33) We did attempt initially to refine a model with half-chloride and half-carbonyl ligands in each coordination site, but this led to high correlation effects and singularities in the least-squares refinement because of the closeness in coordinates of the superimposed ligands.

(34) (a) J. D. Forrester, A. Zalkin, and D. H. Templeton, *Inorg. Chem.*, **3**, 1500 (1964); (b) J. D. Forrester, A. Zalkin, and D. H. Templeton, *ibid.*, **3**, 1507 (1964); (c) W. D. Horrocks, Jr., D. H. Templeton, and A. Zalkin, *ibid.*, **7**, 2303 (1968).

In addition, there are no Rh–Rh distances less than 7.0 Å in the crystal, indicating that there are no metal–metal interactions. This is in contrast with what has been observed in crystals of the chlorodicarbonylrhodium dimer[8] and in other crystals containing nonclosed-shell d^8 Rh(I) or Ir(I) complexes.[35]

The cations and anions in the crystal are stacked in approximately parallel planes. Table IV contains the equations for the least-squares planes through the cation, defined by N, C_{12}, C_{14}, C_{22}, C_{24}, C_{32}, C_{34}, C_{42}, and C_{44}, and through the anion, defined by Rh′, C′, Cl′, X_1′, and X_2′. (The primed atoms are related to those in the asymmetric unit by the twofold screw axis; the coordinates are $1 - x$, $^1/_2 + y$, and $^1/_2 - z$.) The dihedral angle between these planes is 9° but is subject to some uncertainty because of the difficulty of defining a plane through the alkylammonium cation. Its small value does, however, indicate the layered structure of the crystal.

We find no outstanding structural feature of the complex which would indicate why its coordinated CO should be so amenable to oxidation by O_2. The crystallographic results show the complex to be ideally square planar, with the *cis*-carbonyl groups apparently engaged in unusually strong π bonding to the rhodium. It would be satisfying if we could substantiate this structural finding of supposedly strong Rh–CO bonds in $RhCl_2(CO)_2^-$ with other chemical or physical information. In this regard it has been found in other metal carbonyl complexes that infrared spectral data on the reduction in the coordinated CO stretching frequencies usually show a good correlation with the degree of metal–carbon monoxide back-bonding as gauged from the metal–carbon bond lengths. Vallarino[7] has recorded the infrared spectrum of the $RhCl_2(CO)_2^-$ anion and has assigned the two strong bands at 2058 and 1974 cm^{-1} in its spectrum to the symmetric and antisymmetric stretches of the cis carbonyl groups. It is incorrect to attempt to correlate C–O stretching frequencies with bond strength where extensive coupling between vibrations undoubtedly exists. Since, however, a normal-coordinate analysis, which would reveal the force constants for these bonds, has not been performed, we are limited to offering a comparison of the frequency range of the C–O stretches in $RhCl_2(CO)_2^-$ with those of other rhodium cis dicarbonyls for which structural data have been reported. For the parent dimer, $[RhCl(CO)_2]_2$, the CO frequencies are grouped higher in energy and are observed at 2105, 2089, 2035, and 2003 cm^{-1}.[36] Similarly the CO stretches of the terminal $Rh(CO)_2$ fragments of the polynuclear $Rh_6(CO)_{16}$ occur at 2073 and 2026 cm^{-1}.[37] For both of these compounds the Rh–C bonds are marginally longer than that of $RhCl_2(CO)_2^-$. In Bonati and Wilkinson's acetylacetonate complex, Rh(acac)$(CO)_2$, which has Rh–C bond lengths comparable to that of $RhCl_2(CO)_2^-$, the CO stretching frequencies are observed at 2083, 2066, 2015, and 1987 cm^{-1}.[38] Finally, in the isoelectronic, but considerably more unstable, platinum complex, $PtCl_2(CO)_2$, the CO stretches are observed at 2220 and 2162 cm^{-1}.[39] While these data do not prove that the short Rh–C bond in $RhCl_2(CO)_2^-$ is unusually strong, they are certainly not inconsistent with that hypothesis.

When we originally began our search for metal carbonyl complexes within which the coordinated CO might be activated toward oxidation, we felt that the role of the metal would be to weaken the strong C≡O triple bond and to orient the molecule for the attack by the oxidant. While these conditions certainly appear to be satisfied for the CO in this complex, increasing experimental evidence on oxidative addition reactions of coordinatively unsaturated d^8 metal complexes seems to indicate that the electron density at the metal atom may play a large part in determining the reactivity of the complex.[40] It does not seem unreasonable to speculate that the oxidation may proceed through the initial formation of an oxygen adduct, such as have been isolated with Rh(I)[41] and Ir(I)[42] complexes, though with somewhat stronger σ-donating ligands, rather than through direct attack of O_2 upon the coordinated CO. If this were the case, the oxidation of CO could then proceed through the insertion of the CO ligand into the metal–oxygen bond. This type of insertion reaction has been observed for a large variety of metals and ligands.[43]

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