

- (17) M. G. B. Drew and A. Kay, *J. Chem. Soc. A*, 1846 (1971).
 (18) L. Ricard, C. Martin, R. West, and R. Weiss, *Inorg. Chem.*, **14**, 2300 (1975).
 (19) B. Spivack, Z. Dori, and E. I. Stiefel, *Inorg. Nucl. Chem. Lett.*, **11**, 501 (1975).
 (20) M. G. B. Drew and A. Kay, *J. Chem. Soc. A*, 1851 (1971).
 (21) D. H. Brown and J. A. D. Jeffreys, *J. Chem. Soc., Dalton Trans.*, 732 (1973).
 (22) L. Ricard, J. Estienne, and R. Weiss, *Inorg. Chem.*, **12**, 2182 (1973).
 (23) J. I. Gelder and J. H. Enemark, *Inorg. Chem.*, **15**, 1839 (1976).
 (24) B. Spivack and Z. Dori, *Coord. Chem. Rev.*, **17**, 99 (1975), and references therein.
 (25) F. A. Cotton and S. M. Morehouse, *Inorg. Chem.*, **4**, 1377 (1965).
 (26) G. T. J. Delbaere and C. K. Prout, *Chem. Commun.*, 162 (1971).
 (27) B. Spivack, A. P. Gaughan, and Z. Dori, *J. Am. Chem. Soc.*, **93**, 5265 (1971).
 (28) B. Spivack and Z. Dori, *J. Chem. Soc., Dalton Trans.*, 1173 (1973).
 (29) (a) J. Chatt and J. R. Dilworth, *J. Less-Common Met.*, **86**, 531 (1974); (b) M. W. Bishop, J. Chatt, and J. R. Dilworth, *J. Organomet. Chem.*, **73**, C59 (1974); (c) M. W. Bishop, J. Chatt, J. R. Dilworth, G. Kaufman, S. Kim, and J. A. Zubieta, *J. Chem. Soc., Chem. Commun.*, 70 (1977).
 (30) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).
 (31) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
 (32) J. M. Stewart, G. J. Kruger, H. L. Ammon, C. Dickinson, and S. R. Hall, Technical Report TR-192, University of Maryland, June 1972.
 (33) The same procedure has been followed by other authors, e.g., E. Sinn, *Inorg. Chem.*, **15**, 2698 (1976).
 (34) M. J. Bennett, M. Cowie, J. L. Martin, and J. Takats, *J. Am. Chem. Soc.*, **95**, 7504 (1973).
 (35) A. E. Smith, G. N. Schrauzer, V. P. Mayweg, and W. Heinrich, *J. Am. Chem. Soc.*, **87**, 5798 (1965).
 (36) G. F. Brown and E. I. Stiefel, *Chem. Commun.*, 728 (1970).
 (37) R. Hoffmann, J. M. Howell, and A. R. Rossi, *J. Am. Chem. Soc.*, **98**, 2484 (1976).
 (38) J. Hyde, K. Venkatasubramanian, and J. Zubieta, *Inorg. Chem.*, **17**, 414 (1978).
 (39) R. H. Summerville and R. Hoffmann, *J. Am. Chem. Soc.*, **98**, 7240 (1976).
 (40) (a) J. Chatt, L. A. Duncanson, and L. M. Venanzi, *Nature (London)*, **177**, 1042 (1956); (b) R. Eisenberg, *Prog. Inorg. Chem.*, **12**, 295 (1970).
 (41) S. Merlino, *Acta Crystallogr., Sect. B*, **24**, 1441 (1968).
 (42) T. Brennan and I. Bernal, *J. Phys. Chem.*, **73**, 443 (1969).
 (43) L. Pauling, "The Nature of the Chemical Bond", 3rd ed, Cornell University Press, Ithaca, N.Y., 1960.
 (44) O. Bastiansen and A. De Meijera, *Angew. Chem.*, **78**, 142 (1966).
 (45) J. Potenza and D. Mastropaolo, *Acta Crystallogr., Sect. B*, **29**, 1830 (1973).
 (46) J. Potenza, R. J. Johnson, and D. Mastropaolo, *Acta Crystallogr., Sect. B*, **32**, 941 (1976).
 (47) C. S. Harreld and E. O. Schlemper, *Acta Crystallogr., Sect. B*, **27**, 1964 (1971).
 (48) A. Bondi, *J. Phys. Chem.*, **68**, 441 (1964).
 (49) J. G. M. van de Aalsvoort and P. T. Beurskens, *Cryst. Struct. Commun.*, **3**, 653 (1974).
 (50) E. L. Muetterties and L. J. Guggenberger, *J. Am. Chem. Soc.*, **96**, 1748 (1974).
 (51) F. W. Moore and M. L. Larson, *Inorg. Chem.*, **6**, 998 (1967).
 (52) W. Autenrieth and G. Thomas, *Chem. Ber.*, **57**, 423 (1923).
 (53) K. A. Jensen and C. Pedersen, *Acta Chem. Scand.*, **15**, 1087 (1961).
 (54) M. W. Bishop, J. Chatt, J. R. Dilworth, P. Vella, and J. Zubieta, manuscript in preparation.
 (55) J. H. Waters, R. Williams, H. B. Gray, G. N. Schrauzer, and H. W. Finck, *J. Am. Chem. Soc.*, **86**, 4198 (1964).
 (56) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *J. Am. Chem. Soc.*, **86**, 2799 (1964).
 (57) E. I. Stiefel, *Prog. Inorg. Chem.*, **22**, 1 (1977).
 (58) N. Pariyadath, W. E. Newton, and E. I. Stiefel, *J. Am. Chem. Soc.*, **98**, 5388 (1976).
 (59) M. W. Bishop, J. Chatt, J. R. Dilworth, M. B. Hursthouse, and M. Motevalli, *J. Chem. Soc., Chem. Commun.*, 780 (1976).
 (60) G. Bunzey, J. H. Enemark, J. K. Howie, and D. T. Sawyer, *J. Am. Chem. Soc.*, **99**, 4168 (1977).
 (61) E. I. Stiefel, W. E. Newton, and N. Pariyadath, *J. Less-Common Met.*, **54**, 513 (1977).

Contribution from the Department of Chemistry,
 The University of Michigan, Ann Arbor, Michigan 48109

Crystal and Molecular Structure of Bis(triphenylphosphine)rhodium(I) Chloride Dimer-Ethyl Acetate

M. DAVID CURTIS,* WILLIAM M. BUTLER, and JOHN GREENE

Received March 17, 1978

The structure of bis(triphenylphosphine)rhodium(I) chloride dimer has been determined by single-crystal X-ray diffraction techniques. The triclinic crystal ($a = 9.767$ (3), $b = 12.635$ (5), $c = 13.680$ (4) Å; $\alpha = 86.15$ (3), $\beta = 95.80$ (3), $\gamma = 100.84$ (3)°; $V = 1648$ Å³), grown from ethyl acetate/methylene chloride solution, contained one molecule of rhodium dimer and one disordered molecule of ethyl acetate per unit cell. Intensity data were collected out to $2\theta = 45^\circ$ with Mo K α radiation. Of the 4964 reflections observed, 3007 had $I > 3\sigma(I)$ and were used in the full-matrix refinement. Assuming the space group $P\bar{1}$ (C_1^1 , No. 2), the refinement converged at $R_1 = 0.045$ and $R_2 = 0.059$ with the rhodium dimer centered around the origin and the ethyl acetate of solvation disordered around the inversion center at $0, \frac{1}{2}, \frac{1}{2}$. Some final structural parameters are Rh-Cl = 2.394 (2) and 2.424 (2) Å, Rh-P = 2.200 (2) and 2.213 (2) Å, Rh...Rh = 3.662 (2) Å, P-Rh-P = 96.34 (9)°, Rh-Cl-Rh = 98.95 (8)°, and Cl-Rh-Cl = 81.05 (8)°. The RhCl₂Rh ring is planar, in contrast to all but one other of the rhodium(I) chloride dimers whose structures have been determined.

Dahl et al.¹ first reported the structure of a rhodium(I) chloride dimer (CO)₂RhCl₂Rh(CO)₂ and found the complex to be folded along the Cl...Cl axis. This folding has the effect of decreasing the Rh...Rh distance. To explain the observed folding, Dahl et al. proposed the existence of a bent Rh...Rh bond in the dimeric complex. Shortly thereafter, Ibers and Snyder² reported the structure of (COD)RhCl₂Rh(COD), which was found to be not folded as intuitively expected for two halide-bridged, four-coordinate d⁸ centers. Since then, the structures of several other complexes of the general formula L₂RhCl₂RhL₂ have been solved and without exception the complexes have been folded along the Cl...Cl axis.³⁻⁶

The formation of a Rh-Rh bond in rhodium(I) chloride dimers has also received theoretical consideration. Summerville and Hoffmann⁷ have applied the extended Hückel

model to these complexes, focusing their attention on the molecular orbitals composed primarily of metal d orbitals. These authors found no primary interaction which would favor a folded structure over a planar one. In particular, the bonding effect from the overlap of d_{z²} orbitals in the folded structure was cancelled by the corresponding antibonding MO which is also populated. Summerville and Hoffmann concluded that the folding distortion would be "soft" and that packing forces were most likely responsible for the observed distortions from planarity.

Norman and Gmur,⁸ however, found a Rh-Rh bonding interaction in a low-lying MO which is primarily centered on the chloride ligands. The corresponding metal-ligand antibonding MO is not populated so that the net Rh-Rh bond order is greater in the folded structure than in the planar one.

Table I. Summary of Crystal Data and Intensity Collection for $[(PPh_3)_2RhCl]_2$

space group	$P\bar{1}$
$a, b, c, \text{Å}$	9.767 (3), 12.635 (5), 13.680 (4)
$\alpha, \beta, \gamma, \text{deg}$	86.15 (3), 95.80 (3), 100.84 (3)
$V, \text{Å}^3$	1648
mol wt	1413 ($L_2Rh_2Cl_2 \cdot EtOAc$)
Z	1
$d_{\text{obsd}}, \text{g/cm}^3$	1.41 (hexane, C_2Cl_4)
$d_{\text{calcd}}, \text{g/cm}^3$	1.42
crystal dimens, mm	0.331, 0.140, 0.140
radiation	λ (Mo $K\alpha$) 0.709 26–0.713 54 Å, monochromatized from oriented graphite crystal
takeoff angle, deg	4.0
linear abs coeff, $\mu, \text{cm}^{-1}, \text{Mo } K\alpha$	7.02
transmission factors	0.90–0.91
scan speed, deg/min.	variable, 3.0–15, determined as a function of peak intensity
scan range	Mo $K\alpha_1$ – 0.8 to Mo $K\alpha_2$ + 0.8
ratio of background time to peak scan time	0.8
std reflections	(200), (020), (002)
dev of std during data collection	<5%
2θ limit, deg	45
reflections collected	4964
reflections with $F^2 > 3\sigma(F^2)$	3007
$[\sum w(F_o - F_c)^2 / (NO - NV)]^{1/2}$	1.73

This conclusion is supported by the persistence in solution of the folded structure of $(CO)_2RhCl_2Rh(CO)_2$.^{9,10}

We have determined the structure of $(PPh_3)_2RhCl/2$, in which the $RhCl_2Rh$ ring is planar rather than folded. This then represents the second example of a planar rhodium(I) chloride dimer.

Experimental Section

Crystals of $L_2RhCl_2RhL_2$ ($L = PPh_3$) grew from a methylene chloride/ethyl acetate solution of a rhodium complex of tetramethyldisiloxane believed to be $L_4(Me_4Si_2O)_2Rh_2H_2$.^{11,12} Apparently, the silyl complex decomposed and/or reacted with the methylene chloride to produce the chloride dimer. The $L_2RhCl_2RhL_2$ dimer has been previously prepared and is believed to be an intermediate in hydrogenation catalysts prepared from L_3RhCl .^{13–15}

Intensity data were collected on a Syntex $P\bar{1}$ diffractometer. Cell constants were determined from a least-squares fit of 15 accurately centered reflections with $20^\circ < 2\theta < 25^\circ$. Experimental details are collected in Table I. The data reduction procedure and computer programs have been described elsewhere.¹⁶ The intensities of the standard reflections were measured after every 50 reflections. Transmission coefficients were analytically calculated for a variety of crystal settings representing diverse cross sections of the crystal. The small differences observed in calculated transmission coefficients showed that no absorption correction was required. Atomic scattering factors were taken from Cromer and Waber¹⁷ and anomalous dispersion factors were obtained from ref 18.

The rhodium atom position was located in a Patterson map. The space group $P\bar{1}$ (C_2^1 , No. 2) was assumed and the rhodium atoms were used to phase a Fourier synthesis. From the difference map, all nonhydrogen atoms were found except for those of the solvate molecule. Two cycles of least-squares refinement with all atoms isotropic converged at $R_1 = 0.09$ and $R_2 = 0.14$.¹⁹ Hydrogen atom positions on the phenyl rings were computed by assuming the H atoms to lie on the C–C–C bisector at a distance of 1.0 Å from the bonded carbon. Isotropic temperature factors one unit higher than the contiguous carbon were assigned to each H atom. The contributions of the H atoms to the structure factors were then calculated and subtracted from F_o . Continued, anisotropic refinement converged at $R_1 = 0.06$ and $R_2 = 0.11$.

From the density and the difference maps, it was apparent that an ethyl acetate molecule of solvation was present. Extremely diffuse peaks with a maximum electron density of 2 e/Å^3 were scattered about the inversion center at $0, 1/2, 1/2$. In order for one ethyl acetate molecule to be present in the space group $P\bar{1}$, the atomic positions

Table II. Fractional Cell Coordinates^a

atom	x	y	z
Rh	0.1353 (1)	0.0924 (1)	0.0705 (1)
P1	0.2830 (2)	0.2416 (2)	0.0370 (2)
P2	0.1932 (2)	0.0860 (2)	0.2311 (2)
Cl1	0.0288 (2)	0.0747 (2)	–0.0945 (2)
Cl2	0.2650 (8)	0.3559 (6)	0.1067 (6)
C2	0.1299 (9)	0.3725 (7)	0.1108 (7)
C3	0.1046 (11)	0.4577 (8)	0.1597 (8)
C4	0.2123 (13)	0.5259 (8)	0.2090 (8)
C5	0.3462 (12)	0.5097 (7)	0.2061 (7)
C6	0.3745 (9)	0.4273 (7)	0.1561 (6)
C7	0.2693 (8)	0.3003 (6)	–0.0908 (6)
C8	0.2905 (9)	0.2396 (7)	–0.1665 (7)
C9	0.2857 (10)	0.2827 (10)	–0.2626 (7)
C10	0.2620 (11)	0.3846 (10)	–0.2844 (7)
C11	0.2419 (11)	0.4475 (8)	–0.2102 (9)
C12	0.2434 (9)	0.4035 (7)	–0.1124 (7)
C13	0.5040 (9)	0.1309 (6)	0.0675 (6)
C14	0.6426 (10)	0.1154 (7)	0.0636 (7)
C15	0.7431 (9)	0.2012 (9)	0.0376 (7)
C16	0.7104 (9)	0.3012 (9)	0.0155 (8)
C17	0.5733 (9)	0.3180 (7)	0.0183 (7)
C18	0.4688 (8)	0.2314 (6)	0.0453 (6)
C19	0.2803 (8)	–0.0264 (6)	0.2787 (6)
C20	0.3003 (9)	–0.1021 (7)	0.2141 (6)
C21	0.3674 (11)	–0.1860 (7)	0.2485 (8)
C22	0.4140 (11)	–0.1968 (8)	0.3472 (8)
C23	0.3957 (10)	–0.1231 (8)	0.4108 (7)
C24	0.3304 (9)	–0.0371 (7)	0.3771 (6)
C25	–0.1398 (13)	–0.0355 (10)	0.3955 (8)
C26	–0.2313 (11)	0.0305 (11)	0.3649 (8)
C27	–0.1941 (11)	0.1134 (11)	0.2990 (8)
C28	–0.0650 (9)	0.1311 (9)	0.2613 (7)
C29	0.0301 (8)	0.0619 (7)	0.2919 (6)
C30	–0.0084 (10)	–0.0209 (8)	0.3594 (7)
C31	0.3029 (8)	0.1933 (6)	0.3038 (6)
C32	0.2471 (9)	0.2599 (7)	0.3611 (7)
C33	0.3356 (12)	0.3395 (8)	0.4164 (7)
C34	0.4781 (11)	0.3534 (8)	0.4132 (7)
C35	0.5336 (9)	0.2887 (8)	0.3559 (7)
C36	0.4490 (9)	0.2108 (7)	0.3026 (6)

^a Standard deviations for the last significant figure are given in parentheses.

must be averaged to a centrosymmetric arrangement. Several models with half-occupancy for all atoms were tried, but none refined properly. Typically, the thermal parameters would become unreasonably large and the atom positions would oscillate with successive refinement cycles. Furthermore, the positions (Table V) about which the oscillations occurred did not describe a chemically reasonable ethyl acetate molecule.

However, with the solvate fixed at the atom positions in Table V, the rest of the structure converged with $R_1 = 0.045$ and $R_2 = 0.059$. In the final difference map, the largest residue in the solvate region was 0.9 e/Å^3 , and 0.57 e/Å^3 (a Rh shadow) was the largest peak outside the solvate region. The number of variables was 361, giving a data:variable ratio of 8.3:1.

Results

The final positional and thermal parameters for the refinement with the fixed solvate included are presented in Tables II and III, respectively. The calculated positions of the phenyl hydrogens and their isotropic thermal parameters are in Table VII (supplementary material). In Table IV are the positional and thermal parameters of the solvate. Table V gives the bond distances and angles for the rhodium chloride dimer.

Figure 1 is an ORTEP drawing of the rhodium dimer and Figure 2 is the bc face of the unit cell showing the solvate in the void at $0, 1/2, 1/2$.

Discussion

Although the solvate molecule at $0, 1/2, 1/2$ could not be properly located due to a disorder, the effect of this inadequacy in the structural model on the atomic positions of interest is

Table III. Anisotropic Temperature Factors^a

atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Rh	0.0065 (1)	0.0046 (1)	0.0038 (0)	-0.0001 (0)	0.0004 (0)	-0.0000 (0)
P1	0.0070 (3)	0.0042 (2)	0.0043 (1)	0.0004 (2)	0.0005 (2)	-0.0000 (1)
P2	0.0069 (3)	0.0051 (2)	0.0037 (1)	0.0008 (2)	0.0005 (2)	-0.0000 (1)
Cl	0.0123 (3)	0.0072 (2)	0.0039 (1)	-0.0037 (2)	-0.0009 (2)	0.0008 (1)
C1	0.0072 (10)	0.0045 (6)	0.0054 (6)	0.0007 (6)	0.0013 (6)	0.0005 (5)
C2	0.0094 (12)	0.0062 (8)	0.0079 (8)	0.0012 (8)	0.0013 (8)	-0.0005 (6)
C3	0.0135 (15)	0.0077 (9)	0.0105 (9)	0.0037 (10)	0.0044 (10)	-0.0007 (7)
C4	0.0209 (18)	0.0057 (8)	0.0099 (9)	0.0022 (10)	0.0038 (10)	-0.0025 (7)
C5	0.0179 (18)	0.0050 (8)	0.0067 (7)	0.0006 (9)	0.0007 (9)	-0.0012 (6)
C6	0.0112 (13)	0.0046 (7)	0.0054 (6)	0.0008 (8)	-0.0000 (7)	0.0005 (5)
C7	0.0065 (10)	0.0043 (6)	0.0050 (6)	-0.0005 (6)	-0.0001 (6)	0.0006 (5)
C8	0.0099 (12)	0.0069 (7)	0.0059 (7)	-0.0009 (7)	0.0012 (7)	-0.0006 (6)
C9	0.0128 (14)	0.0117 (11)	0.0048 (7)	-0.0008 (10)	0.0007 (8)	-0.0009 (7)
C10	0.0135 (15)	0.0119 (11)	0.0053 (7)	0.0024 (10)	0.0013 (8)	0.0025 (7)
C11	0.0144 (15)	0.0086 (9)	0.0082 (9)	0.0040 (9)	0.0011 (9)	0.0032 (7)
C12	0.0119 (13)	0.0077 (8)	0.0054 (6)	0.0026 (8)	0.0003 (7)	0.0009 (6)
C13	0.0089 (11)	0.0048 (6)	0.0061 (7)	0.0009 (7)	0.0008 (7)	-0.0005 (5)
C14	0.0112 (13)	0.0067 (8)	0.0066 (7)	0.0022 (8)	0.0003 (7)	-0.0009 (6)
C15	0.0078 (11)	0.0104 (10)	0.0058 (7)	0.0021 (9)	0.0009 (7)	-0.0011 (7)
C16	0.0066 (11)	0.0097 (10)	0.0077 (8)	-0.0007 (8)	0.0015 (7)	-0.0000 (7)
C17	0.0085 (12)	0.0063 (7)	0.0060 (6)	-0.0003 (7)	0.0013 (7)	0.0007 (5)
C18	0.0073 (10)	0.0047 (6)	0.0041 (5)	0.0008 (6)	0.0005 (6)	-0.0010 (5)
C19	0.0078 (10)	0.0056 (7)	0.0052 (6)	0.0017 (7)	0.0007 (6)	0.0009 (5)
C20	0.0112 (12)	0.0061 (7)	0.0046 (6)	0.0003 (8)	0.0003 (7)	-0.0003 (5)
C21	0.0159 (15)	0.0053 (7)	0.0083 (8)	0.0031 (9)	0.0015 (9)	-0.0000 (6)
C22	0.0151 (15)	0.0069 (8)	0.0076 (9)	0.0042 (9)	0.0007 (9)	0.0025 (7)
C23	0.0136 (14)	0.0082 (9)	0.0053 (7)	0.0029 (9)	0.0003 (8)	0.0021 (6)
C24	0.0109 (12)	0.0063 (7)	0.0040 (6)	0.0017 (7)	0.0003 (7)	0.0003 (5)
C25	0.0150 (17)	0.0119 (11)	0.0070 (8)	-0.0025 (11)	0.0030 (10)	0.0003 (8)
C26	0.0093 (14)	0.0173 (14)	0.0060 (8)	0.0004 (11)	0.0021 (9)	-0.0024 (9)
C27	0.0102 (15)	0.0171 (14)	0.0068 (7)	0.0061 (12)	0.0015 (8)	-0.0003 (8)
C28	0.0092 (12)	0.0117 (10)	0.0066 (7)	0.0033 (9)	0.0015 (7)	0.0011 (7)
C29	0.0075 (11)	0.0082 (8)	0.0037 (5)	0.0003 (7)	0.0010 (6)	-0.0012 (5)
C30	0.0118 (13)	0.0097 (9)	0.0060 (7)	-0.0006 (9)	0.0029 (8)	0.0001 (7)
C31	0.0093 (11)	0.0052 (6)	0.0039 (5)	0.0010 (7)	-0.0001 (6)	-0.0001 (5)
C32	0.0116 (12)	0.0071 (8)	0.0062 (7)	0.0029 (8)	0.0014 (8)	-0.0007 (6)
C33	0.0168 (18)	0.0091 (9)	0.0066 (8)	0.0016 (10)	0.0002 (9)	-0.0033 (7)
C34	0.0163 (16)	0.0064 (8)	0.0068 (7)	-0.0001 (9)	-0.0028 (9)	-0.0003 (6)
C35	0.0086 (11)	0.0071 (8)	0.0061 (7)	0.0000 (8)	-0.0014 (7)	0.0005 (6)
C36	0.0092 (12)	0.0063 (7)	0.0048 (6)	0.0015 (7)	-0.0007 (7)	0.0000 (5)

^a Standard deviations of the last significant figure are in parentheses. The form of the temperature factor is $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

Table IV. Positional and Isotropic Thermal Parameters for Ethyl Acetate^a

atom	x	y	z	B, Å ²
O(1)	0.054182	0.719508	0.484465	15.17
O(2)	0.171905	0.584492	0.415848	19.68
C(37)	0.065982	0.622123	0.595126	17.02
C(38)	0.064216	0.628832	0.478184	17.00
C(39)	0.170094	0.563347	0.511627	15.85
C(40)	0.048772	0.466151	0.497772	16.80

^a C(37)-C(38)=(O(1))-O(2)-C(39)-C(40).

Table V. Bond Distances (Å) and Angles (deg) for [(PPh₃)₂RhCl]₂^{a,b}

Rh-P1	2.200 (2)	Rh··Rh'	3.662 (2)
Rh-P2	2.213 (2)	Cl··Cl'	3.131 (4)
Rh-Cl	2.394 (2)	P-C	1.839 ± 0.009 ^c
Rh-Cl'	2.424 (2)	C-C	1.382 ± 0.018 ^c
P1-Rh-P2	96.34 (9)	Cl-Rh-Cl'	81.05 (8)
P1-Rh-Cl	94.95 (8)	Rh-Cl-Rh'	98.95 (8)
P1-Rh-Cl'	175.7 (1)	C-P-C	191.9 ± 4.0 ^c
P2-Rh-Cl'	87.77 (8)	C-P-Rh	116.2 ± 6.2 ^c
P2-Rh-Cl	168-01 (7)	C-C-C	120.00 ± 0.09 ^c

^a Standard deviations from covariance matrix in parentheses.

^b With solvate model included in refinement; $R_1 = 0.045$, $R_2 = 0.059$. ^c Average values. Standard deviation, $\sigma = [\sum(x - \bar{x})^2 / (n - 1)]^{1/2}$. The minimum and maximum values for the P-C and C-C distances and the C-P-C, C-P-Rh, and C-C-C angles are, respectively, 1.827 (8), 1.854 (8); 1.35 (2), 1.41 (2); 97.6 (4), 108.5 (4); 107.4 (3), 127.0 (3); and 117.6 (8), 121.4 (9).

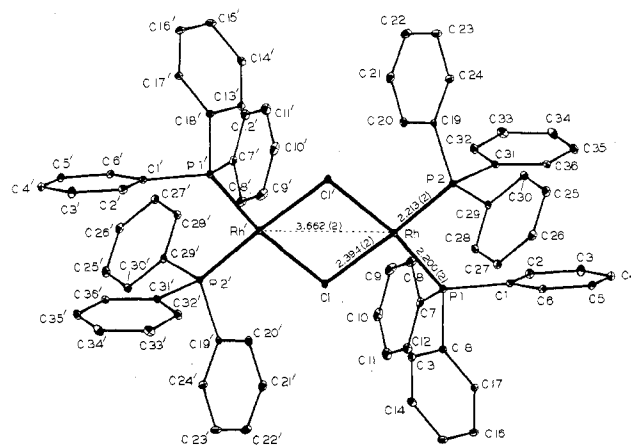


Figure 1. ORTEP drawing of bis(triphenylphosphine)rhodium(I) chloride dimer showing the numbering scheme. Thermal ellipsoids are drawn at the 50% probability level.

minimal. The changes in the structural parameters when the solvate was not included in the refinement were of the same magnitude as their standard deviations. In a similar structure, that of $(PPh_3)_2(CO)(H)Ir(Me_4Si_2O) \cdot EtOH$, the ethanol solvate refined properly.¹² Here also it was found that the atomic positions of the iridium moiety were relatively insensitive to the presence or absence of the solvate in the refinement.

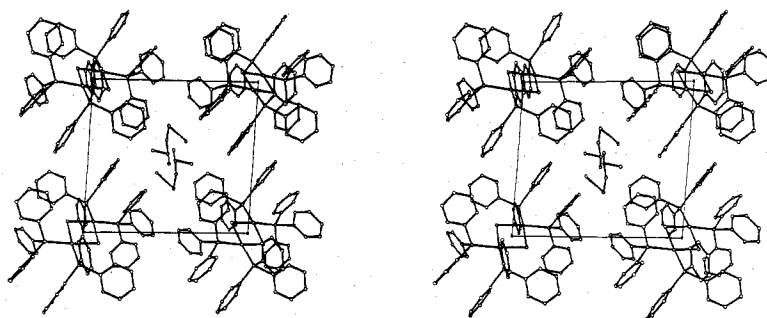


Figure 2. ORTEP drawing of the *bc* face of the unit cell of $[(\text{PPh}_3)_2\text{RhCl}]_2$, showing the ethyl acetate of solvation around $0, \frac{1}{2}, \frac{1}{2}$. The *a* axis is out of the paper, the *b* axis is vertical, and the *c* axis is horizontal.

Table VI. Comparisons of Some Structural Parameters for Various Rhodium(I) Chloride Dimers

complex	$\lambda, ^\circ$ deg	Rh...Rh, Å	Rh-Cl, Å	L-Rh-L, deg	Cl-Rh-Cl, deg	ref
$(\text{PPh}_3)_2\text{Rh}_2\text{Cl}_2$	180	3.662	2.40	96.3	81.0	This work
$(\text{COD})_2\text{Rh}_2\text{Cl}_2$	180	3.50	2.38	90	85	2
$(\text{CO})_4\text{Rh}_2\text{Cl}_2$	124	3.12	2.35	91.0	85.0	1
<i>cis</i> - $(\text{CO})_2(\text{L})_2\text{Rh}_2\text{Cl}_2^b$	123	3.167	2.43, ^c 2.41	90.5	84.4	6
$(\text{COD})\text{RhCl}_2\text{RhL}_2^{d,2}$	123	3.138	2.405, ^c 2.385	91.3	82.9	4
$(\text{C}_2\text{H}_5)_2\text{Rh}_2\text{Cl}_2$	116	3.02	2.40		84	3
$\text{L}_4\text{Rh}_2\text{Cl}_2^e$	116	3.040	2.405	93.4	81.4	5

^a Fold angle. ^b L = PhPMe_2 . ^c Trans to L. ^d L = $\text{P}(\text{O}i\text{Pr})_3$. ^e L = η^2 -2-methyl-2,4-pentadiene.

There is a rather large variation in the C-P2-Rh angles ($\text{C}29\text{-P}2\text{-Rh} = 107.4(3)^\circ$ and $\text{C}31\text{-P}2\text{-Rh} = 127.0(3)^\circ$). Thus, the P2 phosphine ligand is canted with respect to the molecular plane. This distortion may be due to interligand, steric crowding, or intermolecular packing constraints. The C-P-Rh angles about P1 show much smaller deviations (range = 3.20°).

The structure of $\text{L}_2\text{RhCl}_2\text{RhL}_2$ (L = PPh_3) is essentially square planar about each rhodium, and the molecule is not folded across the Cl...Cl axis. Table VI lists some structural parameters of the rhodium(I) chloride dimers whose structures have been determined. Bonnet et al.⁶ state that the Rh-Cl distance increases as the fold angle, λ , decreases and that the increase in bond length is related to the formation of the weak Rh-Rh bond in the folded complex. However, the data in Table VI do not substantiate this idea. The Rh-Cl bond length does appear to be weakly coupled to the nature of the trans ligand, tending to be somewhat shorter trans to olefins or carbonyls and longer trans to phosphorus. Even here, however, the differences are approximately equal to the standard deviations.

The ClRhCl and LRhL angles are related. As the latter increases, the former decreases (correlation coefficient = 0.90). This angle relation is probably partly steric and partly electronic.⁷ The RhClRh angle is geometrically connected to the fold angle λ . As λ decreases, the RhClRh angle decreases for a constant Rh-Cl distance and a constant ClRhCl angle, making comparisons difficult.

It is obvious that the structural details of rhodium dimers of the type $\text{L}_2\text{RhCl}_2\text{RhL}_2$ are the result of extremely subtle electronic and steric effects of the ligands. It is interesting to note, however, that acyclic olefins tend to cause the greatest deviations from planarity (smallest λ). Also, there does not appear to be any "middle ground". The complexes are either planar ($\lambda = 180^\circ$) or folded considerably ($\lambda \leq 124^\circ$). This observation suggests that a Rh...Rh bonding interaction is either present with reasonable strength or completely absent. Since the Rh...Rh bonding interaction arises from molecular orbitals which are primarily metal-ligand in character,⁸ it is not unreasonable to suggest that relatively small changes in

the metal-ligand orbitals could completely quench the Rh...Rh bonding interaction.

Acknowledgment. The authors thank the National Science Foundation for their support through Grant CHE77-01577.

Registry No. $[(\text{PPh}_3)_2\text{RhCl}]_2 \cdot \text{H}_3\text{CCO}_2\text{Et}$, 67351-11-5.

Supplementary Material Available: A listing of structure factor amplitudes and Table VII, showing fixed positional and isotropic thermal parameters for the phenyl hydrogens of $[(\text{PPh}_3)_2\text{RhCl}]_2$ (14 pages). Ordering information is given on any current masthead page.

References and Notes

- L. F. Dahl, C. Martell, and D. L. Wampler, *J. Am. Chem. Soc.*, **83**, 1761 (1961).
- J. A. Ibers and R. G. Snyder, *Acta Crystallogr.*, **15**, 923 (1962).
- K. Klenderman and L. F. Dahl, quoted in L. R. Bateman, P. M. Maitlis, and L. F. Dahl, *J. Am. Chem. Soc.*, **91**, 7292 (1969).
- J. Coetzer and G. Gafner, *Acta Crystallogr., Sect. B*, **26**, 985 (1970).
- M. G. B. Drew, S. M. Nelson, and M. Sloan, *J. Chem. Soc., Dalton Trans.*, **1484** (1973).
- J. J. Bonnet, Y. Jeannin, P. Kalck, A. Maisonnat, and R. Poilbanc, *Inorg. Chem.*, **14**, 743 (1975).
- R. H. Summerville and R. Hoffmann, *J. Am. Chem. Soc.*, **98**, 7240 (1976).
- J. G. Norman, Jr., and D. J. Gmur, *J. Am. Chem. Soc.*, **99**, 1446 (1977).
- C. W. Garland and J. R. Wilt, *J. Chem. Phys.*, **36**, 1094 (1962).
- J. G. Bullitt and F. A. Cotton, *Inorg. Chim. Acta*, **5**, 637 (1971).
- J. Greene and M. D. Curtis, *J. Am. Chem. Soc.*, **99**, 5176 (1977); M. D. Curtis and J. Greene, *ibid.*, in press.
- J. Greene, Ph.D. Thesis, The University of Michigan, Ann Arbor; M. D. Curtis, J. Greene, and W. M. Butler, *J. Organomet. Chem.*, in press.
- M. A. Bennett and P. A. Longstaff, *Chem. Ind. (London)*, **20**, 846 (1965).
- J. A. Osborne, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc. A*, 1711 (1966).
- C. A. Tolman, P. Z. Meakin, D. L. Lindner, and J. P. Jesson, *J. Am. Chem. Soc.*, **96**, 2762 (1974).
- R. J. Klingler, W. M. Butler, and M. D. Curtis, *J. Am. Chem. Soc.*, **100**, 5034 (1978). A cell reduction was done using program "TRACER", by S. C. Lawton.
- D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).
- C. H. MacGillivray, G. D. Riech, and K. Lonsdale, "International Tables for X-Ray Crystallography", Vol. III, Kynoch Press, Birmingham, England, 1962.
- $R_1 = \sum |F_o| - |F_c| / \sum |F_o|$; $R_2 = [\sum (|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2}$, where the weighting factor is $w = 4F^2 / (\sigma^2(I) + P^2I^2)$ with $P = 0.04$. The function minimized during least squares was $w(|F_o| - |F_c|)^2$.
- The calculated density is quite sensitive to the presence of the EtOAc. Thus, $\rho_{\text{calcd}} = 1.33 \text{ g/cm}^3$ with no EtOAc included in the cell, and $\rho_{\text{calcd}} = 1.51 \text{ g/cm}^3$ with 2 molecules of EtOAc/cell.