Supplementary Material Available. A listing of the structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number AIC405727.

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Dinuclear-Bridged d^8 Metal Complexes. IV. Crystal and Molecular Structure of $[RhCl(CO)(P(CH_3)_2C_6H_5)]_2$ and Isomerization in Solution of $[RhCl(CO)(PR_3)]_2$ Complexes[1]

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The crystal and molecular structure of *cis*-di-μ-chloro-dicarbonylbis(dimethylphenylphosphine)dirhodium(I) has been solved by single-crystal X-ray diffraction. The compound crystallizes in space group $P\bar{1}$ with two asymmetric units per unit cell. Lattice constants are $a = 10.495 \pm 0.009$, $b = 12.086 \pm 0.009$, and $c = 10.337 \pm 0.007$ Å; $\alpha = 112.71 \pm 0.04$, $\beta = 97.50 \pm 0.04$, and $\gamma = 103.69 \pm 0.04°$. The structure has been refined by a full-matrix least-squares procedure to a conventional R factor of 0.037 for 2370 observed reflections. Each rhodium atom is surrounded approximately in a square-planar fashion but there is a dihedral angle of 123° between these two planes. Bond distances of interest are as follows: two Rh–Cl trans to phosphorus, 2.410 (3) and 2.427 (3) Å; two Rh–Cl trans to carbonyl groups, 2.408 (3) and 2.406 (2) Å; Rh–P 2.230 (3) and 2.220 (2) Å; Rh–Rh, 3.167 (1) Å. In conjunction with X-ray results, a careful discussion of the infrared spectra in the solid state and in solution indicates an isomerization phenomenon in solution which is extented to the parent compounds.

Introduction

A previous infrared and nmr study[2] showed that complexes of the type $[RhCl(CO)(PR_3)]_2$ have a double square-planar structure. However a definitive conclusion about the cis or trans configuration could not be clearly set up. Moreover, nmr spectra[2] of $[RhCl(CO)(P(CH_3)_2C_6H_5)]_2$ at room temperature showed an apparent equivalence of the methyl protons which could be interpreted as an entirely planar structure. However, previous crystal structures of dinuclear chloro-bridged rhodium(I) complexes such as $[RhCl(CO)_2]_2$,[3] $[RhCl(C_2H_4)_2]$,[4] $C_8H_{12}Rh_2Cl_2[P(OC_6H_5)_3]_2$,[5] $[RhCl(C_6H_{10})_2]_2$,[6] and $[RhCl(C_8H_{12})]_2$[7] showed that each rhodium atom is in a square-planar configuration but the dihedral angle between these two planes departs from 180° except in the last case. The present study was undertaken to elucidate these two points of interest.

The X-ray structural determination has been carried out on a single crystal of $[RhCl(CO)(P(CH_3)_2C_6H_5)]_2$. Discussing results in comparison with those of a careful infrared study in the solid state and in solution, an interpretation of isomerization is given; it is extented to the parent compounds such as trimethyl- and tris(dimethylamino)phosphine complexes of Rh(I).

Experimental Section

The compounds $[RhCl(CO)PR_3]_2$ were prepared as previously described.[2] All attempts to crystallize the $[RhCl(CO)P(CH_3)_3]_2$ compound failed to give suitably sized crystals. However beautiful clear brown-yellow prisms of $[RhCl(CO)(P(CH_3)_2C_6H_5)]_2$ were obtained using the following technique. Hexane, in which the compound is slightly soluble, was added to a solution of the complex in toluene without stirring. At −20° the slow diffusion of toluene in hexane and of hexane in toluene led to suitable crystals. *Anal.* Calcd for $RhClC_9H_{11}OP$: C, 35.49; H, 3.65; P, 10.17; Cl, 11.64. Found: C, 34.77; H, 3.81; P, 10.35; Cl, 11.62.

Infrared Studies. The infrared spectra were recorded with a Perkin-Elmer 225 grating spectrometer equipped with a scale expander, either in cyclohexane solutions or in cesium bromide pellets. In the carbonyl stretching region, the spectra were calibrated by water vapor lines. Line shape analyses were performed with a Dupont 310 curve resolver. The part due to diffusion in the Lorentz shape analysis of the spectra in the solid state has not been taken into account. We checked that this neglected part does not affect our conclusions.

Crystal Data. Examination of crystals of $Rh_2Cl_2(CO)_2(P(CH_3)_2C_6H_5)_2$ by precession methods using Mo Kα radiation did not reveal any symmetry but the center imposed by the Friedel law. Hence the space group is either $P1$ or $P\bar{1}$. The lattice constants, obtained after alignment of a crystal on a four-circle diffractometer, are $a = 10.495 \pm 0.009$, $b = 12.086 \pm 0.009$, and $c = 10.337 \pm 0.007$ Å; $\alpha = 112.71 \pm 0.04$, $\beta = 97.50 \pm 0.04$, and $\gamma = 103.69 \pm 0.04°$ (T 21°, λ(Mo Kα) 0.71069 Å).

Based on a calculated volume of 1139 Å^3 and two asymmetric units per unit cell, the calculated density of 1.783 g cm^{-3} is in good agreement with the density of 1.77 g cm^{-3} measured by flotation in an aqueous solution of zinc chloride.

Data Collection. Diffraction data were collected at room temperature from a truncated hexagonal bipyramid of average dimension

0.3 mm with a manually operated four-circle X-ray diffractometer. The crystal was mounted on a glass fiber about an axis roughly normal to the (100) planes. The linear absorption coefficient μ of the compound for Mo Kα radiation is 17.7 cm^{-1}; for Cu Kα it is 87.7 cm^{-1}. Because Cu Kα radiation does seriously worsen the absorption problem, Mo Kα has been chosen, with a pyrolytic graphite monochromator set just in front of the counter aperture.

The takeoff angle was 4°; at this angle the peak intensity of a typical reflection is about 80% of the maximum value obtained by increasing this angle. The X-ray tube focus–crystal distance was 22 cm and the crystal–counter distance was 21 cm. The receiving aperture selected to minimize extraneous background had a diameter of 4 mm. The apparatus was equipped with a scintillation counter and a pulse height analyzer adjusted to admit about 90% of the Kα peak.

Peak intensities were recorded using the θ–2θ scan technique at a rate of 1° in θ/min from 0.6° in θ below the Kα_1 peak to 0.6° above the Kα_2 peak to a maximum Bragg angle of 23.5° ($(\sin\theta)/\lambda \leq 0.56$).

Stationary-crystal, stationary-counter background measurements of 20-sec duration were made at each end of the scan interval. Beyond $\theta = 20°$, background measurements were increased to 30 sec. A total of 3173 intensities of independent reflections were measured ($h \geq 0,\pm k,\pm l$). As a check on electronic and crystal stability during the period of data collection the intensities of three standard reflections—340, $50\bar{2}$, $10\bar{4}$—were measured every 50 reflections. No systematic drift in these standards was observed.

Strong reflections, corresponding to a count higher than 4000 counts/sec during the scan, have been corrected for lost counts due to the dead time of the counter, using a computer correction curve as previously described.[8]

Data processing was carried out with a local program. Peak counts were corrected for background to yield the net integrated intensity I. These intensities were assigned standard deviations according to the formula

$$\sigma(I) = [\mathrm{CT} + 0.25(t_c/t_b)^2(B_1 + B_2) + (pI)^2]^{1/2}$$

where CT is the total integrated peak count obtained during a scan time t_c, B_1 and B_2 are background counts each obtained during a time t_b, and $I = \mathrm{CT} - 0.5(t_c/t_b)(B_1 + B_2)$. The value of p was selected as 0.03 in such a way that all integrated intensities of the three standard reflections were included in the $I \pm \sigma(I)$ range. The values of I and $\sigma(I)$ were next corrected for Lorentz and polarization effects.

No absorption corrections were made because of the relatively low absorption coefficient value (17.7 cm^{-1} for Mo Kα) and because no significant intensity variation for a given reflection was observed when rotating around the ψ angle.

Structure Solution and Refinement. The structure was solved by standard Patterson and Fourier methods and refined by full-matrix least-squares techniques.[9] The quantity minimized is $\sum w(|F_o| - |F_c|)^2$ where F_o and F_c are the observed and calculated structure amplitudes put on a same scale where the weights w are taken as $4F_o^2/\sigma^2(F_o^2)$. The agreement indices are defined as $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2}$. Values of the atomic scattering factors and the anomalous terms were those published by Cromer and Waber;[10] 236 variables were refined using 2370 observed reflections having higher than 3 times its standard deviations ($F_o^2 \geq 3\sigma(F_o^2)$).

It has been assumed that the correct space group was $P\bar{1}$ rather than $P1$. This was confirmed by the subsequent structure solution.

From the Patterson function, both rhodium and both chlorine atoms were located, $R = 0.33$. On subsequent difference Fourier maps, all other atoms, but hydrogen, were found. A least-squares refinement with all atoms and variable isotropic thermal parameters led to values of R and R_w of 0.141 and 0.144. In a next step, variable anisotropic thermal parameters were used; the values of R and R_w were respectively 0.050 and 0.060.

Examination of $|F_c| - |F_o|$ values showed that some differences were very high (more than $20\sigma(F)$) indicating without any doubt a human error due to missetting of the Euler angles during data collection. Twelve such reflections were omitted from the next cycle which led to $R = 0.045$ and $R_w = 0.052$.

It was then observed that a number of strong low Bragg angle reflections had large positive values for $|F_c| - |F_o|$ which was attributed to the secondary extinction effect. A correction was applied to the reflections accordingly to Larson and Cromer's scheme.[11] The agreement indices took the values $R = 0.040$ and $R_w = 0.050$, and the value of the isotropic extinction parameter was 0.12×10^{-5} e^{-2}.

In the next difference Fourier map, the positions of 17 hydrogen atoms among 22 present in an asymmetric unit were visible. However those of phenyl groups were idealized. The hydrogen atoms were included in a final cycle of refinement but were not refined. This cycle converged to final values of R and R_w of 0.037 and 0.049, respectively. The largest parameter shifts in this last cycle were less than 0.1 of their estimated standard deviations. A final difference Fourier map was essentially featureless since the observed peaks of the order 0.7 e/Å^3 were approximately 15% of the heights of carbon atom peaks found in earlier Fourier maps. For all reflections, including those for which $I < 3\sigma(I)$, a structure factor calculation showed that among the 802 "unobserved" reflections only 24 had $|F_o^2 - F_c^2| > 3\sigma(F_o^2)$.

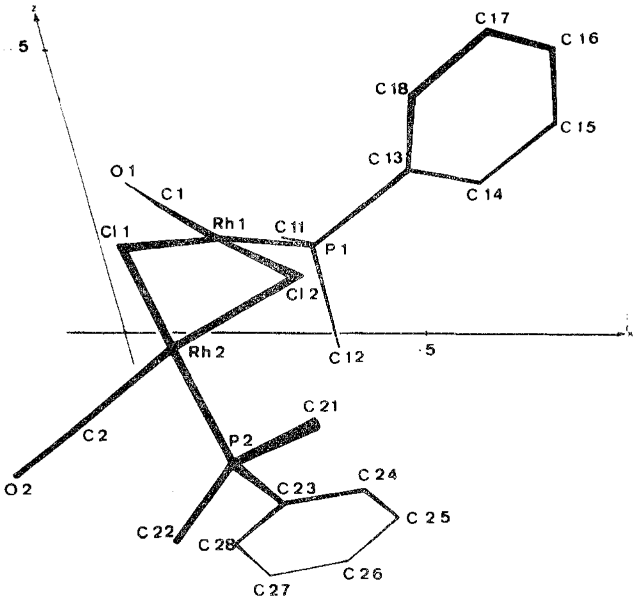

Figure 1. Perspective view of the asymmetric unit down the y axis.

Consequently these 802 were omitted from Table I where values of $|F_o|$ and $|F_c|$ for reflections used in the refinement procedure are presented. The atomic parameters with their standard deviations are given in Table II. The idealized hydrogen positions (those of the phenyl groups) together with the hydrogen positions found in the Fourier map are presented in Table III.

Discussion of the Structure

The unit cell contains two dimeric units of formula $[\mathrm{RhCl(CO)(P(CH_3)_2C_6H_5)}]_2$. The first one, the geometry of which is described in Figure 1, is defined by the parameters listed in Table II. The second one is obtained from the first one by symmetry from the center of inversion which is the origin.

Table IV lists intramolecular bond distances and bond angles with their standard deviations derived from the error matrix after the final least-squares cycle in which the full matrix was inverted.

As expected from a previous ir study[2] each rhodium atom is in an approximately square-planar configuration, being bonded to two chlorine, one phosphorus and one carbon atoms (Figure 2). However in the dimeric unit, both square-planar arrangements are not perfect, since, the four atoms bonded to a rhodium atom do not strictly lie in the same plane (Table V).

An interesting feature is that this double square-planar structure is bent with a dihedral angle of 123.0 (1)°. This value is quite comparable with that of 122.6 (2)° obtained by Coetzer and Gafner[5] in $\mathrm{Rh_2(P(OC_6H_5)_3)_2C_8H_{12}Cl_2}$ but is significantly higher than the 115.8° value observed by Drew, *et al.*,[6] for $\mathrm{Rh_2Cl_2(C_6H_{10})_4}$. This bent, bridged geometry, if comparable in some cases, however is not general for di-μ-chloro complexes of Rh(I); indeed Ibers and Snyder[7] showed that the 1,5-cyclooctadiene complex $[\mathrm{Rh(C_8H_{12})Cl}]_2$ has a strictly planar Rh–Cl$_2$–Rh bridge.

Table II. Atomic Parameters for $Rh_2Cl_2(CO)_2(P(CH_3)_2C_6H_5)_2$ with Their Standard Deviations

Atom	x	y	z	β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Rh(1)	0.1548 (1)	0.2368 (1)	0.1620 (1)	0.0099 (1)	0.0111 (1)	0.0107 (1)	0.0022 (1)	0.0018 (1)	0.0047 (1)
Rh(2)	0.0788 (1)	0.3529 (1)	−0.0533 (1)	0.0078 (1)	0.0088 (1)	0.0121 (1)	0.0025 (1)	0.0018 (1)	0.0041 (1)
Cl(1)	−0.0111 (2)	0.3423 (2)	0.1478 (2)	0.0126 (2)	0.0162 (3)	0.0166 (3)	0.0063 (2)	0.0066 (2)	0.0072 (2)
Cl(2)	0.2924 (2)	0.3891 (2)	0.0994 (2)	0.0089 (2)	0.0127 (2)	0.0137 (3)	0.0012 (2)	0.0005 (2)	0.0062 (2)
P(1)	0.3107 (2)	0.1382 (2)	0.1489 (2)	0.0134 (2)	0.0117 (2)	0.0126 (3)	0.0042 (2)	0.0008 (2)	0.0058 (2)
P(2)	0.1831 (2)	0.3699 (2)	−0.2214 (2)	0.0084 (2)	0.0094 (2)	0.0126 (3)	0.0020 (1)	0.0013 (2)	0.0052 (2)
C(1)	0.0549 (11)	0.1306 (11)	0.2178 (13)	0.0160 (13)	0.0158 (12)	0.0197 (16)	0.0005 (10)	0.0049 (11)	0.0090 (12)
C(2)	−0.0839 (8)	0.3138 (9)	−0.1720 (10)	0.0093 (9)	0.0150 (10)	0.0158 (12)	0.0035 (7)	0.0028 (9)	0.0069 (9)
O(1)	−0.0079 (12)	0.0669 (12)	0.2578 (14)	0.0261 (16)	0.0281 (16)	0.0378 (23)	0.0015 (13)	0.0127 (16)	0.0229 (17)
O(2)	−0.1860 (7)	0.2876 (10)	−0.2449 (11)	0.0086 (7)	0.0284 (14)	0.0292 (15)	0.0026 (7)	−0.0008 (8)	0.0172 (12)
C(11)	0.2668 (13)	−0.0122 (11)	0.1641 (17)	0.0195 (16)	0.0130 (11)	0.0309 (24)	0.0027 (10)	0.0003 (15)	0.0117 (14)
C(12)	0.3553 (15)	0.0979 (15)	−0.0255 (12)	0.0261 (20)	0.0269 (20)	0.0134 (13)	0.0169 (17)	0.0069 (13)	0.0090 (13)
C(13)	0.4526 (8)	0.2310 (9)	0.2832 (10)	0.0106 (9)	0.0145 (10)	0.0154 (13)	0.0031 (7)	0.0019 (8)	0.0093 (9)
C(14)	0.5938 (13)	0.2217 (11)	0.2600 (18)	0.0160 (15)	0.0129 (12)	0.0352 (29)	0.0069 (11)	0.0012 (16)	0.0014 (15)
C(15)	0.7128 (13)	0.2929 (17)	0.3632 (30)	0.0119 (14)	0.0203 (19)	0.0470 (46)	0.0051 (13)	0.0023 (20)	0.0122 (24)
C(16)	0.7110 (13)	0.3728 (21)	0.4920 (22)	0.0134 (15)	0.0315 (30)	0.0318 (30)	−0.0004 (16)	−0.0043 (17)	0.0237 (28)
C(17)	0.6001 (17)	0.3887 (31)	0.5170 (14)	0.0163 (19)	0.0613 (60)	0.0115 (16)	0.0037 (25)	−0.0013 (13)	0.0015 (23)
C(18)	0.4769 (11)	0.3158 (25)	0.4101 (13)	0.0099 (11)	0.0538 (44)	0.0116 (14)	0.0014 (17)	0.0015 (10)	−0.0010 (19)
C(21)	0.3147 (10)	0.5193 (9)	−0.1541 (12)	0.0135 (10)	0.0110 (9)	0.0224 (16)	0.0012 (8)	0.0028 (10)	0.0082 (10)
C(22)	0.0868 (9)	0.3631 (9)	−0.3860 (10)	0.0125 (9)	0.0140 (10)	0.0160 (12)	0.0050 (8)	0.0003 (8)	0.0079 (9)
C(23)	0.2643 (7)	0.2482 (8)	−0.2882 (8)	0.0094 (8)	0.0118 (8)	0.0117 (9)	0.0031 (6)	0.0026 (6)	0.0069 (7)
C(24)	0.4021 (8)	0.2734 (10)	−0.2649 (13)	0.0069 (8)	0.0156 (11)	0.0261 (18)	0.0033 (8)	0.0032 (9)	0.0082 (12)
C(25)	0.4552 (11)	0.1754 (14)	−0.3159 (18)	0.0123 (12)	0.0216 (19)	0.0351 (28)	0.0082 (13)	0.0103 (15)	0.0137 (19)
C(26)	0.3727 (13)	0.0532 (12)	−0.3921 (14)	0.0197 (16)	0.0179 (15)	0.0242 (19)	0.0110 (13)	0.0124 (14)	0.0112 (14)
C(27)	0.2390 (12)	0.0271 (10)	−0.4159 (13)	0.0190 (15)	0.0118 (10)	0.0208 (17)	0.0044 (10)	0.0081 (12)	0.0052 (10)
C(28)	0.1852 (8)	0.1246 (9)	−0.3639 (12)	0.0084 (8)	0.0122 (10)	0.0229 (16)	0.0026 (7)	0.0024 (9)	0.0052 (10)

[a] The form of the anisotropic thermal ellipsoid is $\exp(-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl))$.

Table III. Hydrogen Atom Fractional Coordinates

Atom	x	y	z
HC(14)	0.596	0.186	0.200
HC(15)	0.765	0.287	0.351
HC(16)	0.762	0.401	0.538
HC(17)	0.600	0.431	0.574
HC(18)	0.425	0.324	0.423
HC(24)	0.438	0.327	−0.232
HC(25)	0.515	0.186	−0.304
HC(26)	0.397	0.012	−0.415
HC(27)	0.202	−0.027	−0.450
HC(28)	0.126	0.114	−0.374
H1C(22)	0.030	0.300	−0.410
H2C(22)	0.150	0.375	−0.320
H3C(22)	0.030	0.425	−0.350
H1C(21)	0.270	0.590	−0.110
H1C(11)	0.280	0.010	0.260
H2C(11)	0.370	0.000	0.135
H1C(12)	0.450	0.075	−0.050

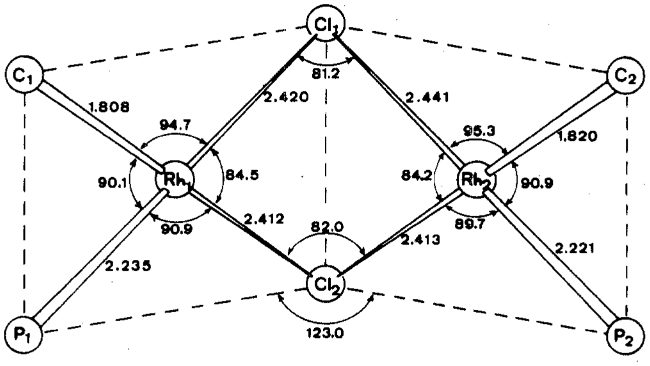

Figure 2. Sketch showing the double square-planar environment of each rhodium. Bond distances in angstroms are those corrected for thermal motion (Table IV). Bond angles are in degrees.

Table IV. Selected Intramolecular Bond Distances and Angles in $[RhCl(CO)(P(CH_3)_2C_6H_5)]_2$

	Distances, Å		
Rh(1)–Cl(1)	2.410 (3)	Rh(2)–P(2)	2.220 (2)
	2.420 (3)[a]		2.221 (2)[a]
Rh(1)–Cl(2)	2.408 (2)	Rh(2)–C(2)	1.808 (9)
	2.412 (2)[a]		1.820 (9)[a]
Rh(1)–P(1)	2.230 (3)	C(1)–O(1)	1.124 (13)
	2.235 (3)[a]	C(2)–O(2)	1.124 (12)
Rh(1)–C(1)	1.782 (11)	P(1)–C(11)	1.839 (11)
	1.808 (11)[a]	P(1)–C(12)	1.832 (11)
Rh(2)–Cl(1)	2.427 (3)	P(1)–C(13)	1.831 (8)
	2.441 (3)[a]	P(2)–C(21)	1.803 (9)
Rh(2)–Cl(2)	2.406 (2)	P(2)–C(22)	1.824 (8)
	2.413 (2)[a]	P(2)–C(23)	1.824 (8)
	Angles, Deg		
Cl(1)–Rh(1)–Cl(2)	84.5 (1)	Rh(2)–C(2)–O(2)	178.6 (9)
Cl(1)–Rh(1)–P(1)	173.1 (1)	Rh(1)–P(1)–C(11)	117.6 (5)
Cl(1)–Rh(1)–C(1)	94.7 (4)	Rh(1)–P(1)–C(12)	110.7 (4)
Cl(2)–Rh(1)–P(1)	90.9 (1)	Rh(1)–P(1)–C(13)	115.1 (3)
Cl(2)–Rh(1)–C(1)	176.9 (4)	Rh(2)–P(2)–C(21)	112.1 (4)
P(1)–Rh(1)–C(1)	90.1 (4)	Rh(2)–P(2)–C(22)	119.5 (3)
Cl(1)–Rh(2)–Cl(2)	84.2 (1)	Rh(2)–P(2)–C(23)	112.2 (2)
Cl(1)–Rh(2)–P(2)	173.8 (1)	C(11)–P(1)–C(12)	104.1 (7)
Cl(1)–Rh(2)–C(2)	95.3 (3)	C(11)–P(1)–C(13)	103.7 (5)
Cl(2)–Rh(2)–P(2)	89.7 (1)	C(12)–P(1)–C(13)	104.2 (6)
Cl(2)–Rh(2)–C(2)	175.9 (3)	C(21)–P(2)–C(22)	101.6 (5)
P(2)–Rh(2)–C(2)	90.9 (3)	C(21)–P(2)–C(23)	106.3 (4)
Rh(1)–C(1)–O(1)	177.6 (12)	C(22)–P(2)–C(23)	103.8 (4)

[a] Distances corrected for thermal motion taking light atoms riding on rhodium.

In the present molecule the Rh···Rh distance is 3.167 (1) Å. This value is similar to those found in most other structures of bent di-μ-chloro complexes of Rh(I) and may be considered as a weak metal–metal interaction. It is of interest to note that the structure of the present compound (as that of $Rh_2[P(OC_6H_5)_3]_2C_8H_{12}Cl_2$ described by Coetzer and Gafner[5]) is different from that of $Rh_2(CO)_4Cl_2$ studied by Dahl, *et al.*[3] Indeed for this last complex an octahedral hybridization for the Rh atoms has been postulated because an intermolecular Rh–Rh distance of 3.31 Å was found. In the present structure, the closest approach of two Rh atoms belonging to closest separated molecules is found equal to 5.3 Å. Thus it can be concluded that the observed bent structure for the present compound is due to an intramolecular metal–metal interaction.

The two Rh–Cl bond distances trans to the phosphorus atoms are 2.410 (3) and 2.427 (3) Å; the two Rh–Cl distances trans to the carbonyl groups are 2.408 (3) and 2.405 (3) Å. These Rh–Cl distances corrected for thermal motion are 2.420 (3) and 2.441 (3) Å for the chlorine atoms trans to the

Table V. Equation of the Best Planes around Rh(1) and Rh(2)[a]

Atoms defining the plane	Plane no.	Equation of the best plane	Rh(1)	Rh(2)	Cl(1)	Cl(2)	P(1)	P(2)	C(1)	C(2)
			Distances of atoms (Å) to the best plane							
Rh(1), Cl(1), Cl(2), P(1), C(1)	1	$-0.1818X - 0.1877Y - 0.9653Z + 1.9874 = 0$	−0.018	1.490	0.082	−0.069	0.089	2.608	−0.072	2.723
Rh(2), Cl(1), Cl(2), P(2), C(2)	2	$-0.0257X - 0.9250Y - 0.3791Z + 3.7760 = 0$	1.484	−0.022	−0.036	0.046	2.900	−0.041	2.482	0.056
Cl(1), Cl(2), P(1), C(1)	3	$-0.1816X - 0.1873Y - 0.9654Z + 1.9820 = 0$	−0.022	1.487	0.078	−0.073	0.085	2.605	−0.078	2.720
Cl(1), Cl(2), P(2), C2	4	$-0.0254X - 0.9251Y - 0.3788Z + 3.7708 = 0$	1.480	−0.028	−0.042	0.042	2.897	−0.047	2.478	0.049

[a] The dihedral angle between planes 1 and 2 is 123.0 (1)°; that between planes 3 and 4 is 122.9 (1)°.

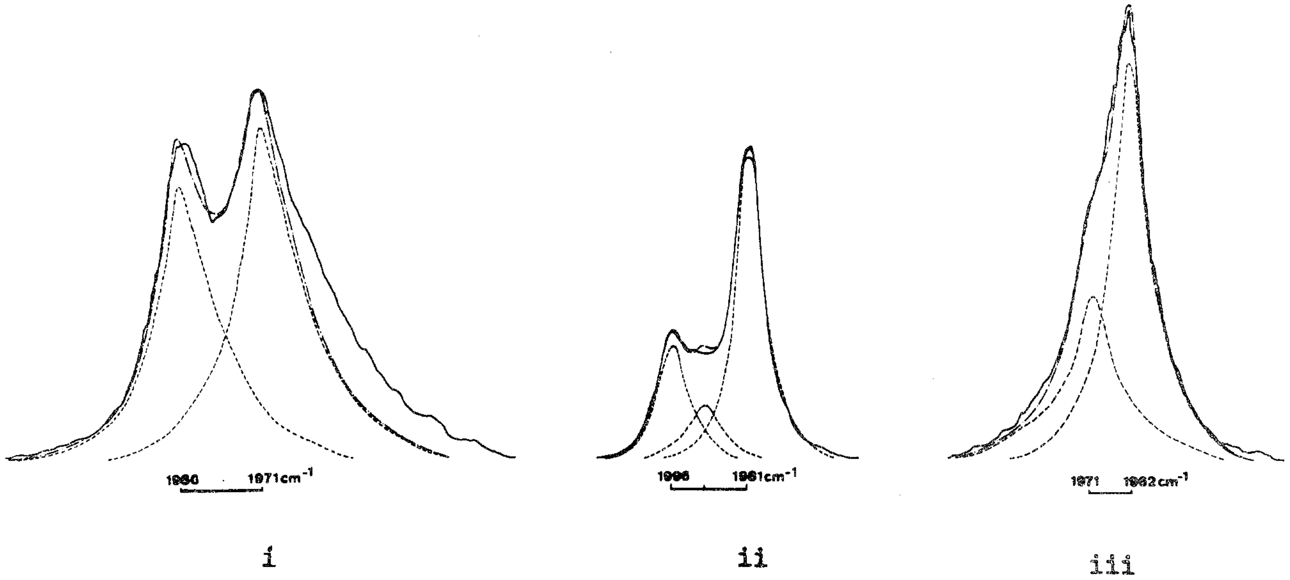

Figure 3. Infrared spectra of (i) $[RhCl(CO)PMe_2Ph]_2$ in solid state, (ii) $[RhCl(CO)PMe_2Ph]_2$ in cyclohexane solution, and (iii) $[RhCl(CO)P(NMe_2)_3]_2$ in solid state: - - - -, lorentzian components of infrared bands; – – –, envelope of the lorentzian curves; ——, experimental curve.

phosphorus atoms and 2.412 (2) and 2.413 (2) Å for those trans to the carbonyl groups taking chlorine atoms as light atoms riding on rhodium atoms. Two points of interest arise. First, the mean distance in the present compound is longer than those observed in square-planar mononuclear complexes of Rh(I) such as 2.373 and 2.375 Å in tris(triphenylphosphine)rhodium(I) chloride and bis(triphenylphosphine)(tetrafluoroethylene)rhodium(I) chloride,[12] respectively, and 2.381 (2) Å in $Rh[C_6H_5P(CH_2CH_2CH_2P(C_6H_5)_2)_2]Cl$.[13] Second, in di-μ-chloro-rhodium(I) complexes the Rh–Cl distance is still the same (2.38 Å) if the dihedral angle between the two square planes is equal to 180° as for $[RhCl(C_8H_{12})]_2$.[7] However as the dihedral angle decreases, the Rh–Cl bond distances increase; for example Rh–Cl = 2.410 (3) and 2.402 (2) Å in $[RhCl(C_6H_{10})_2]_2$ in which the dihedral angle is equal to 115.8°. This lengthening is related to the weak metal–metal interaction which does not occur in mononuclear complexes or even in the strictly planar $[RhCl(C_8H_{12})]_2$ complex. Let us add that in the present compound, although the value of the dihedral angle (123°) is higher in $[RhCl(C_6H_{10})_2]_2$, the Rh–Cl distances trans to the phosphine are still longer: 2.420 (3) and 2.441 (3) Å. This additional lengthening can be explained by the trans influence of the phosphine ligands which are strong σ donors and poor π acceptors while the carbonyl groups are good π acceptors. This trans influence has been already observed and discussed for platinum complexes.[14]

The P–C distances and C–P–C angles are well within the range that has been observed in a number of complexes of phosphines.

There is no report of analogous dinuclear complexes of Rh(I) with phosphines which would allow us to compare our Rh–P bond distances of 2.229 (2) and 2.220 (2) Å. However, our values are quite similar to those observed for mononuclear complexes of rhodium(I) with phosphines: 2.218 Å in tris(triphenylphosphine)rhodium(I) chloride,[12] for example. Moreover the present values are satisfactory compared with 2.230 Å for Pt–P found in a dinuclear complex of platinum(II) with tripropylphosphine.[15] Another interesting discussion can be made considering Rh–P distances of the phosphorus atom belonging to a phosphite group. For instance 2.146 (5) and 2.138 (5) Å have been found for $Rh_2(P(OC_6H_5)_3)_2C_8H_{12}Cl_2$.[5] These values are significantly shorter than ours. This result has been explained[16] considering a phosphite as a better π acceptor than a phosphine. This point is confirmed by the fact that no trans influence of a phosphite group is observed as in $Rh_2[P(OC_6H_5)_3]_2C_8H_{12}Cl_2$.

Discussion of the Infrared Spectra: Isomerization in Solution

Infrared spectra of selected crystals with the same morphology as that studied by X-ray analysis, in cesium bromide pellets exhibit two CO stretching bands at 1986 and 1971 cm^{-1} (Figure 3). The presence of only two ν_{CO} bands of almost identical intensities (respectively proportional to 7.9 and 10.0) is in agreement with the cis structure revealed by the X-ray determination. All attempts to find different crystals of the trans isomer or to detect some mixture of both isomers in the solid state failed. But cyclohexane solutions of the crystals revealed a system of three CO bands, as shown by shape analysis with a curve resolver (Figure 3) at 1996 cm^{-1} (24% of the total intensity), 1990 cm^{-1} (14%), and 1981 cm^{-1} (62%). Assuming, as previously,[2] the transferability of interaction force constants k_{cis} and k_{trans}, the splitting of 15 cm^{-1} between utmost bands appears to be in accord with the cis isomer. Assuming the same intensity ratio as for the solid state, we can evaluate a contribution of this isomer of 30% to the band at 1981 cm^{-1}. Due to the value of the small splitting (9 cm^{-1}) of the two frequencies 1990 and 1981 cm^{-1} [2] and to their relative intensities (4.7 and 10.0, respectively) it sounds quite reasonable to assign them to the trans isomer in which the angle between the two CO vibrators is 113° (*vide infra*). Thus starting from *cis*-$[RhCl(CO)PMe_2Ph]_2$ in the solid state, a mixture of cis and trans isomers occurs in cyclohexane solutions. Inversely, the cis isomer is the only one recovered from these solutions and the trans isomer disappeared upon isomerization.

Similarly, we have studied the complex $[RhCl(CO)PMe_3]_2$. All crystals studied correspond to the cis isomer; *i.e.*, two CO stretching bands at 1984 cm^{-1} (9.2) and 1969 cm^{-1} (10.0) are found. In cyclohexane solutions, we also observed a mixture of both isomers, with the following assignments: *cis*-$[RhCl(CO)PMe_3]_2$, 1995 cm^{-1} (14% of total intensity) and 1980 cm^{-1} (15%); the trans isomer, 1989 cm^{-1} (16%) and 1980 cm^{-1} (55%).

The complex $[RhCl(CO)P(NMe_2)_3]_2$ exhibits two CO bands at 1971 and 1962 cm^{-1} in the solid state. The occurrence of a small splitting of frequencies (9 cm^{-1}) and a rather small intensity ratio (5.6/10.0) prompt us to assign a trans geometry to this complex. In solution, a small proportion of cis isomer also is detected (1994 and 1978 cm^{-1}) in addition to the trans one (1988 and 1978 cm^{-1}).

From X-ray determinations, the angle between both CO vectors was calculated to be $\omega = 80.4°$. Using the usual approximation in which each CO oscillator is treated as a dipole vector,[16] the angle ω can be calculated from the intensities of the symmetric (I_{sym}) and antisymmetric bands (I_{asym}) with the formula $I_{sym}/I_{asym} = \cot^2(\omega/2)$. In the case of the compound *cis*-$[RhCl(CO)(PMe_2Ph]_2$ of C_s symmetry such a calculation gives $I_{sym}/I_{asym} = 58/42$ from $\omega = 80.4°$ whereas the experimental ratio of higher and lower frequency bands is $\sim 44/56$!

In the trans isomer of $[RhCl(CO)PMe_2Ph]_2$ the same ambiguity does not occur, the angle ω between CO vibrators being calculated as 113°, a value consistent with both CO groups in trans positions.

The discrepancy in the case of the cis isomer is under investigation.[17]

Registry No. *cis*-$[RhCl(CO)PMe_2Ph]_2$, 53187-76-1; *trans*-$[RhCl(CO)PMe_2Ph]_2$, 53187-77-2; *cis*-$[RhCl(CO)PMe_3]_2$, 53187-78-3; *trans*-$[RhCl(CO)PMe_3]_2$, 36713-90-3; *cis*-$[RhCl(CO)P(NMe_2)_3]_2$, 53187-79-4; *trans*-$[RhCl(CO)P(NMe_2)_3]_2$, 53187-80-7.

Supplementary Material Available. Table I, a listing of structure factor amplitudes, will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $4.00 for photocopy or $2.00 for microfiche, referring to code number AIC40493V.

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Hindered Ligand Systems. VIII. Syntheses of the Iron(III), Cobalt(III), and Nickel(II) Compounds of *cis,cis*-1,3,5-Tris(salicylaldimino)cyclohexane and the Crystal Molecular Structure of the Cobalt(III) Complex

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The Fe(III), Co(III), and Ni(II) complexes of *cis,cis*-1,3,5-tris(salicylaldimino)cyclohexane ($(sal)_3tach$) have been prepared and characterized. The diamagnetic Co(III) and high-spin Fe(III) compounds are mononuclear but the Ni(II) complex has been shown to be $Ni_3((sal)_3tach)_2$ with a magnetic moment of 3.2 BM/Ni atom. The crystal structure of $Co((sal)_3tach)$ was determined from three-dimensional X-ray data collected by counter methods. The compound crystallizes in the hexagonal space group $P\bar{3}$ with two molecules in the unit cell whose dimensions are $a = 11.80$ (2) and $c = 9.52$ (1) Å. Least-squares refinement of the structure led to a final residual, R, of 0.052 for the 616 unique reflections. The complex, which has crystallographic threefold symmetry, has a twist angle of 59°. The anomalously long Co–N bond distance of 1.942 (4) Å, the nonplanar nature of the chelate rings, and rotations about C=N bonds as well as those about the C—C bonds immediately adjacent are ascribed to the rigidity of the cyclohexane backbone and the overwhelming tendency of the Co atom to introduce large twist angles.

Although considerable study has been directed to metal complexes of the adduct of pyridine-2-carboxaldehyde with *cis,cis*-1,3,5-triaminocyclohexane ($(py)_3tach$),[1-5] the corresponding complexes of *cis,cis*-1,3,5-tris(salicylaldimino)cyclohexane ($(sal)_3tach$) have received little attention.[1,6] Unlike $(py)_3tach$, the larger chelate rings of $(sal)_3tach$ cannot accommodate trigonal-prismatic coordination to a metal atom without severe distortions to bond angles within the chelate rings. Thus, the twist angle[7] is expected to approach 60°. Optimal values of this angle cannot be determined from the