Contribution from the Department of Chemistry,
The University of Alberta, Edmonton, Alberta, Canada T6G 2E1

Crystal and Molecular Structure of Chloro(dioxygen)tris(triphenylphosphine)rhodium(I)

MICHAEL J. BENNETT and PETER B. DONALDSON*

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The compound chloro(dioxygen)tris(triphenylphosphine)rhodium(I), $RhCl(O_2)(P(C_6H_5)_3)_3 \cdot 2CH_2Cl_2$, has been identified as one of the species formed by the oxygenation of $RhCl(P(C_6H_5)_3)_3$. The crystal structure of this compound has been determined from three-dimensional x-ray data collected on a manual four-circle diffractometer at room temperature. The compound crystallizes in the orthorhombic space group *Pbca* with 8 molecules per unit cell ($\rho_{obsd} = 1.411$, $\rho_{calcd} = 1.416$ g cm^{-3}). The axial parameters are $a = 24.817$ (4), $b = 18.359$ (2), $c = 23.200$ (4) Å. Least-squares refinement of absorption- and decomposition-corrected intensity data converged at a conventional *R* factor of 0.049 based on 2073 significant reflections. The geometry about the rhodium atom may be described as a trigonal bipyramid with three phosphine ligands occupying one equatorial (Rh–P(2) = 2.357 (3) Å) and the two axial positions (Rh–P(1) = 2.365 (4), Rh–P(3) = 2.391 (4) Å). The remaining equatorial sites are occupied by the chlorine (Rh–Cl(1) = 2.401 (3) Å) and the dioxygen molecule. The dioxygen molecule is π bonded and a slight asymmetry in the rhodium–oxygen bond lengths (Rh–O(1) = 2.081 (8), Rh–O(2) = 2.005 (8) Å) is observed. One of the dichloromethanes of crystallization appears to be hydrogen bonded to the coordinated dioxygen.

Introduction

In a previous paper[1] we have described preliminary results on the nature of crystalline materials obtained from the reaction of molecular oxygen with chlorotris(triphenylphosphine)rhodium(I) in dichloromethane. Two products have been characterized using x-ray diffraction. In one of these compounds the rhodium atoms fulfilled the effective atomic number rule through a most unusual doubly bridged dioxygen structure $Cl(P(C_6H_5)_3)_2Rh(O_2)_2Rh(P(C_6H_5)_3)_2Cl$. While this compound is structurally interesting, its insolubility suggests that it is of doubtful significance in the oxidation of organic substrates by $RhCl(P(C_6H_5)_3)_3$.[2,3] The second crystalline compound which was isolated from this system and tentatively assigned the formulation $RhCl(O_2)(P(C_6H_5)_3)_3 \cdot xCH_2Cl_2$ (x = 2–3) has been properly characterized by x-ray diffraction as having $x = 2$. In this paper we report the details of synthesis and characterization of this compound.

Experimental Section

(a) Synthesis. We have been unable to prepare good crystalline samples of $RhCl(O_2)(P(C_6H_5)_3)_3 \cdot 2CH_2Cl_2$ without contamination by the dimeric bis(phosphine) complex. In the most economical synthesis oxygen was bubbled through a solution of 0.25 g of $RhCl(P(C_6H_5)_3)_3$ and 0.25 g of triphenylphosphine in 15 mL of dichloromethane (Fisher Scientific Co. analytical reagent grade) for 2 min at room temperature. After 2 days of slow evaporation at 7 °C the crystals were filtered and washed with cooled cyclohexane. Hand sorting was facilitated by the tendency of the tris(phosphine) complex crystals to form clusters of needles. This procedure was carried out to provide sufficient material for the various facets of the investigation but a complete separation was not obtained and hence we cannot give a reliable measure of the yield (mp 82–84 °C, dec pt 126–128 °C).

Microanalytical analyses were in reasonable agreement with the formulation. Anal. Calcd: C, 59.7; H, 4.4. Found: C, 59.3; H, 4.4. Chlorine analyses (calcd 15.7%, found 15.0–16.6%) on several samples proved difficult owing to rhodium interference. The infrared spectrum (Nujol mull) showed an absorption at 880 cm^{-1} assigned to the coordinated dioxygen. Similar studies on the products after heating to 200 °C in vacuo indicated the presence of triphenylphosphine oxide in the solid residue and oxygen was identified in the gaseous products by gas chromatography.

(b) X-Ray Crystallography. A single crystal was cut to the desired length of about 0.2 mm and mounted on a thin glass fiber so that the needle axis was approximately coincident with the goniometer head. In order to hinder possible loss of solvent of crystallization the crystal was dipped in a thin solution of polystyrene in dichloromethane. Examination of preliminary Weissenberg and precession photographs indicated that the crystal possessed orthorhombic symmetry. The systematic absences ($hk0$, $h = 2n + 1$; $h0l$, $l = 2n + 1$; $0kl$, $k = 2n + 1$) were consistent with the unique choice of the space group *Pbca*. The crystal was mounted on a Picker manual diffractometer so that the "b" axis (needle axis) was coincident with the diffractometer ϕ axis. Precise lattice parameters were determined as $a = 24.817$ (4), $b = 18.359$ (2), and $c = 23.200$ (4) Å from the setting angles of 12 accurately centered high-angle reflections at 22 °C. All peaks showed good resolution of the Kα_1, Kα_2 doublet and only the α_1 peaks (λ 1.540 51 Å) were used. The density of the complex was determined by the flotation method in aqueous potassium iodide as ρ_{obsd} 1.411 g cm^{-3} which is in excellent agreement with the calculated density of 1.416 g cm^{-3} assuming 8 formula units per unit cell.

A careful examination of peak profiles showed no obvious physical defects in the study crystal. Intensity data were collected with copper Kα radiation using the coupled ω–2θ method with a 2° takeoff angle. The diffractometer was equipped with a graphite crystal monochromator (002 reflecting plane). Each data point was scanned from $(2\theta - 1)°$ to $(2\theta + 1)°$ with a scan speed of 2° min^{-1}. Background counts were estimated from a linear interpolation of 30-s stationary counts taken at the limits of the scan. During the data collection, the intensities of six reflections were monitored at periodic intervals to allow for correction of crystal decomposition and to detect crystal misalignment. Data were only measured to 80° in 2θ as indicated by the preliminary photography. Data collection was terminated after 1755 reflections for this first crystal when the standard reflections had decreased in intensity by 10–20%. The crystal faces were identified as the forms {100}, {010}, and {001}, and the perpendicular distances between the opposite members of each form were measured as 0.010, 0.028, and 0.018 cm, respectively. The variation in intensity of the $0k0$ reflections with the setting angle ϕ was measured to provide experimental evidence for the correctness of subsequent absorption corrections. A second crystal of the same habit and with dimensions (0.008 × 0.009 × 0.032 cm) was used to collect the remaining 1970 reflections. The variation of I_{0k0} with ϕ was studied for this second crystal. All intense reflections with count rates in excess of 10^4 counts s^{-1} were remeasured under conditions such that the scattered x rays did not exceed the linear response range of the scintillation counter.

Finally, representative reflections from the first crystal were remeasured with the second crystal to improve the merging of the two data sets. Both crystals appeared to have similar rates of decomposition (directly proportional to $(\sin\theta)/\lambda$ and logarithmically related to time) and only decomposed when exposed to x rays. Of the total 3745 reflections measured, 2073 were found to be statistically reliable using the criterion $I \geq 3\sigma$. Decomposition and absorption corrections were then applied ($\mu = 62.1$ cm^{-1}) with the transmission factors varying from 0.517 to 0.637 in the first crystal and from 0.356 to 0.544 in the second. The data were then corrected for Lorentz and polarization effects and the derived structure amplitudes and their standard deviations calculated ($p = 0.03$[4]) after the two data sets had been scaled.

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* To whom correspondence should be addressed at the Research School of Chemistry, Australian National University, Canberra, ACT, Australia.

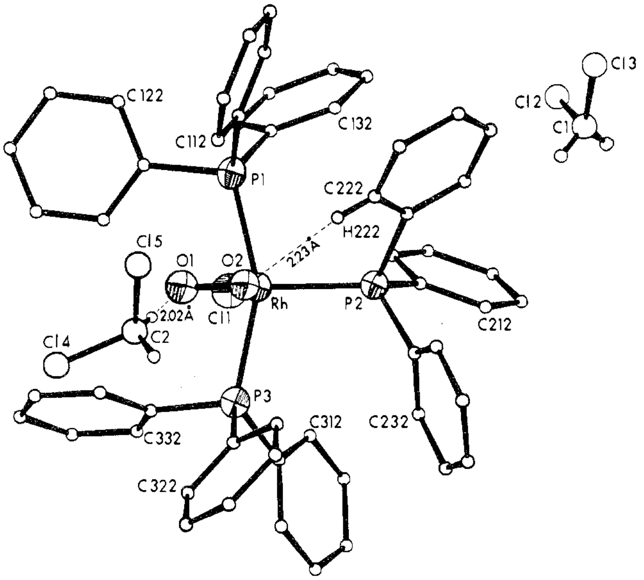

Figure 1. General view of $RhCl(O_2)(P(C_6H_5)_3)_3 \cdot 2CH_2Cl_2$.

Solution of Structure and Refinement

The structure was solved using normal heavy-atom techniques. The solution was not quite straightforward in that the "y" and "z" coordinates of the rhodium assumed semispecial values approximating to 0.25. Nevertheless the solution proceeded without serious difficulty. The final model, which was to a certain extent dictated by the number of observed intensities, utilized anisotropic thermal parameters for all heavy atoms (Rh, Cl, P) and for the carbon atoms of the two dichloromethane molecules where the thermal motion was extensive. The remaining light atoms were restrained to isotropic motion and the carbons of the phenyl rings were constrained further to conform to a rigid-body description with D_{6h} symmetry and a carbon–carbon length of 1.392 Å. Contributions of the hydrogen atoms to the scattering were calculated with isotropic thermal parameters 10% greater than those of the carbon atom to which they were attached and assuming a carbon–hydrogen bond length of 1.0 Å, a value representing a reasonable internuclear distance modified for the effects of the distortion of the electron density due to chemical bonding. All scattering factors except hydrogen were obtained from Cromer's coefficients[5] and the hydrogen scattering factors were those of Mason and Robertson.[6] Real and imaginary contributions of anomalous scattering for the atoms Rh, Cl, and P[7] were included.

Refinement was considered complete ($R_1 = 0.049$; $R_2 = 0.059$)

$$R_1 = \frac{\Sigma(||F_o| - |F_c||)}{\Sigma |F_o|}$$

$$R_2 = \left[\frac{\Sigma w(|F_o| - |F_c|)^2}{\Sigma w |F_o|^2}\right]^{1/2}$$

when the maximum parameter shift was one-seventh of the corresponding standard deviation. The standard deviation of an observation of unit weight was 1.79 at convergence which is reasonable in view of the constraints imposed upon the model. A final electron density difference map was calculated and the largest positive and negative peaks (0.38 and −0.36 e Å^{-3}; cf. carbon value of 3 e Å^{-3}) were located near the methylene chloride molecules. Major programs used in this study included SFLS5HR,[8] GONO9,[9] ORFFE II,[10] FORDAP,[11] and ORTEP.[12] Sundry local programs were also used.

Results

Table I gives the refined and derived positional coordinates of the atoms and their isotropic thermal parameters. Tables II and III give the anisotropic thermal parameters and the coordinates of the phenyl ring rigid bodies, respectively. Other tables give the interatomic distances (Table IV), intramolecular angles (Table V), and intra- and intermolecular nonbonded contacts (Tables VI and VII, respectively). A comparison of $|F_o|$ and $|F_c|$ (electrons × 10) is available (see paragraph at end of paper regarding supplementary material).

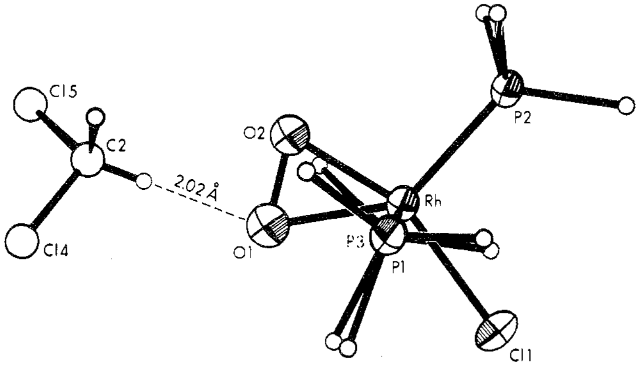

Figure 2. Equatorial plane geometry of $RhCl(O_2)(P(C_6H_5)_3)_3 \cdot 2CH_2Cl_2$.

Discussion

The complex has a trigonal-bipyramidal structure if dioxygen is treated as occupying a single coordination site. Alternatively if dioxygen is treated as a bidentate ligand, then the structure is approximately octahedral. A general view of the molecule including important interactions with a methylene chloride is shown in Figure 1. In the trigonal-bipyramidal description, the two axial sites are occupied by triphenylphosphine ligands while the equatorial sites (Figure 2) contain the third phosphine ligand, the chlorine atom Cl(1), and the dioxygen molecule (with both atoms in the equatorial plane). The molecule is then coordinatively saturated.

The rhodium–phosphorus bond lengths (Rh–P(1) = 2.365 (4), Rh–P(2) = 2.357 (3), Rh–P(3) = 2.391 (3) Å) show significant variation. However the apparent significance in the difference between the chemically equivalent axial rhodium–phosphorus distances ($\Delta/\sigma > 3$) suggests that subtle intramolecular (and perhaps less likely intermolecular) interactions are operative and hence a discussion of differences in axial and equatorial bond lengths would seem unwise. Similar observations have been made elsewhere.[14] The rhodium–chlorine bond length of 2.401 (3) Å is normal.[15,16] The phosphorus–carbon bond lengths average 1.829 Å in accord with general observations for triphenylphosphine complexes.[17-19] The distribution of these distances is consistent with a standard deviation of 0.01 Å which is only slightly larger than the average value of 0.009 Å as suggested by the least-squares refinement.

The dioxygen ligand is sideways bonded and is reasonably described within the framework as discussed by Hoffmann et al.[20] The oxygen–oxygen distance of 1.413 (9) Å is not significantly different from that observed in the dimer (1.44 (1) Å). Both of these distances compare favorably with recently reported oxygen–oxygen bond lengths.[21,22] The dioxygen ligand is attached assymmetrically as judged by the apparent significant difference in rhodium–oxygen bond lengths (Rh–O(1) = 2.081 (8), Rh–O(2) = 2.005 (8) Å). This may reflect differences in the trans ligand (O(1) is pseudotrans to P(2) and O(2) is pseudotrans to Cl(1)). In view of the observed differences in the axial rhodium–phosphorus bond lengths this apparent difference must be treated with some caution. However in the case of the rhodium–oxygen distances the magnitude of the difference is much larger. Also a similar trend has been observed in the structure of the compound $IrCl(O_2)(CO)(P(C_6H_5)_2(C_2H_5))_2$ where the longer metal–oxygen distance is once again pseudotrans to the better π-bonding ligand (in this case carbon monoxide).

It should be noticed that both oxygens are involved in secondary interactions. The most significant, of approximately 2.0 Å, involved O(1) with a hydrogen atom of one di-

Table I. Fractional Atomic Coordinates and Isotropic Thermal Parameters for $RhCl(O_2)(P(C_6H_5)_3) \cdot 2CH_2Cl_2$[a]

(I) Refined Positional Parameters

Atom	x	y	z	B	Atom	x	y	z	B	Atom	x	y	z	B
Rh	0.16618(4)	0.23480(5)	0.23730(4)	2.3*	Cl(2)	0.4111(3)	0.2504(5)	0.4869(4)	17.4*	C(2)	0.0846(9)	0.410(1)	0.1009(9)	11.2*
Cl(1)	0.1727(1)	0.1049(2)	0.2386(1)	3.4*	Cl(3)	0.3976(3)	0.0987(4)	0.4933(3)	14.9*	O(1)	0.1447(3)	0.2832(4)	0.1595(3)	3.4(3)
P(1)	0.0722(1)	0.2154(2)	0.2424(1)	2.8*	C(1)	0.3687(9)	0.179(1)	0.506(1)	12.9*	O(2)	0.1534(3)	0.3341(4)	0.2041(3)	2.9(3)
P(2)	0.1877(1)	0.2637(2)	0.3333(1)	2.4*	Cl(4)	0.1302(2)	0.4769(3)	0.0778(3)	13.1*					
P(3)	0.2531(2)	0.2252(2)	0.1938(1)	2.9*	Cl(5)	0.0451(4)	0.3844(4)	0.0444(3)	18.7*					

*These values are equivalent isotropic temperature factors corresponding to the anisotropic temperature factors given in Table 2.

(II) Calculated Positional Parameters[b]

C(111)[c]	0.0411	0.1660	0.3022	3.4(3)	C(235)	0.2176	0.1625	0.4872	5.7(4)	H(135)	-0.0858	0.3449	0.1734	7.7
C(112)	-0.0131	0.1760	0.3152	6.4(4)	C(236)	0.2003	0.2120	0.4457	3.9(4)	H(136)	-0.0303	0.2399	0.1880	7.0
C(113)	-0.0363	0.1386	0.3612	8.0(5)										
C(114)	-0.0052	0.0912	0.3941	6.1(4)	C(311)	0.2469	0.1793	0.1236	2.7(3)	H(212)	0.1682	0.4194	0.3557	4.0
C(115)	0.0491	0.0812	0.3811	5.6(4)	C(312)	0.1977	0.1526	0.1039	3.3(3)	H(213)	0.0956	0.4842	0.4000	4.9
C(116)	0.0723	0.1186	0.3352	4.1(4)	C(313)	0.1949	0.1171	0.0509	4.5(4)	H(214)	0.0215	0.4188	0.4409	4.9
					C(314)	0.2412	0.1084	0.0177	3.9(4)	H(215)	0.0200	0.2886	0.4374	5.0
C(121)	0.0546	0.1579	0.1814	2.4(3)	C(315)	0.2903	0.1352	0.0375	5.4(4)	H(216)	0.0927	0.2238	0.3931	4.3
C(122)	0.0437	0.0840	0.1880	3.8(4)	C(316)	0.2931	0.1707	0.0905	4.5(4)					
C(123)	0.0327	0.0413	0.1398	4.9(4)						H(222)	0.2172	0.3811	0.2607	2.9
C(124)	0.0326	0.0725	0.0851	4.9(4)	C(321)	0.3020	0.1683	0.2319	2.5(3)	H(223)	0.2830	0.4763	0.2630	3.5
C(125)	0.0436	0.1464	0.0786	5.3(4)	C(322)	0.3099	0.0958	0.2164	4.2(4)	H(224)	0.3485	0.4800	0.3385	3.7
C(126)	0.0546	0.1891	0.1267	4.5(4)	C(323)	0.3463	0.0529	0.2470	5.7(4)	H(225)	0.3483	0.3882	0.4118	3.7
					C(324)	0.3747	0.0825	0.2931	5.5(4)	H(226)	0.2826	0.2930	0.4095	3.0
C(131)	0.0302	0.2949	0.2324	3.4(3)	C(325)	0.3669	0.1550	0.3086	4.8(4)					
C(132)	0.0465	0.3625	0.2533	3.4(3)	C(326)	0.3304	0.1979	0.2780	3.9(4)	H(232)	0.2369	0.1208	0.3288	3.6
C(133)	0.0142	0.4235	0.2448	4.2(4)						H(233)	0.2667	0.0358	0.4000	6.0
C(134)	-0.0345	0.4169	0.2154	5.5(4)	C(331)	0.2902	0.3077	0.1720	3.1(3)	H(234)	0.2545	0.0622	0.5002	5.8
C(135)	-0.0508	0.3493	0.1945	7.0(5)	C(332)	0.3452	0.3168	0.1814	4.9(4)	H(235)	0.2125	0.1736	0.5290	6.3
C(136)	-0.0185	0.3882	0.2030	6.4(4)	C(333)	0.3703	0.3814	0.1653	6.1(4)	H(236)	0.1827	0.2587	0.4577	4.3
					C(334)	0.3405	0.4370	0.1399	5.0(4)					
C(211)	0.1364	0.3164	0.3707	2.4(3)	C(335)	0.2855	0.4279	0.1305	4.0(4)	H(312)	0.1644	0.1589	0.1276	3.6
C(212)	0.1371	0.3921	0.3727	3.6(4)	C(336)	0.2603	0.3632	0.1466	3.0(3)	H(313)	0.1597	0.0979	0.0367	4.9
C(213)	0.0948	0.4298	0.3985	4.5(4)						H(314)	0.2392	0.0829	-0.0202	4.3
C(214)	0.0518	0.3916	0.4224	4.5(4)	H(112)	-0.0353	0.2102	0.2915	7.0[d]	H(315)	0.3236	0.1289	0.0138	5.9
C(215)	0.0511	0.3158	0.4204	4.6(4)	H(113)	-0.0752	0.1460	0.3704	8.8	H(316)	0.3284	0.1899	0.1048	4.9
C(216)	0.0934	0.2782	0.3945	3.9(4)	H(114)	-0.0219	0.0644	0.4271	6.7					
					H(115)	0.0713	0.0471	0.4048	6.2	H(322)	0.2894	0.0745	0.1833	4.6
C(221)	0.2445	0.3293	0.3348	2.5(3)	H(116)	0.1112	0.1112	0.3259	4.5	H(323)	0.3520	0.0009	0.2359	6.3
C(222)	0.2447	0.3828	0.2922	2.6(3)						H(324)	0.4008	0.0518	0.3150	6.0
C(223)	0.2830	0.4381	0.2937	3.2(3)	H(122)	0.0437	0.0615	0.2272	4.2	H(325)	0.3872	0.1763	0.3417	5.3
C(224)	0.3211	0.4400	0.3377	3.4(3)	H(123)	0.0248	-0.0118	0.1444	5.4	H(326)	0.3247	0.2499	0.2891	4.3
C(225)	0.3209	0.3866	0.3803	3.4(3)	H(124)	0.0247	0.0419	0.0505	5.4					
C(226)	0.2825	0.3312	0.3788	2.7(3)	H(125)	0.0436	0.1689	0.0393	5.8	H(332)	0.3666	0.2769	0.1998	5.4
					H(126)	0.0625	0.2422	0.1221	4.9	H(333)	0.4098	0.3879	0.1721	6.7
C(231)	0.2074	0.1967	0.3875	2.2(3)						H(334)	0.3586	0.4834	0.1283	5.5
C(232)	0.2318	0.1319	0.3706	3.3(3)	H(132)	0.0815	0.3669	0.2743	3.7	H(335)	0.2641	0.4678	0.1121	4.4
C(233)	0.2492	0.0823	0.4121	5.5(4)	H(133)	0.0261	0.4719	0.2598	4.6	H(336)	0.2208	0.3568	0.1398	3.3
C(234)	0.2421	0.0976	0.4704	5.3(4)	H(134)	-0.0576	0.4609	0.2094	6.0					

(a) Estimated standard deviation (in parentheses) in this and the following tables in the text, refer to the last significant digit in each case.

(b) Phenyl ring carbon and hydrogen positional parameters derived from rigid body parameters in Table 3.

(c) The numbering of the phenyl ring carbon and hydrogen atoms proceeds as follows: for the atom C(*ijk*), *i* is the number of the phosphorus atom to which the ring is attached, *j* is the ring number in each triphenylphosphine ligand and *k* is the individual atom number.

(d) Hydrogen thermal parameters set at 10% greater than those of the corresponding carbon atoms.

chloromethane molecule where the hydrogen coordinates were estimated from the known heavy-atom coordinates and reasonable geometric parameters for dichloromethane.[23] This hydrogen is also relatively close to O(2) (2.2 Å) but the angular and distance arguments suggest that the major interaction is with O(1) and that a hydrogen bond[24,25] is indicated. The hydrogen bonding may be compared to that observed in potassium decacyano-μ-peroxo-dicobaltate dinitrate tetrahydrate[26] where water molecules are hydrogen bonded to the bridging peroxo group. Of similar importance is the contact with a phenyl hydrogen (O(2)–H(222) = 2.23 Å). In this particular case it is perhaps more dubious to deduce hydrogen bonding; however, similar intramolecular bonds have been observed.[27,28] It is interesting to note that the coordinated dioxygen in this complex exhibits a certain degree of basicity as indicated by the hydrogen-bond formation. Clearly the evidence is not as dramatic as that observed in the bridging structure of the dimer but nevertheless it appears to be a genuine feature in this series of compounds.

The identification and characterization of the two compounds $RhCl(O_2)(P(C_6H_5)_3)_3$ and $[RhCl(O_2)(P(C_6H_5)_3)_2]_2$ and their solubility properties give a certain insight into the nature of the solution species. Ignoring the steps involving the initial bonding of oxygen and triphenylphosphine oxide for-

Table II. Anisotropic Temperature Factors ($Å^2 \times 10^3$)[a]

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Rh	34.0 (9)	24.8 (9)	26.8 (9)	0.9 (7)	−2.6 (7)	3.0 (6)
Cl(1)	25 (2)	51 (3)	55 (2)	4 (2)	1 (2)	1 (2)
P(1)	41 (3)	30 (3)	35 (3)	2 (2)	−5 (2)	2 (2)
P(2)	36 (3)	25 (3)	30 (2)	−2 (2)	−2 (2)	5 (2)
P(3)	43 (3)	33 (3)	33 (2)	0 (3)	0 (2)	4 (2)
Cl(2)	144 (6)	186 (7)	330 (10)	36 (6)	6 (6)	4 (7)
Cl(3)	182 (7)	185 (8)	198 (7)	37 (6)	40 (5)	−43 (5)
C(1)	140 (20)	38 (15)	312 (30)	−7 (16)	100 (20)	−72 (17)
Cl(4)	142 (6)	115 (6)	242 (7)	20 (5)	33 (5)	14 (5)
Cl(5)	327 (11)	213 (8)	172 (6)	−54 (7)	−119 (7)	47 (6)
C(2)	165 (21)	123 (19)	140 (18)	−87 (17)	−66 (16)	87 (14)

[a] Anisotropic temperature factors are in the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

Table III. Refined Rigid-Body Parameters[a]

Phenyl ring	x	y	z	D	E	F
11	0.0180 (3)	0.1286 (3)	0.3482 (3)	2.290 (5)	0.372 (8)	0.85 (1)
12	0.0436 (2)	0.1152 (3)	0.1332 (3)	0.208 (5)	1.666 (5)	2.528 (6)
13	−0.0022 (3)	0.3559 (4)	0.2239 (2)	2.956 (5)	2.644 (5)	2.183 (7)
21	0.0941 (2)	0.3540 (3)	0.3965 (2)	0.035 (5)	0.499 (5)	2.622 (7)
22	0.2827 (2)	0.3846 (3)	0.3363 (2)	0.592 (5)	2.300 (6)	2.064 (7)
23	0.2247 (2)	0.1472 (3)	0.4289 (3)	2.677 (6)	1.545 (6)	2.322 (7)
31	0.2440 (3)	0.1439 (2)	0.0707 (2)	1.062 (5)	0.38 (1)	1.86 (1)
32	0.3383 (2)	0.1254 (3)	0.2625 (2)	2.861 (5)	2.276 (5)	2.512 (7)
33	0.3153 (2)	0.3723 (3)	0.1560 (2)	0.394 (5)	2.933 (5)	1.177 (7)

[a] The fractional coordinates x, y, and z describe the position of the center of the ring and the angles D, E, and F (in radians) describe rotations about an internal coordinate system.[13]

Table IV. Selected Interatomic Distances (Å)

Rh–Cl(1)	2.391 (3) [2.401 (3)[a]]	P(2)–C(221)	1.836 (9)
Rh–P(1)	2.362 (4) [2.365 (4)]	P(2)–C(231)	1.818 (9)
Rh–P(2)	2.357 (3) [2.357 (3)]	P(3)–C(311)	1.840 (10)
Rh–P(3)	2.387 (4) [2.391 (4)]	P(3)–C(321)	1.829 (9)
Rh–O(1)	2.081 (8)	P(3)–C(331)	1.842 (9)
Rh–O(2)	2.005 (8)	O(1)–O(2)	1.413 (9)
P(1)–C(111)	1.828 (10)	C(1)–Cl(2)	1.74 (2)
P(1)–C(121)	1.819 (9)	C(1)–Cl(3)	1.67 (2)
P(1)–C(131)	1.809 (9)	C(2)–Cl(4)	1.75 (2)
P(2)–C(211)	1.836 (8)	C(2)–Cl(5)	1.70 (2)

[a] A riding correction was performed on these bond lengths with the second atom assumed to ride on the first atom.

Table V. Selected Intramolecular Angles (deg)

Cl(1)--Rh--P(1)	85.1 (1)	Rh--P(3)--C(321)	115.9 (4)
Cl(1)--Rh--P(2)	101.3 (1)	Rh--P(3)--C(331)	120.4 (5)
Cl(1)--Rh--P(3)	82.5 (1)	P(1)--C(111)--C(114)	179.3 (9)
Cl(1)--Rh--O(2)	157.4 (2)	P(1)--C(121)--C(124)	177.0 (9)
Cl(1)--Rh--O(1)	117.0 (2)	P(1)--C(131)--C(134)	179.2 (8)
P(1)--Rh--P(2)	102.7 (1)	P(2)--C(211)--C(214)	176.0 (8)
P(1)--Rh--P(3)	154.4 (1)	P(2)--C(221)--C(224)	174.1 (7)
P(1)--Rh--O(2)	90.0 (2)	P(2)--C(231)--C(234)	176.6 (8)
P(1)--Rh--O(1)	81.7 (2)	P(3)--C(311)--C(314)	178.0 (9)
P(2)--Rh--P(3)	101.6 (1)	P(3)--C(321)--C(324)	178.2 (8)
P(2)--Rh--O(2)	101.3 (2)	P(3)--C(331)--C(334)	176.5 (9)
P(2)--Rh--O(1)	141.7 (2)	O(1)--O(2)--Rh	66.9 (4)
P(3)--Rh--O(2)	92.8 (2)	Rh--O(1)--C(2)	157 (1)
P(3)--Rh--O(1)	84.1 (2)	O(2)--O(1)--C(2)	84 (1)
O(1)--Rh--O(2)	40.4 (3)	O(1)--C(2)--Cl(4)	111 (1)
Rh--P(1)--C(111)	122.0 (5)	O(1)--C(2)--Cl(5)	114 (1)
Rh--P(1)--C(121)	106.6 (5)	O(2)--C(2)--Cl(4)	99 (1)
Rh--P(1)--C(131)	116.2 (5)	O(2)--C(2)--Cl(5)	133 (1)
Rh--P(2)--C(211)	113.4 (4)	Cl(2)--C(1)--Cl(3)	111 (1)
Rh--P(2)--C(221)	110.1 (4)	Cl(4)--C(2)--Cl(5)	109 (1)
Rh--P(2)--C(231)	124.2 (4)	C(222)--H(222)--O(2)	157.8
Rh--P(3)--C(331)	109.4 (5)		

Table VI. Selected Intramolecular Nonbonded Contacts (Å)

O(1)--C(2)	3.08 (2)	Rh--H(312)	2.90
O(2)--C(2)	3.26 (2)	Cl(1)--H(116)	2.54
O(2)--H(222)	2.23	H(332)--H(326)	2.37

Table VII. Selected Intermolecular Distances

Atom 1	Atom 2	Symmetry operation (on atom 2)	Dist, Å
Cl(1)	H(122)	$\frac{1}{2} - x, \frac{1}{2} + y - 1, z$	2.66
H(122)	H(134)	$\bar{x}, \frac{1}{2} + y - 1, \frac{1}{2} - z$	2.39
H(136)	H(325)	$\frac{1}{2} + x - 1, y, \frac{1}{2} - z$	2.45
H(213)	H(324)	$\frac{1}{2} - x, \frac{1}{2} + y, z$	2.33
H(225)	H(315)	$x, \frac{1}{2} - y, \frac{1}{2} + z$	2.46

mation, the potential equilibria may be represented by the reactions

$$RhCl(O_2)(P(C_6H_5)_3)_3 \rightleftarrows RhCl(O_2)(P(C_6H_5)_3)_2 + P(C_6H_5)_3 \qquad (1)$$

$$2RhCl(O_2)(P(C_6H_5)_3)_2 \rightleftarrows [RhCl(O_2)(P(C_6H_5)_3)_2]_2 \qquad (2)$$

$$[RhCl(O_2)(P(C_6H_5)_3)_2]_2 + 2CH_2Cl_2 \rightleftarrows [RhCl(O_2)(P(C_6H_5)_3)_2]_2 \cdot 2CH_2Cl_2 \qquad (3)$$

In a freshly prepared solution equilibrium 1 is probably achieved in a short period of time. Reaction 2 would be expected to be extremely slow owing to the special geometric requirements of the dimer formation. This would appear to be indicated by the insolubility of the dimer complex coupled with the large time interval required for crystal formation. The studies of the equilibrium constant for reaction 1 are being carried out elsewhere. A recent paper[30] states that the dimer in solution resembles the oxygenation product of $[RhCl(P(C_6H_5)_3)_2]_2$. Oxygenation is reversible in ethanol. However, the necessary presence of additional triphenylphosphine suggests that it may be the tris-phosphine complex that may be deoxygenated.

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Registry No. $RhCl(O_2)(P(C_6H_5)_3)_3 \cdot 2CH_2Cl_2$, 62521-14-6; $RhCl(P(C_6H_5)_3)_3$, 14694-95-2.

Supplementary Material Available: Listing of structure factor amplitudes (5 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry,
The University of Alberta, Edmonton, Alberta, Canada T6G 2E1

Crystal and Molecular Structure of Bis(chloro(dioxygen)bis(triphenylphosphine)rhodium(I))

MICHAEL J. BENNETT and PETER B. DONALDSON*

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The compound bis(chloro(dioxygen)bis(triphenylphosphine)rhodium(I)), $[RhCl(O_2)(P(C_6H_5)_3)_2{\cdot}CH_2Cl_2]_2$, has been formed by the oxygenation of $RhCl(P(C_6H_5)_3)_3$. The crystal structure has been determined from three-dimensional x-ray data at room temperature. The compound crystallized in space group $P\bar{1}$ with one molecule per unit cell ($\rho_{obsd} = 1.470$, $\rho_{calcd} = 1.469$ g cm^{-3}). The axial parameters are $a = 13.889$ (7), $b = 13.678$ (6), $c = 11.433$ (5) Å; $\alpha = 105.73$ (4), $\beta = 115.74$ (3), $\gamma = 100.97$ (4)°. Least-squares refinement of absorption- and decomposition-corrected intensity data converged at a conventional R factor of 0.044 based on 1658 significant reflections. The structure may be described as a dimer having two trigonal-bipyramidal subunits, the bridge being formed by one oxygen atom of each subunit having a third bond to the second subunit. The dioxygen molecules thus have features similar to those of both π-bonded ligands and chelating peroxo groups.

Introduction

Two crystalline materials have been isolated in the products formed in the reaction of molecular oxygen with solutions of chlorotris(triphenylphosphine)rhodium(I) in methylene chloride. In a previous paper[1] we have given complete details of the synthesis and structural characterization of the monomeric species $RhCl(O_2)(P(C_6H_5)_3)_3{\cdot}2CH_2Cl_2$. In this paper we present structural details for the dimeric species $[RhCl(O_2)(P(C_6H_5)_3)_2{\cdot}CH_2Cl_2]_2$ on which we have published a previous communication.[2]

Experimental Section

(a) Synthesis. On bubbling oxygen for 5 min through a solution containing 0.25 g of $RhCl(P(C_6H_5)_3)_3$ in 15 mL of methylene chloride and slowly evaporating the solution at 7 °C for 2 days, red-brown diamagnetic crystals were obtained (~50% yield). All measurements were made on this material which appeared to be homogeneous. Carbon and hydrogen analyses[3] are in reasonable agreement with the formulation $RhCl(O_2)(P(C_6H_5)_3)_2{\cdot}CH_2Cl_2$. The chlorine analysis proved difficult owing to rhodium interference in the method used. Anal. Calcd: C, 57.0; H, 4.1; Cl, 13.6. Found: C, 57.7; H, 4.2; Cl, ~15. The infrared spectrum (Nujol mull) shows an absorption at 845 cm^{-1} attributable to oxygen–oxygen stretching.[4] The complex is also formed by dissolution of $RhCl(O_2)(P(C_6H_5)_3)_3$ in methylene chloride. Yields vary with concentration (less than 1×10^{-2} M solutions give ~50% yield after standing at 7 °C for 2 days). Oxygen was positively identified in the gaseous thermal decomposition products by gas chromatography after heating the complex in vacuo to 200 °C. The residue showed an absorption at 1120 cm^{-1} consistent with the formation of complexed triphenylphosphine oxide.[5,6] The complex undergoes a series of transformations on heating: 80–85 °C, dissolution in solvent of crystallization; 110–120 °C, loss of solvent; 133–134 °C, explosive decomposition.

Black diamagnetic crystals of the iodo analogue may be prepared in the same manner from $RhI(P(C_6H_5)_3)_3$ in 62% yield (mp 166–168 °C). Microanalytical analyses were satisfactory for the formulation $RhI(O_2)(P(C_6H_5)_3)_2$. Anal. Calcd: C, 54.9; H, 3.8; I, 16.1. Found: C, 54.5; H, 4.0; I, 16.2. No evidence of chlorine was found in the analysis. However, it appears that some methylene chloride of crystallization (ν 740 cm^{-1}) is initially present but is removed under vacuum. The infrared spectrum was very similar to that observed for the chloro species. However, the dioxygen stretching band is shifted slightly at 857 cm^{-1}. In both complexes the oxygen is irreversibly bound.[1]

The chloro complex is extremely stable chemically, being inert to both strong acid and base and almost insoluble in all solvents tested.

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* To whom correspondence should be addressed at the Research School of Chemistry, Australian National University, Canberra, ACT, Australia 2600.