The Molecular Structure of $Rh_2Cl_2(\mu\text{-}CO)(\mu\text{-}(C_6H_5)_2PCH_2P(C_6H_5)_2)\cdot 2C_6H_6$: A Rhodium 'A-Frame' Complex

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In recent years considerable interest has focused on the notion of employing complexes containing two metal centers to activate small molecules [1]. Of the numerous bimetallic compounds studied to date, Pd [2–6], Pt [7–11], Rh [12–20] and Ir [21, 22] complexes using bis-(diphenylphosphino)methane, dppm, or related phosphine ligands [23, 24] as a bridging moiety have drawn considerable attention. One of the reasons for this is that dppm can bring together two metal atoms in close proximity allowing binuclear reactions involving formation and/or cleavage of metal–metal bonds. Furthermore, the geometry of such complexes facilitates the simultaneous interaction of the two metal centers with a substrate molecule, giving rise to what is termed an 'A–frame' geometry. One such compound is the rhodium complex $Rh_2Cl_2(\mu\text{-}CO)(\mu\text{-}dppm)_2$ [18]. This coordinatively unsaturated species is known to react with a number of small molecules such as CO [18], acetylenes [12], heteroallenes [17] and SO_2 [20]. The results of a crystallographic study of this rhodium 'A-frame' are the subject of this report.

Experimental Section

X-Ray Data Collection and Reduction

Red crystals of the title compound were obtained by slow cooling of a benzene solution. Diffraction experiments were performed on a four-circle Syntex $P2_1$ diffractometer with graphite-monochromatized Mo Kα radiation. The initial orientation matrix was obtained from 15 machine-centered reflections selected from a rotation photograph. These data were used to determine the crystal system. Partial rotation photographs around each axis were consistent with an orthorhombic crystal system. Ultimately, 25 high-angle reflections ($14 < 2\theta < 25°$) were used to obtain the final lattice parameters and the orientation matrix. Machine parameters, crystal data, and data collection parameters are summarized in Table I. The observed extinctions were consistent with the space group *Pbca*. $+h$, $+k$, $+l$ data were collected in one shell ($4.5 < 2\theta < 45.0°$). Three standard reflections were recorded every 97 reflections; their intensities showed no statistically significant change over the duration of data collection. The data were processed by using the SHELX-76 program package on the computing facilities at the University of Windsor. A total of 1887 reflections with $F_o^2 > 3\sigma(F_o^2)$ were used in the refinement.

Structure Solution and Refinement

Non-hydrogen atomic scattering factors were taken from the tabulation of Cromer and Waber [25, 26]. The Rh atom positions were determined by the heavy atom (Patterson) method. The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. Refinement was carried out using full-matrix least squares techniques on F, minimizing the function $\Sigma w(|F_o| - |F_c|)^2$ where the weight w is defined as $4F_o^2/\sigma^2(F_o^2)$ and F_o and F_c are the observed and calculated structure factor amplitudes. In the final cycles of least-squares refinement, all Rh, P, O and Cl atoms were assigned anisotropic temperature factors, all C atoms were assigned isotropic temperature factors and all phenyl ring geometries were constrained to regular hexagons with a C–C bond length of 1.39 Å. The hydrogen atom contributions were included, C–H bond lengths of 0.95 Å were assumed, and hydrogen atom temperature factors were fixed at 1.10 times the isotropic temperature factor of the bonded carbon atom. This gave $R_1 = \Sigma|F_o| - |F_c|/\Sigma|F_o| = 0.0751$ and $R_w = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2)^{1/2} = 0.0746$. The maximum Δ/σ on any of the parameters in the final cycles was 0.001. A final difference Fourier map calculation showed no peaks of chemical significance; the largest peak was 0.6 electrons and was associated with one of the rhodium atoms. The following data are tabulated: positional parameters (Table II); interatomic distances and angles (Table III).

Temperature factors (Table S-I), hydrogen atom parameters (Table S-II) angles and values of $10|F_o|$ and $10|F_c|$ (Table S-IV) have been deposited as supplementary material.

Results and Discussion

An ORTEP drawing of the molecule showing the numbering scheme is shown in Fig. 1. Selected interatomic distances and angles are listed in Table III. The unit cell contains eight discrete molecules of

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TABLE I. Summary of Crystal Data, Intensity Collection and Structure Solution.

formula	$Rh_2Cl_2P_4OC_{63}H_{56}$
crystal color, form	wine-red, blocks
a (Å)	15.483 (3)
b (Å)	31.112 (7)
c (Å)	23.723 (6)
crystal system	orthorhombic
space group	*Pbca*
V (Å^3)	11429 (5)
d calcd (g cm^{-3})	1.43
Z	8
crystal dimens (mm)	0.12 × 0.31 × 0.19
crystal faces	(100) (−101) (010) (0 − 10) (001) (00 − 1)
abs. coeff (μ), (cm^{-1})	7.79
radiation (λ, Å)	Mo Kα (0.71069) (graphite monochromator)
temp (°C)	24
scan speed (deg/min)	2.05–5.0° ($\theta/2\theta$ scan)
scan range (deg)	2.0° below K_{α_1}, 1.0° above K_{α_2}
bkgd/scan time ratio	0.5
data collecd	20 of 4.5–45.0° (+*h*, +*k*, +*l*)
total No. of data collecd	8206
No. of unique data ($F_o^2 > 3\sigma F_o^2$)	1887
No. of variables	216
R (%)	7.57
R_w (%)	7.46

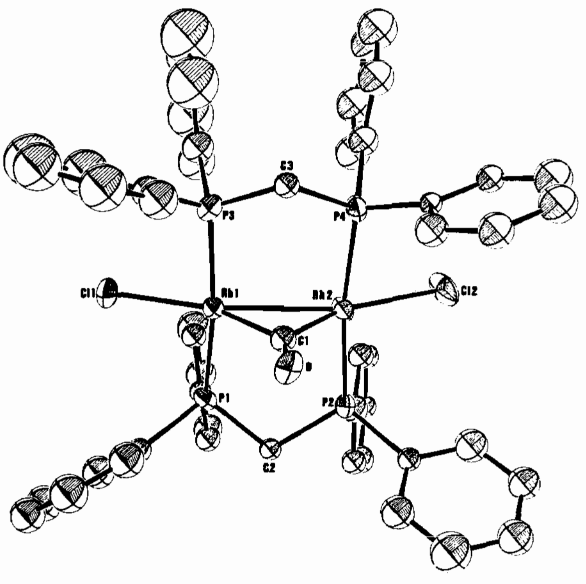

Fig. 1. ORTEP drawing of the molecule (1), 30% thermal ellipsoids are shown, hydrogen atoms are omitted for clarity.

$Rh_2Cl_2(\mu\text{-}CO)(\mu\text{-}dppm)_2$ and sixteen molecules of benzene. There are no unusual contacts between the complex molecules and the solvent molecules in the cell. The closest non-bonded contact between complex molecules is 2.863 Å (H22. . .Cl2).

The geometry about each Rh atom of the complex molecule is approximately trigonal bipyramidal. Both coordination spheres consist of trans dppm phosphorus atoms, and a 'trigonal' plane made up of a terminal chloride, a bridging carbonyl moiety and a formal Rh–Rh bond. The perturbation from trigonal bipyramidal geometry is clearly shown by the Cl1–Rh1–Rh2, Cl1–Rh1–C1 and C1–Rh1–Rh2 angles of 162.3(3), 154(1) and 44.1(9)° and the Cl2–Rh2–Rh1, Cl2–Rh2–C1, and C1–Rh2–Rh1 angles of 160.6(3), 155(1) and 44(1)° respectively. The overall geometry of the complex molecule is that of a distorted 'A-frame' structure. It resembles closely the previously characterized complexes, $Rh_2Br_2(\mu\text{-}CO)(\mu\text{-}dppm)_2$ [19] and $Rh_2Cl_2(\mu\text{-}SO_2)(\mu\text{-}dppm)_2$ [20] in which the 'A-frame' configuration is flattened due to the presence of the Rh–Rh bond.

The Rh–Cl bond distances of 2.348(8) Å are well within the range of normal terminal Rh–Cl distance of 2.34–2.39 Å found for this class of compounds [17, 18, 20, 23]. The geometry of the Rh–dppm framework is similar to that observed in other dppm-bridged complex of rhodium [12–20] and most parameters are as expected. The average Rh–P distances of 2.306(9) Å and the average P–C bond lengths of 1.82(3) Å are typical [12–20]. The methylene linkages of the dppm ligands are oriented towards the side of the molecule containing the bridging CO fragment. This is commonly found in these systems as it minimizes unfavourable intramolecular contacts involving the bulky phenyl rings [12–20]. The Rh–F–C(phenyl) angles are of two types. At each P atom there is both an angle close to the expected tetrahedral value and one that is significantly larger. For example, at P4 the Rh–P–C(phenyl) angles are 112.2(7) and 120.1(8)°. In the compound $Rh_2Br_2(\mu\text{-}CO)(\mu\text{-}dppm)_2$ similar yet larger distortions of the Rh–P–C(phenyl) angles were observed [19]. Angles of 121.8(2) and 123.1(2)° were seen for the two phenyl rings that exhibited Br–H contacts (3.15 and 2.75 Å) which are less than the sum of the van der Waals radii. It was concluded that these steric interactions between the bromo ligands and the phenyl rings were cause of the observed distortion of the angles at phosphorus. In the structure of $Rh_2Cl_2(\mu\text{-}SO_2)(\mu\text{-}dppm)_2$ which contains the less bulky chloro ligand the distortions at phosphorus were less marked. The maximum Rh–P–C(phenyl) angle observed in that case was 118.9(2)°. Although it is tempting to adopt a similar rationale for the observed distortions in the present structure, it is not clear why the closest phenyl hydrogen–chloro contact of 2.76 Å is associated with the Rh–P–C(phenyl) angle of 114.9(8)° and yet for the larger Rh–P–C(phenyl) angles no close contacts are observed. It is possible that crystal packing forces effect the orientation of

TABLE II. Positional Parameters[a].

Atom	*x*	*y*	*z*
Rh1	1149(1)	1200(1)	495(1)
Rh2	−127(1)	984(1)	1233(1)
Cl1	2132(5)	1600(3)	−47(4)
Cl2	−1291(5)	1049(3)	1862(4)
P1	2161(5)	1239(3)	1202(4)
P2	791(5)	917(3)	1997(3)
P3	229(6)	1223(3)	−270(4)
P4	−1183(5)	995(3)	550(4)
O	784(13)	297(7)	686(8)
C1	654(18)	680(11)	763(12)
C2	1949(16)	870(9)	1762(11)
C3	−758(18)	896(10)	−179(12)
C11	3243(15)	1041(6)	977(8)
C12	3987(15)	1284(6)	1070(8)
C13	4767(15)	1162(6)	822(8)
C14	4802(15)	797(6)	482(8)
C15	4059(15)	554(6)	389(8)
C16	3279(15)	676(6)	637(8)
C21	2299(11)	1745(6)	1553(9)
C22	2759(11)	1780(6)	2057(9)
C23	2809(11)	2174(6)	2334(9)
C24	2399(11)	2534(6)	2108(9)
C25	1939(11)	2500(6)	1604(9)
C26	1889(11)	2105(6)	1327(9)
C31	593(11)	454(8)	2437(8)
C32	1117(11)	90(8)	2405(8)
C33	906(11)	−277(8)	2713(8)
C34	172(11)	−281(8)	3053(8)
C35	−352(11)	83(8)	3085(8)
C36	−142(11)	451(8)	2777(8)
C41	822(11)	1342(5)	2501(9)
C42	1374(11)	1322(5)	2965(9)
C43	1394(11)	1658(5)	3353(9)
C44	862(11)	2016(5)	3277(9)
C45	310(11)	2036(5)	2813(9)
C46	290(11)	1699(5)	2425(9)
C51	−145(15)	1756(11)	−427(10)
C52	63(15)	2104(11)	−81(10)
C53	−286(15)	2508(11)	−192(10)
C54	−842(15)	2565(11)	−649(10)
C55	−1050(15)	2218(11)	−994(10)
C56	−701(15)	1813(11)	−883(10)
C61	618(14)	1022(9)	−934(12)
C62	502(14)	601(9)	−1120(12)
C63	838(14)	473(9)	−1639(12)
C64	1290(14)	766(9)	−1972(12)
C65	1406(14)	1188(9)	−1786(12)
C66	1070(14)	1316(9)	−1267(12)
C71	−1851(12)	1467(9)	460(8)
C72	−1639(12)	1830(9)	777(8)
C73	−2107(12)	2209(9)	708(8)
C74	−2787(12)	2226(9)	322(8)
C75	−2999(12)	1863(9)	6(8)
C76	−2531(12)	1483(9)	75(8)
C81	−1946(10)	558(7)	630(7)
C82	−1727(10)	145(7)	453(7)
C83	−2284(10)	−198(7)	560(7)
C84	−3061(10)	−127(7)	843(7)
C85	−3280(10)	286(7)	1020(7)
C86	−2723(10)	629(7)	913(7)
C91	2815(16)	4158(12)	1525(13)
C92	2227(16)	3827(12)	1628(13)
C93	1439(16)	3820(12)	1343(13)
C94	1239(16)	4142(12)	956(13)
C95	1828(16)	4472(12)	853(13)
C96	2616(16)	4480(12)	1138(13)
C101	4303(31)	3359(18)	2815(13)
C102	3784(31)	3626(18)	3144(13)
C103	3712(31)	3553(18)	3723(13)
C104	4158(31)	3212(18)	3971(13)
C105	4677(31)	2946(18)	3641(13)
C106	4750(31)	3019(18)	3063(13)

[a] Parameters given × 10^4.

TABLE III. Selected Bond Distances and Angles[a].

Rh1–Cl1	2.348(8)	Rh2–Cl2	2.348(8)
Rh1–P1	2.300(8)	Rh2–P2	2.311(8)
Rh1–P3	2.308(9)	Rh2–P4	2.304(9)
Rh1–C1	1.90(3)	Rh2–C1	1.90(3)
Rh1–Rh2	2.726(3)		
P1–C2	1.79(3)	P2–C2	1.88(3)
P1–C11	1.86(2)	P2–C31	1.81(2)
P1–C21	1.80(2)	P2–C41	1.79(2)
P3–C3	1.85(3)	P4–C3	1.88(3)
P3–C51	1.79(3)	P4–C71	1.81(3)
P3–C61	1.80(3)	P4–C81	1.81(2)
C1–O	1.22(3)		
P1–Rh1–Rh2	92.1(2)	P2–Rh2–Rh1	94.6(2)
P1–Rh1–Cl1	86.0(3)	P2–Rh2–Cl2	89.0(3)
P1–Rh1–P3	173.2(4)	P2–Rh2–P4	171.7(3)
P1–Rh1–C1	94.3(9)	P2–Rh2–C1	91.4(9)
P3–Rh1–Rh2	93.8(2)	P4–Rh2–Rh1	93.3(2)
P3–Rh1–Cl1	87.3(3)	P4–Rh2–Cl2	84.3(3)
P3–Rh1–C1	92.3(9)	P4–Rh2–C1	92.6(9)
Cl1–Rh1–Rh2	162.3(3)	Cl2–Rh2–Rh1	160.6(3)
Cl1–Rh1–C1	154(1)	Cl2–Rh2–C1	155(1)
C1–Rh1–Rh2	44.1(9)	C1–Rh2–Rh1	44(1)
Rh1–P1–C2	112.6(9)	Rh2–P2–C2	111.2(9)
Rh1–P1–C11	112.7(7)	Rh2–P2–C31	114.9(8)
Rh1–P1–C21	117.7(7)	Rh2–P2–C41	118.4(7)
C2–P1–C11	100(1)	C2–P2–C31	106(1)
C2–P1–C21	104(1)	C2–P2–C41	103(1)
C11–P1–C21	108.4(9)	C31–P2–C41	102.1(9)
Rh1–P3–C3	114(1)	Rh2–P4–C3	113.4(9)
Rh1–P3–C51	113.0(9)	Rh2–P4–C71	120.1(8)
Rh1–P3–C61	118.1(8)	Rh2–P4–C81	112.2(7)
C3–P3–C51	105(1)	C3–P4–C71	103(1)
C3–P3–C61	101(1)	C3–P4–C81	102(1)
C51–P3–C61	104(1)	C71–P4–C81	104.4(9)
Rh1–C1–Rh2	92(1)		
Rh1–C1–O	136(2)	Rh2–C1–O	133(2)
P1–C2–P2	110(1)	P3–C3–P4	108(1)

[a] Bond lengths in Å, angles in degrees.

the phenyl rings and are thus at least partly responsible for the observed distortions. In this regard we note that pairs of phenyl rings on each of the dppm moieties are positioned so as to be approximately parallel. This type of packing arrangement has been observed in other systems where distortions of the metal–P–C(phenyl) angles occur [27].

The Rh–Rh distance of 2.726(3) Å and the Rh–C–Rh angle of 92(2) are similar to those observed for $Rh_2Br_2(\mu\text{-}CO)(\mu\text{-}dppm)_2$ [19] and $Rh_2Cl_2(\mu\text{-}SO_2)(\mu\text{-}dppm)_2$ [20] and well within the range of values observed for other complexes known to contain a Rh–Rh single bond.

The carbonyl ligand symmetrically bridges the Rh–Rh bond as is shown by the identical Rh–C bond lengths of 1.90(3) Å. These distances are considerably shorter than those observed in other rhodium systems containing bridging carbonyls [13]. In fact, these distances are slightly shorter than the values of 1.958(8) and 1.961(8) Å seen for $Rh_2Br_2(\mu\text{-}CO)(\mu\text{-}dppm)_2$ [19] presumably reflecting the greater trans influence of bromide versus chloride. The Cl–O bond distance is 1.22(3) Å. The observed carbonyl stretching frequency in the infrared spectrum is 1745 cm^{-1} which is considerably lower than typical bridging carbonyls [18]. These parameters are consistent with a decreased bond order of the carbonyl moiety. This is in contrast to that observed for $Rh_2Br_2(\mu\text{-}CO)(\mu\text{-}dppm)_2$ where although the CO stretching frequency is also 1745 cm^{-1} the C–O bond length of 1.167(9) Å (1.192(9) Å corrected) does not reflect a decreased bond order [19].

The crystallographic study described above provides detailed structural data about a coordinatively unsaturated binuclear rhodium species containing CO. Further studies designed to examine the chemistry of other unsaturated species with small molecule substrates are underway [28]. Such studies will undoubtedly yield chemistry which is both interesting and relevent to the understanding of catalytic processes.

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Supplementary Material Available

Tables S-I–S-III list temperature factors, hydrogen atom parameters, and observed and calculated structure factors (14 pages). Ordering information is given on any current masthead page.

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