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A Rhodium A-Frame Complex: Crystal Structure of $[Rh_2(dppm)_2(\mu\text{-}OH)(CO)_2][PF_6]\cdot(CH_3)_2CO$

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Abstract

The crystal structure of $[Rh_2(dppm)_2(\mu\text{-}OH)(CO)_2][PF_6]\cdot(CH_3)_2CO$ has been determined. The crystal and structure data are, $M_r = 1250.7$, monoclinic, $P2_1/n$, $a = 10.165(3)$, $b = 21.084(4)$, $c = 25.85(1)$ Å, $\beta = 95.69(3)°$, $V = 5513(3)$ Å^3, $Z = 4$, D_m (295 K) = 1.48, $D_x = 1.51$ g cm^{-3}, Mo Kα, $\lambda = 0.71069$ Å, $\mu = 5.03$ cm^{-1}, $F(000) = 2348$, $R = 0.0433$, $R_w = 0.0462$, 6257 observed reflections $I > 3\sigma(I)$. This molecule was found to be hydrogen-bonded to an acetone molecule in the lattice and has a Rh···Rh separation of 3.139(1) Å, and a Rh(1)–O(3)–Rh(2) angle of 99.1(1)°. No other unusual structural features were observed.

Introduction

There has been considerable interest in recent years in complexes containing bridging ligands that can accommodate the A-frame structure [1]. Most of the attention these complexes are receiving results from the fact that many of these bimetallic compounds activate small molecules [2]. Many of the dirhodium complexes of interest contain two *trans* bis(diphenylphosphino)methane ligands, or related phosphine and arsine ligands. A number of issues associated with these and related compounds are being addressed by current researchers. Among these are the relationship between the bite size of the two *trans* bridging ligands and the metal–metal separation [3, 4], the effects of ligand modifications on electronic and electrochemical properties [5–7] and the effect of changing the apex bridging on the properties of the complex [8]. The title complex could provide additional insight into these phenomena. Its crystal structure is the subject of this paper.

Experimental

The compound $[Rh_2(dppm)_2(\mu\text{-}amp)(CO)_2]PF_6$ (1) (amp = 2-amidopyridine) was prepared by the reaction of $[Rh_2(dppm)_2(\mu\text{-}Cl)(CO)_2]PF_6$ with an alcoholic KOH solution of 2-aminopyridine. Complex **1** was obtained from this solution by evaporation to dryness, followed by extraction with dichloromethane, filtration, and precipitation with an ether/ligroine mixture. The title compound was obtained by the hydrolysis of **1** in acetone. Plate-like yellow crystals of the title compound suitable for X-ray analysis were obtained by recrystallization from acetone. Diffraction experiments were performed on a Nicolet R3m diffractometer with graphite-monochromatized Mo Kα radiation. Accurate unit-cell parameters were obtained from a least-squares refinement of 14 reflections (θ range 11–15°) [9]. The observed extinctions were consistent with the space group $P2_1/n$ a nonstandard setting of $P2_1/c$. Data was taken as $\theta/2\theta$ scans in the range of hkl: $-11 \leqslant h \leqslant 11, 0 \leqslant k \leqslant 23, 0 \leqslant l \leqslant 28$. One standard reflection (121) measured every 40 reflections showed no more than 4% variation over the duration of data collection. A total of 7864 data were measured ($5 \leqslant 2\theta \leqslant 45°$) with 6257 observed reflections $I \geqslant 3\sigma(I)$, corrections were made for Lorentz and polarization effects, decay corrections were ignored. An empirical absorption correction was applied with max. and min. transmission coefficients of 0.582 and 0.543, respectively.

Structure Solution and Refinement

A trial structure was obtained from direct methods. Remaining atoms were found by subsequent difference Fourier maps and refined routinely by block-diagonal least-squares procedures, $\Sigma w(|F_o||F_c|)^2$ minimized, $w = 1/[\sigma^2(F) + G(F)^2]$ and $G = 0.0004$; nonhydrogen atoms anisotropic, H atoms idealized coordinates were calculated, but not refined. Hydrogen thermal parameters were assigned

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as 0.070 Å^2; R = 0.0433, R_w = 0.0462 based on 648 least-squares parameters, scattering factors for Rh, P, F, O, C, and H were obtained from the International Tables for X-ray Crystallography [10], S = 1.625. Anomalous-dispersion corrections for Rh were applied toward the end of the refinement [11]. In the final cycle, the largest shift observed in any parameter was -0.778σ. The final difference map showed no peaks larger than 0.81 e$^-$/Å^3 at 0.67 Å from H(53c). Calculations were carried out with Nicolet XTL and SHELXTL 5.1 structure solving package on a Nicolet R3m/μ crystallographic system [12].

Results and Discussion

The atomic fractional coordinates with their standard deviations and U_{eq} values are given in Table I [13]. The structure and numbering scheme are shown in Fig. 1. Table II contains a listing of selected interatomic bond distances and angles with their standard deviations. The hydrogen bonding interaction between the hydroxy group and the acetone molecule in the lattice is shown in Fig. 2.

As expected, the $[Rh_2(\mu\text{-dppm})_2(CO)_2(\mu\text{-OH})]^+$ cation displays the A-frame structure in which the two rhodium atoms are bridged by two dppm ligands that are in a *trans* disposition. A plane that is perpendicular to the Rh–P vectors contains the hydroxy group that bridges the two metals and the carbonyl ligands that are *trans* to the hydroxy group. Therefore, the geometry about each Rh atom is approximately square planar consisting of the two *trans* phosphorus atoms from the dppm ligands, the

TABLE I. Atomic Coordinates (× 10^4) and Isotropic Thermal Parameters (Å^2 × 10^3)

	x	y	z	U[a]
Rh(1)	−2122(1)	2611(1)	1337(1)	47(1)
Rh(2)	−1008(1)	1488(1)	712(1)	42(1)
P(1)	−791(1)	2320(1)	2082(1)	44(1)
P(2)	−3241(1)	2974(1)	565(1)	45(1)
P(3)	169(1)	1148(1)	1480(1)	41(1)
P(4)	−2047(1)	1900(1)	−57(1)	42(1)
P(5)	2217(2)	5951(1)	1503(1)	77(1)
F(1)	2909(4)	6464(2)	1169(2)	115(2)
F(2)	905(5)	6139(3)	1225(3)	186(3)
F(3)	2424(9)	5445(2)	1111(3)	226(4)
F(4)	2089(9)	6461(3)	1907(2)	215(4)
F(5)	1561(6)	5457(2)	1843(2)	147(3)
F(6)	3563(6)	5807(4)	1798(3)	248(4)
C(1)	−3461(6)	2823(3)	1719(2)	74(2)
O(1)	−4283(4)	2972(3)	1961(2)	110(2)
C(2)	−1393(5)	679(3)	516(2)	57(2)
O(2)	−1628(4)	165(2)	381(2)	85(2)
C(3)	576(5)	1786(2)	1953(2)	46(2)
C(4)	−2393(5)	2749(2)	−4(2)	45(2)
C(5)	137(5)	2998(2)	2379(2)	49(2)
C(6)	−338(6)	3602(2)	2253(2)	61(2)
C(7)	374(7)	4134(3)	2441(3)	79(3)
C(8)	1528(7)	4058(3)	2755(3)	84(3)
C(9)	2004(6)	3468(3)	2873(2)	77(2)
C(10)	1322(5)	2928(3)	2690(2)	63(2)
C(11)	−1570(5)	1921(2)	2601(2)	48(2)
C(12)	−943(6)	1865(3)	3097(2)	76(2)
C(13)	−1535(7)	1536(4)	3473(2)	96(3)
C(14)	−2754(7)	1265(3)	3363(3)	86(3)
C(15)	−3380(6)	1313(3)	2872(3)	81(3)
C(16)	−2791(5)	1639(3)	2494(2)	64(2)
C(17)	−3288(5)	3841(2)	527(2)	51(2)
C(18)	−2939(8)	4181(3)	113(2)	95(3)
C(19)	−3065(10)	4839(3)	110(3)	134(5)
C(20)	−3475(9)	5151(3)	520(3)	113(4)
C(21)	−3806(8)	4825(3)	936(3)	112(4)
C(22)	−3709(7)	4173(3)	941(3)	94(3)
C(23)	−4966(5)	2737(2)	399(2)	49(2)
C(24)	−5690(6)	2997(3)	−24(2)	82(3)
C(25)	−6979(7)	2790(4)	−153(3)	103(3)
C(26)	−7537(6)	2342(3)	137(3)	84(3)
C(27)	−6822(6)	2090(3)	554(3)	81(3)
C(28)	−5549(5)	2288(3)	684(2)	64(2)
C(29)	1807(4)	830(2)	1396(2)	42(2)
C(30)	1931(5)	406(3)	992(2)	60(2)
C(31)	3147(5)	148(3)	908(2)	67(2)
C(32)	4253(5)	326(3)	1208(2)	64(2)
C(33)	4147(6)	744(3)	1608(3)	77(2)
C(34)	2947(5)	993(3)	1705(2)	65(2)
C(35)	−575(5)	518(2)	1843(2)	44(2)
C(36)	−1902(5)	366(2)	1731(2)	56(2)
C(37)	−2458(5)	−119(3)	1998(2)	68(2)
C(38)	−1715(6)	−443(3)	2383(2)	75(2)
C(39)	−421(6)	−293(3)	2490(2)	78(2)
C(40)	174(5)	189(3)	2228(2)	63(2)
C(41)	−1005(4)	1852(2)	−593(2)	46(2)
C(42)	−631(5)	2367(3)	−876(2)	63(2)
C(43)	158(6)	2282(3)	−1275(2)	75(2)
C(44)	592(5)	1696(3)	−1402(2)	71(2)
C(45)	246(6)	1176(3)	−1125(2)	70(2)
C(46)	−524(5)	1252(3)	−722(2)	62(2)
C(47)	−3618(5)	1565(2)	−342(2)	48(2)
C(48)	−4343(5)	1165(3)	−54(2)	59(2)
C(49)	−5559(5)	934(3)	−273(2)	73(2)
C(50)	−6018(6)	1087(3)	−776(3)	77(3)
C(51)	−5299(6)	1481(3)	−1061(3)	79(3)
C(52)	−4098(5)	1720(3)	−849(2)	65(2)
O(3)	−551(3)	2420(1)	904(1)	51(1)
C(53)	710(8)	3873(4)	815(4)	163(5)
C(54)	1804(7)	3593(3)	1179(3)	97(3)
O(4)	1673(5)	2995(2)	1324(2)	111(2)
C(55)	2985(9)	3896(4)	1388(4)	173(6)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.

TABLE II. Selected Bond Distances and Angles

Bond lengths (Å)			
Rh(1)–P(1)	2.326(2)	Rh(1)–P(2)	2.326(2)
Rh(1)–C(1)	1.814(6)	Rh(1)–O(3)	2.068(4)
Rh(2)–P(3)	2.328(2)	Rh(2)–P(4)	2.325(2)
Rh(2)–C(2)	1.809(5)	Rh(2)–O(3)	2.059(3)
P(1)–C(3)	1.846(5)	P(1)–C(5)	1.835(5)
P(1)–C(11)	1.827(5)	P(2)–C(4)	1.837(5)
P(2)–C(17)	1.829(5)	P(2)–C(23)	1.831(5)
P(3)–C(3)	1.836(5)	P(3)–C(29)	1.825(5)
P(3)–C(35)	1.834(5)	P(4)–C(4)	1.831(5)
P(4)–C(41)	1.829(5)	P(4)–C(47)	1.831(5)
C(1)–O(1)	1.137(8)	C(2)–O(2)	1.159(6)
C(54)–O(4)			
Bond angles (°)			
Rh(2)–Rh(1)–P(1)	91.0(1)	Rh(2)–Rh(1)–P(2)	88.7(1)
P(1)–Rh(1)–P(2)	173.1(1)	Rh(2)–Rh(1)–C(1)	142.4(2)
P(1)–Rh(1)–C(1)	91.1(2)	P(2)–Rh(1)–C(1)	93.3(2)
Rh(2)–Rh(1)–O(3)	40.4(1)	P(1)–Rh(1)–O(3)	89.2(1)
P(2)–Rh(1)–O(3)	86.1(1)	C(1)–Rh(1)–O(3)	177.2(2)
Rh(1)–Rh(2)–P(3)	88.6(1)	Rh(1)–Rh(2)–P(4)	90.1(1)
P(3)–Rh(2)–P(4)	174.9(1)	Rh(1)–Rh(2)–C(2)	140.8(2)
P(3)–Rh(2)–C(2)	91.5(2)	P(4)–Rh(2)–C(2)	92.6(2)
Rh(1)–Rh(2)–O(3)	40.6(1)	P(3)–Rh(2)–O(3)	90.5(1)
P(4)–Rh(2)–O(3)	85.2(1)	C(2)–Rh(2)–O(3)	177.6(2)
Rh(1)–P(1)–C(3)	113.3(2)	Rh(1)–P(1)–C(5)	111.9(2)
C(3)–P(1)–C(5)	100.7(2)	Rh(1)–P(1)–C(11)	118.1(2)
C(3)–P(1)–C(11)	104.1(2)	C(5)–P(1)–C(11)	107.2(2)
Rh(2)–P(4)–C(4)	112.0(1)	Rh(2)–P(4)–C(41)	112.2(2)
C(4)–P(4)–C(41)	104.0(2)	Rh(2)–P(4)–C(47)	120.2(2)
C(4)–P(4)–C(47)	104.0(2)	C(41)–P(4)–C(47)	102.8(2)
Rh(1)–C(1)–O(1)	177.9(6)	Rh(2)–C(2)–O(2)	178.5(5)
P(1)–C(3)–P(3)	116.4(2)	P(2)–C(4)–P(4)	115.0(2)
P(1)–C(5)–C(6)	117.5(4)	P(1)–C(5)–C(10)	122.8(4)
P(1)–C(11)–C(12)	121.8(4)	P(1)–C(11)–C(16)	119.8(4)
P(2)–C(17)–C(18)	123.9(4)	P(2)–C(17)–C(22)	118.2(4)
P(2)–C(23)–C(28)	121.2(4)	C(24)–C(23)–C(28)	118.5(5)
P(3)–C(29)–C(30)	118.6(4)	P(3)–C(29)–C(34)	124.1(4)
P(30)–C(35)–C(36)	120.1(4)	P(3)–C(35)–C(40)	120.5(4)
P(4)–C(41)–C(42)	124.4(4)	P(4)–C(41)–C(46)	118.1(4)
P(4)–C(47)–C(48)	120.7(4)	P(4)–C(47)–C(52)	120.0(4)
Rh(1)–O(3)–Rh(2)	99.1(1)	O(4)–C(54)–C(55)	114.9(7)

hydroxy oxygen, and a carbon from the carbonyl ligand. There is a slight perturbation from square planar geometry that is demonstrated by the P3–Rh2–P4 and P1–Rh1–P2 angles of 173.9(1)° and 173.1(1)°, respectively, and the C2–Rh2–O3 and C1–Rh1–O3 angles of 177.6(2)° and 177.2(2)° respectively.

The rather long Rh–Rh separation of 3.139(1) Å is consistent with no formal Rh–Rh bond. In similar structures where a Rh–Rh bond exists, the Rh–Rh separation is significantly shorter than that observed here [14]. Furthermore, the Rh–Rh separation is larger than the intraligand P–P separations of 3.128 Å and 3.099 Å which is the converse of what is observed when a formal Rh–Rh bond is present [14]. A formal Rh–Rh bond would impart paramagnetism on the complex and this is not observed.

Most of the structural parameters of the title compound are the same, within experimental error, as those observed for the chloro-bridged analogue [15]. The only significant difference in the two structures is the angles formed by the two metal atoms and the apex bridging ligand. The Rh1–O3–Rh2 angle is 99.1(1)° compared to that of 82.38(5)° for the Rh–Cl–Rh angle in the chloro derivative [15]. The apex angle of 99.1(1)° is one of the largest observed when no Rh–Rh bond is present. This larger apex angle is necessitated by the shorter distances between the apex atom and the rhodium atoms in the hydroxy-bridged complex (2.059(3) Å and 2.068(4)

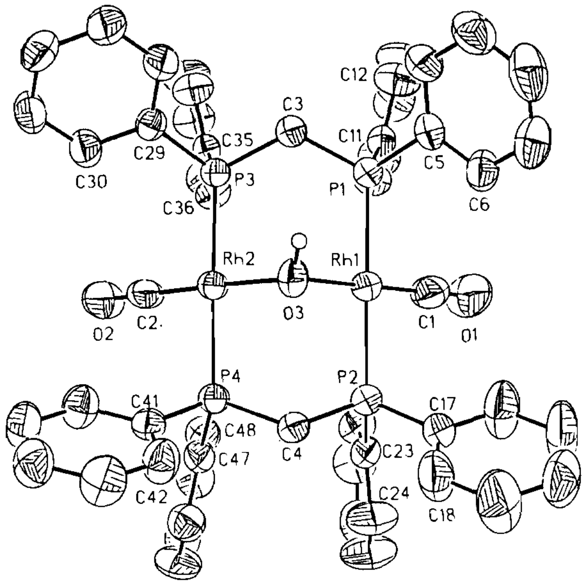

Fig. 1. The structure and numbering scheme for $[Rh_2(dppm)_2(CO)_2(\mu\text{-}OH)]PF_6$. All nonhydrogen atoms are represented as thermal ellipsoids scaled to enclose 50% probability. Hydrogen is represented as a sphere with 0.15 Å radius in this illustration.

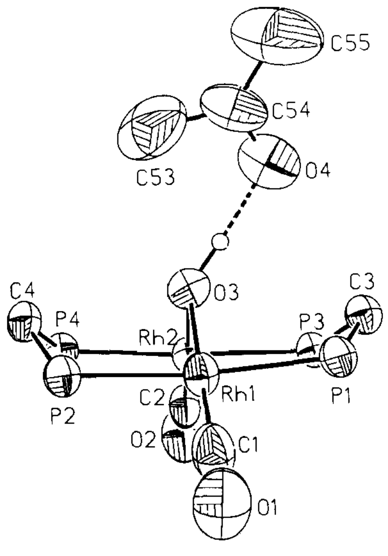

Fig. 2. Inner coordination of $[Rh_2(dppm)_2(CO)_2(\mu\text{-}OH)]PF_6$ showing the hydrogen bonding between the hydroxy hydrogen and the carbonyl oxygen of the acetone.

Å) compared to those of the chloro-bridged complex (2.406(2) Å and 2.380(2) Å). Unlike the chloro-bridged complex, within experimental error the hydroxy-bridged complex displays no assymetry with respect to the apex atom.

The methylene groups of the dppm ligands are folded in a *cis* configuration toward the hydroxy ligand. This configuration is characteristic of most A-frame species containing bridging dppm ligands since it allows the more bulky phenyl groups to occupy a more open site, thus minimizing unfavorable intramolecular contacts. The two types of phenyl groups normally observed for this configuration are found in the title compound. Typically one Rh–P–C(phenyl) angle is close to the true tetrahedral angle and the other one is usually 3 to 8 degrees larger. Viewing down the Rh–Rh axis shows that the Rh–P vectors are nearly eclipsed (Fig. 2), with the P1–Rh1–Rh2–P3 and P2–Rh1–Rh2–P4 torsion angles being 4.9(0.1)° and 3.0(0.1)°, respectively. This feature is very similar to that observed for the chloro-bridged analogue [15]; however, the sulfide-bridged analogue exhibits significant twisting about the Rh–Rh axis [16]. It is possible that the twisting observed for the sulfide complex is the result of crystal packing phenomena.

The separation between the hydroxy hydrogen and O4 of the acetone as depicted in Fig. 2 is 2.089 Å. Though the structure was not reported, a hydroxy-bridged dirhodium complex has been reported in which the hydroxy group is hydrogen bonded to a chloride ion [17]. The nonhydrogen-bonded hydroxy-bridged dimer has also been reported [18]. These two complexes exhibit slightly different reactivities. It would therefore be of interest to see how the reactivity of the title compound compares to those. These studies are in progress.

Supplementary Material

Tables SI–SV list complete bond distances, angles, anisotropic thermal parameters, hydrogen atom coordinates and isotropic thermal parameters, and observed and calculated structure factors. Available from the authors on request.

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