

Two reaction products of $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_2(\text{CH}_3\text{CN})_6][\text{BF}_4]_2$: $[\text{Rh}_2(\text{O}_2\text{CCH}_3)(\text{chp})_2(\text{CH}_3\text{CN})_3][\text{BF}_4]$ and $[\text{Rh}(\text{dpcp})_2][\text{BF}_4]$

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(Received January 19, 1993)

Abstract

Two rhodium complexes have been synthesized from $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_2(\text{CH}_3\text{CN})_6][\text{BF}_4]_2$ as a starting material. A rhodium(II) dinuclear compound, $[\text{Rh}_2(\text{O}_2\text{CCH}_3)(\text{chp})_2(\text{CH}_3\text{CN})_3][\text{BF}_4]_2$ (**1**), has been isolated from the reaction between $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_2(\text{CH}_3\text{CN})_6][\text{BF}_4]_2$ and Hchp (Hchp = 6-chloro-2-hydroxypyridine). A square-planar rhodium(I) mononuclear compound, $[\text{Rh}(\text{dpcp})_2][\text{BF}_4]$ (**2**), has also been prepared by treatment of $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_2(\text{CH}_3\text{CN})_6][\text{BF}_4]_2$ with dpcp ligand where dpcp is (\pm)-*trans*-1,2-bis(diphenylphosphino)cyclopentane. X-ray crystallographic characterization of **1** and **2** gave the following: for **1**·CH₂Cl₂: space group $P\bar{1}$, $a = 13.475(2)$, $b = 13.896(2)$, $c = 7.994(2)$ Å, $\alpha = 99.38(2)$, $\beta = 103.50(2)$, $\gamma = 81.62(2)^\circ$, $V = 1427(1)$ Å³, $Z = 2$; for **2**·CH₂Cl₂: space group $C2/c$, $a = 22.619(4)$, $b = 15.396(3)$, $c = 17.022(3)$ Å, $\beta = 115.13(2)^\circ$, $V = 5367(2)$ Å³, $Z = 4$.

Introduction

The chemistry of the complexes containing the Rh_2^{4+} core, represented by the parent complex, $\text{Rh}_2(\text{O}_2\text{CCH}_3)_4$ [**1**], has been dominated by complexes having four bridging ligands such as carboxylate and hydroxypyridinate [2]. Several Rh_2^{4+} compounds having two bridging ligands have been reported by Garner and Drago research groups [3]. This paper presents the preparation and structures of one Rh_2^{4+} compound with three bridging ligands and of one Rh(I) mononuclear compound obtained from $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_2(\text{CH}_3\text{CN})_6][\text{BF}_4]_2$ as a starting material.

Experimental

Preparative procedures

Starting materials

$[\text{Rh}_2(\text{O}_2\text{CCH}_3)_2(\text{CH}_3\text{CN})_6][\text{BF}_4]_2$ [**3a**] and dpcp [4] were prepared by the literature methods. Hchp was obtained from Aldrich Chemical Company and used without further purification. Solvents were dried and freshly distilled prior to use.

Reaction procedures

All reactions were carried out in an argon atmosphere with the use of standard Schlenk line techniques.

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Preparation of $[\text{Rh}_2(\text{O}_2\text{CCH}_3)(\text{chp})_2(\text{CH}_3\text{CN})_3][\text{BF}_4]$

A mixture of $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_2(\text{CH}_3\text{CN})_6][\text{BF}_4]_2$ (0.18 g, 0.2 mmol) and Hchp (0.06 g, 0.4 mmol) was heated to 140 °C under an argon atmosphere for 40 min. The remaining Hchp was removed by vacuum sublimation. Yield 0.16 g (88%). UV–Vis: 765 and 320 nm in dichloromethane. Green crystals suitable for X-ray crystallographic analysis were obtained by the slow diffusion of hexanes into a dichloromethane solution of $[\text{Rh}_2(\text{O}_2\text{CCH}_3)(\text{chp})_2(\text{CH}_3\text{CN})_3][\text{BF}_4]$.

Preparation of $[\text{Rh}(\text{dpcp})_2][\text{BF}_4]$

A flask containing $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_2(\text{CH}_3\text{CN})_6][\text{BF}_4]_2$ (0.18 g, 0.2 mmol), dpcp (0.84 g, 1.2 mmol), and methanol (10 ml) was heated to gentle reflux for 15 h during which time the green solution was gradually replaced by a yellow solution. The volume of solvent was reduced to 1 ml and a yellow precipitate was filtered off and washed with diethyl ether. Yellow crystals suitable for X-ray crystallographic analysis were obtained by the slow diffusion of hexanes into a dichloromethane solution of $[\text{Rh}(\text{dpcp})_2][\text{BF}_4]$.

X-ray crystallography

The structures of $[\text{Rh}_2(\text{O}_2\text{CCH}_3)(\text{chp})_2(\text{CH}_3\text{CN})_3][\text{BF}_4]$ and $[\text{Rh}(\text{dpcp})_2][\text{BF}_4]$ were determined by a general procedure that has been fully described elsewhere [5]. The diffraction data for **1** and **2** were collected on an Enraf-Nonius CAD-4S diffractometer with graphite monochromated Mo $K\alpha$ ($\lambda_\alpha = 0.71073$ Å) radiation.

Data reduction was carried out by standard methods using well-established computational procedures on a local area VAX cluster employing the VAX/VMS V4.6 software. The crystal parameters and basic information pertaining to data collection and structure refinement are summarized in Table 1. Tables 2 and 3 list the positional parameters and isotropic equivalent thermal parameters for **1** and **2**, respectively. Lists of selected bond distances and angles for the two compounds are given in Tables 4 and 5. See also 'Supplementary material'.

[Rh₂(O₂CCH₃)(chp)₂(CH₃CN)₃][BF₄] (1)

A green crystal of **1** (approximate dimensions 0.32×0.15×0.10 mm) was mounted on the tip of a fiber with epoxy cement. The crystal was indexed using 25 strong reflections taken from a rotation photograph. The reduced cell dimensions indicated that the crystal belonged to the triclinic crystal system. A 2θ-ω scan motion was employed to scan a possible 5015 data points in the range of 4 ≤ 2θ ≤ 50°. Three standard reflections did not show any loss or gain in intensity during the data collection. Azimuthal scans of six reflections with Eulerian angle χ near 90° were used as the basis for an empirical absorption correction [6]. The structure factors were obtained after Lorentz and polarization corrections. The direct methods program in SHELXS-86 [7] led to the location of the positions of the rhodium atoms. The remaining atoms were found in a series of alternating difference Fourier maps and least-square cycles led to full development of the coordination sphere. Anisotropic refinement on all the

TABLE 1. Crystallographic data for **1** and **2**

Formula	Rh ₂ Cl ₄ F ₄ O ₄ N ₅ B ₁ C ₁₉ H ₂₀	Rh ₂ Cl ₇ P ₄ C ₃₉ H ₅₉
Formula weight	816.83	1151.62
Space group	P1 (No 2)	C2/c (No 15)
<i>a</i> (Å)	13.475(2)	22.619(4)
<i>b</i> (Å)	13.896(2)	15.396(3)
<i>c</i> (Å)	7.994(2)	17.022(3)
α (°)	99.38(2)	90.00
β (°)	103.50(2)	115.13(2)
γ (°)	81.62(2)	90.00
<i>V</i> (Å ³)	1427(1)	5367(2)
<i>Z</i>	2	4
<i>D</i> _{calc} (g/cm ³)	1.92	1.43
μ (Mo Kα) (cm ⁻¹)	15.80	5.81
λ (Mo Kα) (Å)	0.71073	0.71073
Temperature (°C)	20 ± 1	20 ± 1
Transmission factors	0.99–0.85	0.99–0.93
<i>R</i> ^a	0.0433	0.0426
<i>R</i> _w ^b	0.0626	0.0619
Quality-of-fit ^c	1.83	1.55
Largest shift/e.s.d.	0.03	0.85
Largest peak (e/Å ³)	0.92	0.55

^a*R* = Σ||*F*_o| - |*F*_c||/Σ|*F*_o|. ^b*R*_w = [Σ*w*(|*F*_o| - |*F*_c|)²/Σ*w*|*F*_o|²]^{1/2}; *w* = 1/σ²(|*F*_o|). ^cQuality-of-fit = [Σ*w*(|*F*_o| - |*F*_c|)²/(*N*_{obs} - *N*_{param})]^{1/2}

TABLE 2 Positional and isotropic equivalent thermal parameters (Å²) and their e.s.d.s for [Rh₂(OAc)(chp)₂(CH₃CN)₃][BF₄]·CH₂Cl₂

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²) ^a
Rh(1)	0.38040(3)	0.30437(3)	0.18061(5)	1.950(8)
Rh(2)	0.37972(3)	0.18867(3)	0.38004(5)	1.765(8)
Cl(1)	0.5024(1)	0.1119(1)	0.7101(2)	3.54(3)
Cl(2)	0.2705(1)	0.0142(1)	0.4257(2)	3.91(3)
O(1)	0.4703(1)	0.3831(3)	0.3779(5)	2.61(8)
O(2)	0.2908(3)	0.2201(3)	-0.0065(5)	2.70(8)
O(3)	0.5091(3)	0.2227(3)	0.1313(5)	2.75(8)
O(4)	0.4899(3)	0.1048(3)	0.2761(5)	2.28(8)
N(1)	0.4919(3)	0.2594(3)	0.5467(5)	1.93(9)
N(2)	0.2724(3)	0.1225(3)	0.1906(6)	2.35(9)
N(3)	0.2744(3)	0.2630(3)	0.5013(6)	2.28(9)
N(4)	0.2557(3)	0.3899(3)	0.2237(6)	2.5(1)
N(5)	0.3889(4)	0.3976(4)	-0.0041(6)	2.8(1)
C(1)	0.5198(4)	0.3433(4)	0.5141(7)	2.2(1)
C(2)	0.6016(4)	0.3878(4)	0.6304(8)	2.7(1)
C(3)	0.6539(5)	0.3446(5)	0.7744(8)	3.2(1)
C(4)	0.6245(5)	0.2580(4)	0.8054(7)	3.0(1)
C(5)	0.5445(4)	0.2201(4)	0.6893(7)	2.4(1)
C(6)	0.2471(4)	0.1506(4)	0.0311(7)	2.5(1)
C(7)	0.1704(5)	0.1046(5)	-0.1000(8)	3.3(1)
C(8)	0.1281(5)	0.0300(6)	-0.0648(9)	4.1(2)
C(9)	0.1568(5)	-0.0025(5)	0.0994(9)	3.8(1)
C(10)	0.2278(4)	0.0472(4)	0.2203(8)	2.8(1)
C(11)	0.5361(4)	0.1407(4)	0.1850(7)	2.4(1)
C(12)	0.6317(5)	0.0804(5)	0.1423(8)	3.5(1)
C(13)	0.2159(4)	0.2985(4)	0.5779(7)	2.5(1)
C(14)	0.1385(4)	0.3473(5)	0.6765(9)	3.6(1)
C(15)	0.1857(5)	0.4440(4)	0.2370(7)	2.7(1)
C(16)	0.0958(5)	0.5155(5)	0.257(1)	4.2(2)
C(17)	0.3803(4)	0.4500(4)	-0.1049(7)	2.7(1)
C(18)	0.3696(6)	0.5189(5)	-0.2273(9)	4.5(2)
C(19)	0.1024(7)	0.8397(7)	0.522(1)	6.0(2)
Cl(3)	0.0960(2)	0.7869(2)	0.3056(3)	6.45(6)
Cl(4)	-0.0234(2)	0.8776(2)	0.5572(3)	5.98(5)
B(1)	0.8925(8)	0.3502(7)	0.174(1)	4.9(2)
F(1)	0.8495(4)	0.4301(4)	0.0887(6)	6.2(1)
F(2)	0.8275(4)	0.2809(4)	0.1354(8)	8.5(2)
F(3)	0.9134(5)	0.3820(5)	0.3462(7)	9.5(2)
F(4)	0.9817(5)	0.3165(5)	0.127(1)	12.0(3)

^aAnisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as: (4/3)[*a*²β₁₁ + *b*²β₂₂ + *c*²β₃₃ + *ab*(cos γ)β₁₂ + *ac*(cos β)β₁₃ + *bc*(cos α)β₂₃]

non-hydrogen atoms was successfully completed to give *R* = 0.0433 and *R*_w = 0.0626.

[Rh(dpcp)₂][BF₄] (2)

A yellow crystal of **2** (approximate dimensions 0.30×0.40×0.50 mm) was mounted on a fiber with epoxy cement. Preliminary examination showed that the unit cell was monoclinic and C-centered. Choice of the centrosymmetric monoclinic space group *C2/c* revealed the correct positions of the rhodium and phosphine atoms via Patterson maps. The method used

TABLE 3. Positional and isotropic equivalent thermal parameters (\AA^2) and their e.s.d.s for $[\text{Rh}(\text{dpcp})_2][\text{BF}_4] \cdot \text{CH}_2\text{Cl}_2$

Atom	x	y	z	B (\AA^2) ^a
Rh(1)	0.250	0.250	0.000	2.29(1)
P(1)	0.26449(5)	0.20527(7)	-0.12079(6)	2.74(3)
P(2)	0.17455(4)	0.13875(6)	-0.03660(6)	2.72(2)
C(1)	0.3412(1)	0.1567(2)	-0.1085(1)	3.2(1)
C(2)	0.3915(1)	0.1485(2)	-0.0254(1)	3.7(1)
C(3)	0.4505(1)	0.1101(2)	-0.0139(1)	5.1(1)
C(4)	0.4591(1)	0.0799(2)	-0.0856(1)	5.3(2)
C(5)	0.4089(1)	0.0881(2)	-0.1687(1)	4.8(2)
C(6)	0.3499(1)	0.1265(2)	-0.1802(1)	4.0(1)
C(7)	0.2421(1)	0.2849(2)	-0.2090(2)	3.0(1)
C(8)	0.2798(1)	0.3018(2)	-0.2541(2)	4.0(1)
C(9)	0.2561(1)	0.3567(2)	-0.3261(2)	5.0(2)
C(10)	0.1946(1)	0.3947(2)	-0.3530(2)	5.4(2)
C(11)	0.1568(1)	0.3777(2)	-0.3078(2)	5.5(2)
C(12)	0.1806(1)	0.3228(2)	-0.2358(2)	4.2(1)
C(13)	0.2090(2)	0.1127(3)	-0.1692(3)	3.3(1)
C(14)	0.1811(2)	0.0889(3)	-0.2658(3)	4.2(1)
C(15)	0.1234(2)	0.0306(3)	-0.2797(3)	4.4(1)
C(16)	0.1061(2)	0.0438(3)	-0.2025(3)	4.5(1)
C(17)	0.1479(2)	0.1217(3)	-0.1543(3)	3.4(1)
C(18)	0.2088(1)	0.0346(2)	0.0123(2)	3.2(1)
C(19)	0.2768(1)	0.0284(2)	0.0516(2)	4.0(1)
C(20)	0.3067(1)	-0.0517(2)	0.0816(2)	5.0(1)
C(21)	0.2686(1)	-0.1256(2)	0.0724(2)	5.1(2)
C(22)	0.2007(1)	-0.1195(2)	0.0332(2)	4.7(2)
C(23)	0.1708(1)	-0.0394(2)	0.0032(2)	3.8(1)
C(24)	0.0977(1)	0.1463(2)	-0.0277(2)	3.2(1)
C(25)	0.0947(1)	0.1222(2)	0.0496(2)	4.3(1)
C(26)	0.0374(1)	0.1353(2)	0.0599(2)	5.6(2)
C(27)	-0.0170(1)	0.1724(2)	-0.0070(2)	5.6(2)
C(28)	-0.0140(1)	0.1965(2)	-0.0843(2)	5.2(2)
C(29)	0.0434(1)	0.1835(2)	-0.0946(2)	4.1(1)
C(30)	0.500	0.2269(8)	0.750	11.2(6)
Cl(1)	0.4321(1)	0.2878(2)	0.6885(2)	12.6(1)
B(1)	0.500	0.0938(8)	0.250	6.1(3)
F(1)	0.518(1)	0.098(1)	0.190(1)	12.4(9)
F(2)	0.4669(6)	0.150(1)	0.271(1)	14.0(7)
F(3)	0.4727(8)	0.0291(8)	0.1981(9)	14.5(7)
F(4)	0.5655(7)	0.097(2)	0.314(1)	18(1)
H(1)	0.3848(1)	0.1719(2)	0.0301(1)	5.5(5)*
H(2)	0.4894(1)	0.1038(2)	0.0505(1)	5.5(5)*
H(3)	0.5048(1)	0.0502(2)	-0.0767(1)	5.5(5)*
H(4)	0.4156(1)	0.0647(2)	-0.2242(1)	5.5(5)*
H(5)	0.3109(1)	0.1328(2)	-0.2446(1)	5.5(5)*
H(6)	0.3275(1)	0.2724(2)	-0.2333(2)	8.3(7)*
H(7)	0.2853(1)	0.3698(2)	-0.3611(2)	8.3(7)*
H(8)	0.1762(1)	0.4372(2)	-0.4087(2)	8.3(7)*
H(9)	0.1092(1)	0.4071(2)	-0.3286(2)	8.3(7)*
H(10)	0.1513(1)	0.3097(2)	-0.2008(2)	8.3(7)*
H(11)	0.2434(2)	0.0616(3)	-0.1365(3)	5(1)*
H(12)	0.1656(2)	0.1466(3)	-0.3055(3)	7(1)*
H(13)	0.2170(2)	0.0547(3)	-0.2803(3)	7(1)*
H(14)	0.1359(2)	-0.0364(3)	-0.2837(3)	6.7(9)*
H(15)	0.0820(2)	0.0486(3)	-0.3389(3)	6.7(9)*
H(16)	0.0547(2)	0.0570(3)	-0.2238(3)	7(1)*
H(17)	0.1194(2)	-0.0130(3)	-0.1613(3)	7(1)*
H(18)	0.1164(2)	0.1772(3)	-0.1801(3)	8(2)*
H(19)	0.3062(1)	0.0856(2)	0.0587(2)	5.7(5)*
H(20)	0.3593(1)	-0.0565(2)	0.1120(2)	5.7(5)*

(continued)

TABLE 3. (continued)

H(21)	0.2918(1)	-0.1876(2)	0.0957(2)	5.7(5)*
H(22)	0.1712(1)	-0.1767(2)	0.0261(2)	5.7(5)*
H(23)	0.1182(1)	-0.0346(2)	-0.0272(2)	5.7(5)*
H(24)	0.1368(1)	0.0935(2)	0.1014(2)	6.6(6)*
H(25)	0.0351(1)	0.1166(2)	0.1197(2)	6.6(6)*
H(26)	-0.0613(1)	0.1825(2)	0.0010(2)	6.6(6)*
H(27)	-0.0561(1)	0.2252(2)	-0.1361(2)	6.6(6)*
H(28)	0.0457(1)	0.2021(2)	-0.1544(2)	6.6(6)*

^aStarred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as: $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos \gamma)\beta_{12} + ac(\cos \beta)\beta_{13} + bc(\cos \alpha)\beta_{23}]$.

TABLE 4. Selected bond distances (\AA) and angles ($^\circ$) for compound 1

Distances			
Rh(1)–Rh(2)	2.4439(6)	Rh(1)–O(1)	2.021(3)
Rh(1)–O(2)	2.016(4)	Rh(1)–O(3)	2.012(4)
Rh(1)–N(4)	1.977(4)	Rh(1)–N(5)	2.149(6)
Rh(2)–O(4)	2.003(4)	Rh(2)–N(1)	2.022(4)
Rh(2)–N(2)	2.035(4)	Rh(2)–N(3)	1.977(5)
Angles			
Rh(2)–Rh(1)–O(1)	88.4(1)	Rh(1)–Rh(2)–O(4)	86.7(1)
Rh(2)–Rh(1)–O(2)	88.2(1)	Rh(1)–Rh(2)–N(1)	86.6(1)
Rh(2)–Rh(1)–O(3)	86.3(1)	Rh(1)–Rh(2)–N(2)	87.6(1)
Rh(2)–Rh(1)–N(4)	96.5(2)	Rh(1)–Rh(2)–N(3)	98.9(1)
Rh(2)–Rh(1)–N(5)	175.5(1)	O(4)–Rh(2)–N(1)	87.7(2)
O(1)–Rh(1)–O(2)	176.6(2)	O(4)–Rh(2)–N(2)	89.1(2)
O(1)–Rh(1)–O(3)	87.9(1)	O(4)–Rh(2)–N(3)	174.2(2)
O(1)–Rh(1)–N(4)	91.4(2)	N(1)–Rh(2)–N(2)	173.5(2)
O(1)–Rh(1)–N(5)	92.9(2)	N(1)–Rh(2)–N(3)	91.3(2)
O(2)–Rh(1)–O(3)	91.8(1)	N(2)–Rh(2)–N(3)	92.4(2)
O(2)–Rh(1)–N(4)	89.1(2)	O(2)–Rh(1)–N(5)	90.5(2)
O(3)–Rh(1)–N(4)	177.1(2)	O(3)–Rh(1)–N(5)	89.5(2)
N(4)–Rh(1)–N(5)	87.8(2)		

TABLE 5. Selected bond distances (\AA) and angles ($^\circ$) for $[\text{Rh}(\text{dpcp})_2][\text{BF}_4] \cdot \text{CH}_2\text{Cl}_2$

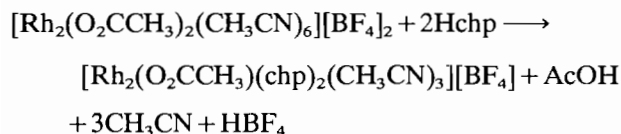
Distances	
Rh(1)–P(1)	2.320(1)
Rh(1)–P(2)	2.309(1)
Angles	
P(1)–Rh(1)–P(1)	180.00(0)
P(1)–Rh(1)–P(2)	84.67(4)
P(1)–Rh(1)–P(2)	95.33(4)

to obtain the structure of this compound was similar to that for 1.

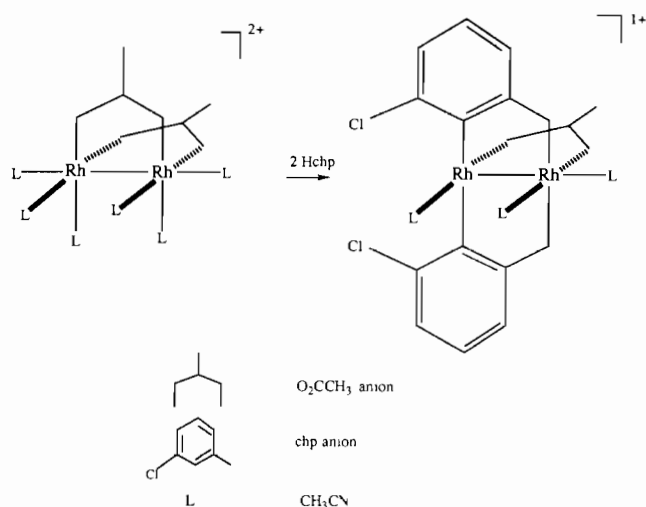
Results and discussion

The green compound, $[\text{Rh}_2(\text{O}_2\text{CCH}_3)(\text{chp})_2(\text{CH}_3\text{CN})_3][\text{BF}_4]$, was obtained by heating a mixture of $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_2(\text{CH}_3\text{CN})_6][\text{BF}_4]_2$ and two equivalents

of Hchp, according to Scheme 1 and the following equation:



Two acetonitrile and one bridging acetate ligands were replaced by two chp ligands. Figure 1 shows an ORTEP plot of the $[\text{Rh}_2(\text{O}_2\text{CCH}_3)(\text{chp})_2(\text{CH}_3\text{CN})_3]$ cation. Two chp ligands are *trans* and are oriented in the same direction thus freeing one rhodium atom for the attachment of the axial acetonitrile ligand. A possible mechanism for the formation of compound **1** is shown in Scheme 2. First, two acetonitrile ligands are replaced by one chp ligand. This leads to the weakening of the



Scheme 1.

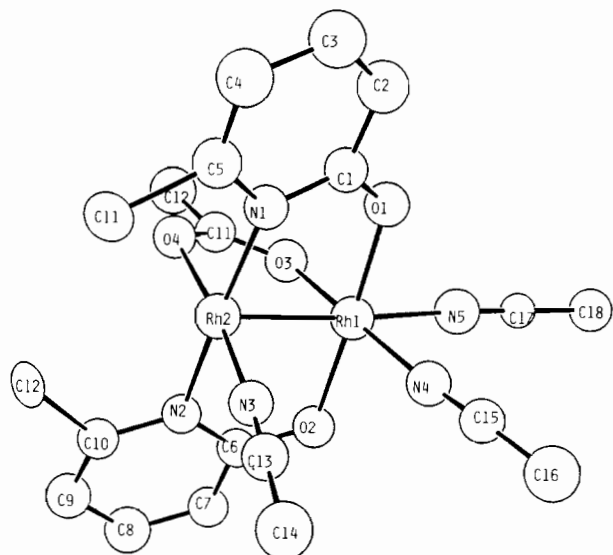
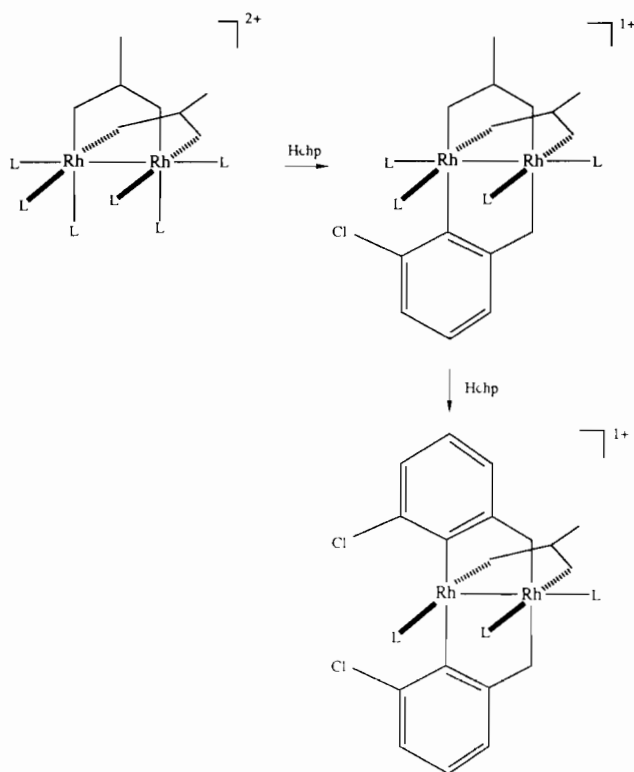


Fig. 1 An ORTEP drawing for $[\text{Rh}_2(\text{OAC})(\text{chp})_2(\text{CH}_3\text{CN})_3][\text{BF}_4]$ (**1**)



Scheme 2

Rh–O bond *trans* to the Rh–N_{eq} bond of the chp ligand and thus, the carboxylate ligand *trans* to the chp ligand would be replaced by the other chp ligand. The question of why two chp ligands are oriented in the same direction even though adjacent chlorine pairs of these chp groups (the distance between two chloride is 3.7 Å) would make contacts close to the sum of van der Waals radii is not clear. Table 4 lists selected bond lengths and angles. The bond lengths in this molecule are of some interest. The Rh–Rh bond length of 2.4439(6) Å in compound **1** having only three bridging ligands is longer than the Rh–Rh bond distances reported for dirhodium(II) compounds with four bridging ligands such as carboxylate or hydroxypyridine ligands. There is a distinction in the lengths of the Rh–N bonds involving the coordinated acetonitrile molecule in the equatorial (1.977(4) Å) as compared to the axial sites (2.149(6) Å) due to the *trans* effect of the Rh–Rh single bond. This Rh–N_{ax} bond distance of 2.149(6) Å is much shorter, i.e. by *c.* 0.08 Å, than the Rh–N_{ax} bond distance of 2.232(4) Å seen in the molecule $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_2(\text{CH}_3\text{CN})_6][\text{BF}_4]_2$. The Rh–Rh–N_{ax} angle is 175.5°; the Rh–N_{ax} bond being bent slightly away from the equatorial acetonitrile ligands.

The yellow rhodium(I) compound was obtained by refluxing a methanol solution containing $[\text{Rh}_2(\text{O}_2\text{CCH}_3)_2(\text{CH}_3\text{CN})_6][\text{BF}_4]_2$ and six equivalents of dpcp ligand. Figure 2 shows an ORTEP plot of the $[\text{Rh}(\text{dpcp})_2]$ cation. $[\text{Rh}(\text{dpcp})_2]$ cation has a square-planar geometry

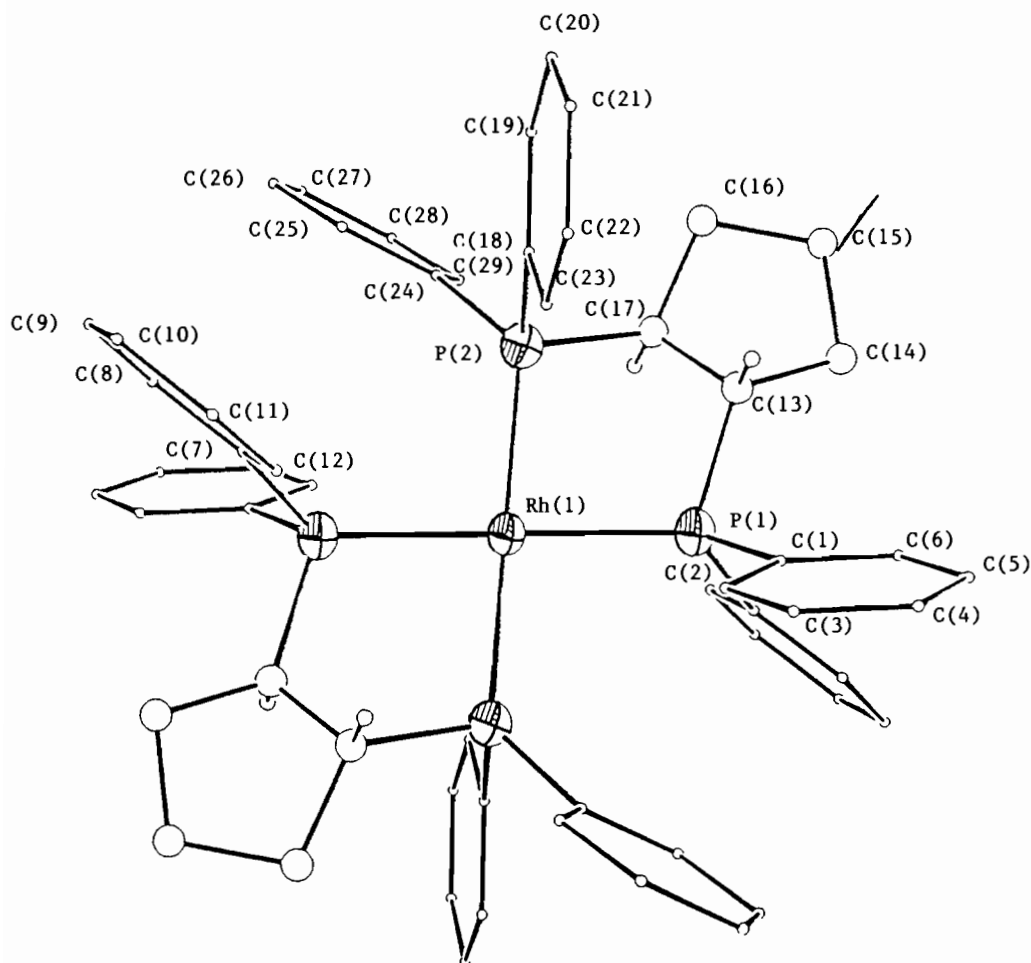


Fig. 2. An ORTEP drawing for $[\text{Rh}(\text{dpcp})_2][\text{BF}_4]$ (**2**).

and has an inversion center on the rhodium atom. Table 5 lists selected bond lengths and angles for compound **2**. The average Rh–P bond length of 2.315[1] Å fits well with the distance reported for rhodium(I) compounds in general. The angle of P(1)–Rh–P(1) is 180° and the angles of P(1)–Rh–P(2) are 85 and 95°. This rhodium(I) mononuclear compound has open axial sites allowing the coordination of small molecules.

Supplementary material

More complete lists of bond distances and angles and tables of anisotropic thermal displacement parameters may be obtained from author F.A.C.

Acknowledgement

We thank the National Science Foundation for support.

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