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Bis(diphenylphosphino)methane complexes of rhodium(III) halides as synthons for dinuclear rhodium(III) complexes

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Abstract

Several rhodium(III) complexes have been synthesized by the reaction of dirhodium tetraacetate, $Rh_2(O_2CCH_3)_4$, with bis(diphenylphosphino)methane (dppm), in the presence of trimethylsilyl halides. Octahedral complexes of formula $RhCl_3(dppm)(CH_3CN)$ (**1**) and $RhI_3(dppm)(CH_3CN)$ (**2**) have been isolated as minor products in the reaction between $Rh_2(O_2CCH_3)_4$, dppm and Me_3SiCl or Me_3SiI, respectively. In addition, the tri-n-butylphosphine complex $RhCl_3(dppm)(P\text{-n-}Bu_3)$ (**3**) has also been prepared either by treatment of **1** with P-n-Bu_3 or from the reaction of $Rh_2Cl_6(P\text{-n-}Bu_3)_4$ with dppm. Dimerization occurs upon heating **3** at 150 °C *in vacuo* for 2 h to form the Rh(II) complex $Rh_2Cl_4(dppm)_2$, which we have previously reported. X-ray crystallographic characterization of **1**, **2** and **3** gave the following: for **1**: space group $I\bar{4}$, $a = 19.090(4)$, $c = 15.100(3)$ Å, $V = 5503(1)$ Å^3, $Z = 8$; for **2**: space group *Cc*, $a = 11.897(2)$, $b = 17.110(3)$, $c = 15.246(1)$ Å, $\beta = 106.04(9)°$, $V = 2983(1)$ Å^3, $Z = 4$; for **3**: space group $P2_12_12_1$, $a = 15.914(4)$, $b = 19.819(6)$, $c = 12.207(3)$ Å, $V = 3850(2)$ Å^3, $Z = 4$.

Introduction

We are investigating the reactivity of dirhodium tetraacetate with tertiary phosphines in the presence of trimethylsilyl halide reagents. Generally these reactions yield binuclear Rh(II) complexes with some, or all, of the acetate groups replaced by chloride and phosphine ligands [1]. In several of the reactions involving the use of bis(diphenylphosphino)methane (dppm), we also isolated a minor product of general formula $RhX_3(dppm)(CH_3CN)$, where X = Cl or I. We have also prepared some analogous complexes with P-n-Bu_3 or MeOH as the donor ligand. Treatment of $Rh_2Cl_6(P\text{-n-}Bu_3)_4$ [2] with dppm gives $RhCl_3(dppm)(P\text{-n-}Bu_3)$ which, when heated to 150 °C in vacuum, dimerizes to form $Rh_2Cl_4(dppm)_2$ [3]. In addition, $RhCl_3 \cdot 3H_2O$ reacts with dppm in the presence of methanol to give $RhCl_3(dppm)(MeOH)$ which, in turn, reacts with CH_3CN displacing the MeOH adduct to form $RhCl_3(dppm)(CH_3CN)$ (**1**). The single crystal X-ray structures of $RhCl_3(dppm)(CH_3CN)$ (**1**), $RhI_3(dppm)(CH_3CN)$ (**2**) and $RhCl_3(dppm)(P\text{-n-}Bu_3)$ (**3**) have been carried out and the results are reported herein.

Experimental

Starting materials

Anhydrous $Rh_2(O_2CCH_3)_4$ [3] and $Rh_2Cl_6(P\text{-n-}Bu_3)_4$ [2] were prepared by the literature methods. Bis(diphenylphosphino)methane (dppm), chlorotrimethylsilane (Me_3SiCl) and iodomethylsilane (Me_3SiI) were 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.

A. Reactions of $Rh_2(O_2CCH_3)_4$

(i) $RhCl_3(dppm)(CH_3CN)$ (1). A flask containing $Rh_2(O_2CCH_3)_4$ (0.15 g, 0.34 mmol), dppm (0.26 g, 0.68 mmol), Me_3SiCl (172 μl, 1.36 mmol) and benzene (20 ml) was heated to gentle reflux for 12 h. The red–orange solution was concentrated to a volume of *c.* 10 ml and a pale orange precipitate was filtered off and washed with benzene followed by diethyl ether. The material was recrystallized from CH_2Cl_2–CH_3CN to give a mixture of red crystals of

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$Rh_2Cl_4(dppm)_2$ and yellow crystals of **1**. The two products were separated in bulk by washing the crude precipitate with methanol which dissolved only the yellow monomer; yield of **1** *c.* 20%. An alternative synthesis of **1** is described in Section B(iii).

(ii) $RhI_3(dppm)(CH_3CN)$ (2). $Rh_2(O_2CCH_3)_4$ (0.200 g, 0.453 mmol) was suspended in 20 ml of benzene along with dppm (0.35 g, 0.905 mmol) and Me_3SiI (258 μl, 1.81 mmol). The reaction mixture was refluxed for 1.5 h during which time the green suspension was gradually replaced by a blood-red solution. The solvent was reduced in volume to *c.* 5 ml and a maroon precipitate was filtered off and washed with diethyl ether. Recrystallization from CH_2Cl_2–CH_3CN (5:1) afforded orange–red crystals of **2**; yield 0.49 g (60%).

(iii) $[RhI_2(dppm)_2]I_3$ (4). In a similar reaction, $Rh_2(O_2CCH_3)_4$ (0.044 g, 0.10 mmol), dppm (0.077 g, 0.20 mmol), Me_3SiI (90 μl, 0.60 mmol) and benzene (10 ml) were refluxed for 8 h. After this time the resulting dark brown solution was cooled and reduced in volume to *c.* 5 ml. The brown precipitate was filtered off in air and washed with benzene and then diethyl ether followed by methanol. This methanol solution was set aside (see below). Yield of **4**: 0.032 g (11%). Dark brown crystals suitable for X-ray crystallographic analysis were obtained by layering a dichloromethane solution with diethyl ether.

The methanol solution was evaporated to dryness and then redissolved in dichloromethane and layered with hexane. Red crystals of **2**, verified by X-ray crystallography, grew within a few days. Yield *c.* 60%.

B. Synthesis of $RhCl_3(dppm)(L)$ where $L = P$-n-Bu_3, MeOH and CH_3CN

(i) $RhCl_3(dppm)(P$-n-$Bu_3)$ (3). $Rh_2Cl_6(P\text{-n-}Bu_3)_4$ [2] (0.201 g, 0.164 mmol) was dissolved in 10 ml of THF in a Schlenk tube. To this solution was added dppm (0.129 g, 0.336 mmol) dissolved in 10 ml of THF. The mixture was refluxed for 45 min. The volume of the resulting yellow solution was reduced to *c.* 2 ml and then carefully layered with 10 ml of benzene. Yellow, air-stable crystals grew on the walls of the tube within 24 h. Yield 0.18 g (70%).

(ii) $RhCl_3(dppm)(MeOH)$. $RhCl_3 \cdot 3H_2O$ (0.127 g, 0.482 mmol) was dissolved in 25 ml of MeOH. To the clear red solution was added dppm (0.187 g, 0.486 mmol). The solution turned orange–red and became cloudy in appearance. The solvent was evaporated by vacuum distillation to leave a salmon-colored residue which was washed with 2 ml of MeOH and dried *in vacuo*. Yield 0.28 g (93%). $^{31}P\{^1H\}$ NMR: $\delta = -24.6$, $^1J_{Rh-P} = 74.8$ Hz.

(iii) $RhCl_3(dppm)(CH_3CN)$ (1). $RhCl_3$(dppm)-(MeOH) (0.150 g, 0.240 mmol) was refluxed in 10 ml of CH_3CN for 30 min. The resulting yellow solution was evaporated to dryness and the yellow solid washed with 2 ml of CH_3CN. Yield 0.15 g (98%). $^{31}P\{^1H\}$ NMR: $\delta = -23.7$, $^1J_{Rh-P} = 74.8$ Hz.

TABLE 1. Summary of the crystallographic parameters for compounds **1**, **2** and **3**

Compound	$RhCl_3(dppm)(CH_3CN)$	$RhI_3(dppm)(CH_3CN)$	$RhCl_3(dppm)(P\text{-n-}Bu_3)$
Formula	$RhCl_3P_2NC_{27}H_{25}$	$RhI_3P_2NC_{27}H_{25}$	$RhCl_3P_3C_{37}H_{49}$
Formula weight	736.6	907.06	795.98
Space group	$I\bar{4}$ (No. 82)	Cc (No. 9)	$P2_12_12_1$ (No. 19)
a (Å)	19.090(4)	11.897(2)	15.914(4)
b (Å)	19.090(4)	17.110(3)	19.819(6)
c (Å)	15.100(3)	15.246(1)	12.207(3)
β (°)		106.04(9)	
V (Å^3)	5503(1)	2983(1)	3850(2)
Z	8	4	4
D_{calc} (g/cm^3)	1.781	2.020	1.373
μ(Mo Kα) (cm^{-1})	16.084	37.591	7.931
Radiation monochromated in incident beam (λ, Å)		Mo Kα ($\lambda_\alpha = 0.71073$ Å)	
Temperature (°C)	22 ± 1	20 ± 1	22 ± 1
Transmission factors (%) (max., min.)	99.73, 83.95	99.99, 94.70	99.88, 97.69
R[a]	0.0751	0.0276	0.0553
R_w[b]	0.0727	0.0351	0.0733

[a] $R = \Sigma \| F_o| - |F_c\| / \Sigma |F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w |F_o|^2]^{1/2}$; $w = 1/\sigma^2\{|F_o|\}$.

C. Preparation of $Rh_2Cl_4(dppm)_2$ [1] from 1 and 3

(i) $RhCl_3(dppm)(CH_3CN)$ (**1**) (0.05 g, 0.08 mmol) was refluxed in toluene (20 ml) for 8 h. The cooled, concentrated solution of *c.* 10 ml was found to exhibit peaks due to the starting material in its $^{31}P\{^1H\}$ NMR spectrum. However, the signal-to-noise ratio was low and trace amounts of other products could have been missed. This solution was set aside for several weeks after which it was noticed that both large amounts of yellow crystals (*c.* 49 mg) and a small amount of poorly formed red crystals (*c.* 1 mg) were present. These red crystals were hand picked from the yellow crystals and dissolved in 5 ml of CH_2Cl_2 for a $^{31}P\{^1H\}$ NMR measurement; $\delta = -19.10$, $^1J_{Rh-P} = 152.9$ Hz. These data agree well with the $^{31}P\{^1H\}$ NMR data for an authentic sample of $Rh_2Cl_4(dppm)_2$ [1].

(ii) $RhCl_3(dppm)(P\text{-}n\text{-}Bu_3)$ (**3**) (0.22 g, 0.28 mmol) was placed in a 30 ml Schlenk tube and heated *in vacuo* at 150 °C for 2 h. During this time the yellow solid turned an orange–red color and free P-n-Bu_3 was liberated (verified by smelling the tube shortly after the reaction time). The orange–red solid was pumped on (*c.* 1×10^{-3} torr) at room temperature for an additional 2 h. The material was then washed with methanol followed by diethyl ether and recrystallized from CH_2Cl_2–CH_3CN. Yield 0.11 g (70%). These red crystals were collected and found to be $Rh_2Cl_4(dppm)_2$ [1] by comparing their IR spectrum, cyclic voltammogram and the unit cell of a single crystal (by X-ray crystallography) with those of an authentic sample.

X-ray crystallography

The structures of $RhCl_3(dppm)(CH_3CN)$ (**1**), $RhI_3(dppm)(CH_3CN)$ (**2**) and $RhCl_3(dppm)(P\text{-}n\text{-}Bu_3)$ (**3**) were determined by general procedures that have been fully described elsewhere [4]. The diffraction data for **1** and **3** were collected on a Nicolet P3/F equivalent diffractometer while the data for **2** were obtained with an Enraf-Nonius CAD-4S diffractometer; both are equipped with graphite monochromated Mo Kα ($\lambda_\alpha = 0.71073$ Å) radiation. Data reductions were carried out by standard methods using well-established computational procedures*. The crystal parameters and basic information pertaining to data collection and structure refinement are summarized in Table 1. Tables 2, 3 and 4 list the positional parameters and isotropic equivalent thermal parameters for **1**, **2** and **3**, respectively. A list of selected bond distances and angles for all three compounds may be found in Table 5. See also 'Supplementary material'.

TABLE 2. Atomic positional parameters and equivalent isotropic displacement parameters (Å^2) and their e.s.d.s for $RhCl_3(dppm)(CH_3CN)$ (**1**)

Atom	*x*	*y*	*z*	*B* (Å^2)
Rh(1)	0.22520(4)	0.21975(4)	0.01047(5)	2.42(2)
Cl(1)	0.2965(1)	0.1553(1)	−0.0953(2)	3.77(7)
Cl(2)	0.2697(1)	0.3258(1)	−0.0352(2)	3.45(6)
Cl(3)	0.1287(1)	0.2274(2)	−0.0950(2)	4.49(7)
P(1)	0.1747(1)	0.2774(1)	0.1251(2)	2.61(6)
P(2)	0.3052(1)	0.2218(1)	0.1199(2)	2.35(6)
N(1)	0.1840(4)	0.1291(4)	0.0522(7)	3.7(2)
C(1)	0.2544(5)	0.2806(5)	0.1947(7)	3.1(2)
C(2)	0.1445(5)	0.3671(5)	0.1167(7)	2.9(2)
C(3)	0.1521(5)	0.4086(6)	0.1873(8)	3.4(3)
C(4)	0.1268(6)	0.4814(6)	0.1806(9)	4.8(3)
C(5)	0.0958(6)	0.5058(5)	0.1072(9)	4.2(3)
C(6)	0.0893(6)	0.4620(5)	0.0344(9)	5.3(3)
C(7)	0.1127(6)	0.3881(7)	0.0370(9)	5.0(3)
C(8)	0.1062(5)	0.2290(5)	0.1792(8)	3.2(3)
C(9)	0.1154(6)	0.1950(6)	0.2632(8)	4.2(3)
C(10)	0.0600(7)	0.1554(6)	0.299(1)	5.7(3)
C(11)	−0.0043(6)	0.1512(7)	0.255(1)	5.7(4)
C(12)	−0.0133(6)	0.1857(6)	0.176(1)	5.3(3)
C(13)	0.0400(5)	0.2258(6)	0.1377(9)	4.6(3)
C(14)	0.3895(4)	0.2647(5)	0.1025(8)	2.9(2)
C(15)	0.4255(5)	0.2482(5)	0.0249(8)	3.7(3)
C(16)	0.4915(5)	0.2813(6)	0.011(1)	5.0(3)
C(17)	0.5134(6)	0.3321(6)	0.067(1)	6.2(3)
C(18)	0.4774(6)	0.3469(8)	0.142(1)	7.1(4)
C(19)	0.4149(6)	0.3115(6)	0.165(1)	5.2(3)
C(20)	0.3218(5)	0.1394(5)	0.1738(8)	3.4(3)
C(21)	0.3418(5)	0.0821(5)	0.1198(8)	3.6(3)
C(22)	0.3586(6)	0.0178(6)	0.1564(9)	5.2(3)
C(23)	0.3525(7)	0.0090(7)	0.252(1)	5.8(4)
C(24)	0.3296(6)	0.0960(6)	0.3027(9)	4.5(3)
C(25)	0.3154(6)	0.1301(6)	0.2641(7)	3.3(3)
C(26)	0.1601(6)	0.0773(6)	0.073(1)	4.8(3)
C(27)	0.1199(7)	0.0141(7)	0.101(2)	9.9(6)

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

$RhCl_3(dppm)(CH_3CN)$ (1)

A yellow plate-like crystal of **1** (approximate dimensions $0.3 \times 0.2 \times 0.1$ mm) was mounted on the tip of a glass fiber. The crystal was indexed using 25 strong reflections taken from a rotation photograph. The reduced cell dimensions indicated that the crystal belonged to the tetragonal crystal system, which we verified by axial photography. An ω-scan motion was used to scan a possible 2521 data points

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*Crystallographic computing was done on a PDP-11/60 (RSX-11M V4.1) with PDP-11 simulated VAX-SDP, a VAX-11/780 (VMS V4.1), a local area VAX cluster (VMS 5.2) and on a CI cluster with VAX 8650 and VAX 8800 CPUs.

TABLE 3. Atomic positional parameters and equivalent isotropic displacement parameters (Å^2) and their e.s.d.s for $RhI_3(dppm)(CH_3CN)$ (**2**)

Atom	x	y	z	B (Å^2)
Rh(1)	0.448	0.21999(3)	0.288	2.32(1)
I(1)	0.47074(7)	0.14770(4)	0.45312(5)	4.33(1)
I(2)	0.33859(6)	0.33869(4)	0.33598(5)	3.93(1)
I(3)	0.65926(6)	0.29388(4)	0.34492(5)	3.89(1)
P(1)	0.4027(2)	0.2678(1)	0.1427(2)	2.34(4)
P(2)	0.2680(2)	0.1699(1)	0.2127(2)	2.59(4)
N(1)	0.5402(7)	0.1295(5)	0.2522(6)	3.7(2)
C(1)	0.2494(8)	0.2348(5)	0.1134(6)	3.0(2)
C(2)	0.4769(7)	0.2198(5)	0.0691(6)	2.8(2)
C(3)	0.4338(9)	0.1515(6)	0.0214(8)	4.0(2)
C(4)	0.497(1)	0.1136(7)	−0.0298(8)	5.0(2)
C(5)	0.601(1)	0.1448(7)	−0.0354(8)	5.1(3)
C(6)	0.645(1)	0.2146(8)	0.0107(9)	5.9(3)
C(7)	0.5824(9)	0.2501(7)	0.0627(8)	4.8(2)
C(8)	0.3978(7)	0.3697(5)	0.1103(7)	3.1(2)
C(9)	0.325(1)	0.3884(6)	0.0251(7)	4.5(2)
C(10)	0.317(1)	0.4662(7)	−0.004(1)	6.5(4)
C(11)	0.381(1)	0.5229(6)	0.0503(9)	5.2(3)
C(12)	0.457(1)	0.5045(7)	0.1369(9)	5.1(3)
C(13)	0.4633(8)	0.4268(5)	0.1653(8)	3.7(2)
C(14)	0.1359(8)	0.1773(5)	0.2507(7)	3.4(2)
C(15)	0.038(1)	0.2151(6)	0.200(1)	5.6(3)
C(16)	−0.065(1)	0.2138(8)	0.231(1)	6.8(4)
C(17)	−0.067(1)	0.1750(9)	0.305(1)	6.7(3)
C(18)	0.030(1)	0.136(1)	0.3544(9)	9.0(5)
C(19)	0.131(1)	0.134(1)	0.3269(8)	6.9(4)
C(20)	0.2698(8)	0.0695(5)	0.1737(7)	3.9(2)
C(21)	0.329(1)	0.0132(6)	0.2375(9)	5.7(3)
C(22)	0.340(2)	−0.0628(7)	0.207(1)	7.9(4)
C(23)	0.286(1)	−0.0827(8)	0.117(1)	9.0(4)
C(24)	0.224(1)	−0.0295(7)	0.056(1)	7.8(3)
C(25)	0.212(1)	0.0499(7)	0.0831(9)	5.9(3)
C(26)	0.5895(9)	0.0822(6)	0.2299(8)	4.6(2)
C(27)	0.653(2)	0.0191(9)	0.193(1)	8.6(4)

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. Atomic positional parameters and equivalent isotropic thermal parameters (Å^2) and their e.s.d.s for $RhCl_3(dppm)(P\text{-}n\text{-}Bu_3)$ (**3**)

Atom	x	y	z	B (Å^2)[a]
Rh(1)	0.5554(2)	0.0376(2)	0.5150(2)	2.48(5)
Cl(1)	0.5720(8)	−0.0049(6)	0.3289(8)	4.7(3)
Cl(2)	0.5333(6)	−0.0732(6)	0.5807(8)	3.8(3)
Cl(3)	0.5830(7)	0.1471(5)	0.4554(9)	4.6(3)
P(1)	0.5666(7)	0.0707(5)	0.6942(8)	2.7(2)
P(2)	0.6953(7)	0.0197(5)	0.5657(8)	2.0(2)
P(3)	0.4133(7)	0.0594(5)	0.4769(9)	3.6(3)
C(1)	0.670(2)	0.034(2)	0.711(3)	1.6(7)*
C(2)	0.569(2)	0.161(2)	0.728(3)	2.0(7)*
C(3)	0.645(2)	0.199(2)	0.694(3)	2.4(9)*
C(4)	0.638(3)	0.261(2)	0.726(4)	5(1)*
C(5)	0.578(3)	0.303(2)	0.777(3)	4(1)*
C(6)	0.510(3)	0.262(2)	0.814(4)	5(1)*
C(7)	0.505(3)	0.195(2)	0.791(3)	4(1)*
C(8)	0.508(2)	0.034(2)	0.806(3)	1.7(7)*
C(9)	0.545(2)	0.043(2)	0.911(3)	3.9(9)*
C(10)	0.500(3)	0.017(2)	1.005(4)	6(1)*
C(11)	0.425(2)	−0.023(2)	0.978(3)	2.9(8)*
C(12)	0.393(2)	−0.036(2)	0.878(3)	3.5(9)*
C(13)	0.436(3)	−0.000(2)	0.786(3)	5(1)*
C(14)	0.753(2)	−0.061(2)	0.555(3)	2.9(9)*
C(15)	0.809(2)	−0.071(2)	0.639(3)	3.2(9)*
C(16)	0.851(3)	−0.152(3)	0.618(5)	7(2)*
C(17)	0.825(2)	−0.182(2)	0.539(3)	2.9(9)*
C(18)	0.767(2)	−0.172(2)	0.470(3)	3.6(9)*
C(19)	0.726(2)	−0.109(2)	0.468(3)	3.1(9)*
C(20)	0.784(2)	0.078(2)	0.525(3)	2.3(8)*
C(21)	0.841(3)	0.106(2)	0.598(3)	4(1)*
C(22)	0.905(2)	0.146(2)	0.560(3)	2.9(9)*
C(23)	0.902(3)	0.163(2)	0.459(3)	5(1)*
C(24)	0.846(3)	0.146(2)	0.373(4)	6(1)*
C(25)	0.780(2)	0.096(2)	0.412(3)	2.1(9)*
C(26)	0.364(3)	0.124(2)	0.565(3)	4(1)*
C(27)	0.267(3)	0.125(2)	0.561(4)	6(1)*
C(28)	0.237(3)	0.188(2)	0.618(4)	4(1)*
C(29)	0.135(3)	0.190(3)	0.629(5)	8(2)*
C(30)	0.344(3)	−0.019(2)	0.492(4)	6(1)*
C(31)	0.363(3)	−0.067(2)	0.400(3)	4(1)*
C(32)	0.329(3)	−0.135(3)	0.424(4)	8(2)*
C(33)	0.223(3)	−0.126(3)	0.434(4)	7(2)*
C(34)	0.378(3)	0.091(2)	0.340(4)	4(1)*
C(35)	0.406(3)	0.162(3)	0.314(4)	7(1)*
C(36)	0.391(3)	0.177(3)	0.181(4)	7(1)*
C(37)	0.414(4)	0.239(3)	0.157(5)	10(2)*

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

in the range $4 \leqslant 2\theta \leqslant 50°$. Careful analysis of the systematic absences from the data led to the choice of the space group $I\bar{4}$. Three standard reflections, scanned every 2 h of X-ray exposure, did not show any loss or gain in intensity during the 48 h of beam exposure. Azimuthal scans of 8 reflections with Eulerian angle χ near 90° were used as the basis for an empirical absorption correction [5]. The structure factors were obtained after Lorentz and polarization corrections and, after data averaging and rejection of unobserved reflections, there remained 2442 data with $F_o^2 \geqslant 3\sigma(F_o)^2$ to be used in the least-squares calculations.

The program MITHRIL [6] was used to locate the Rh atom and successive difference Fourier maps and least-squares cycles led to full development of the coordination sphere. Anisotropic refinement on all the non-hydrogen atoms was successfully completed to give $R=0.0751$ and $R_w=0.0727$ using 2442 reflections to fit 307 variables. A final difference Fourier map had a maximum peak density of

TABLE 5. Selected bond distances (Å) and angles (°) for compounds **1**, **2** and **3**

$RhCl_3(dppm)(CH_3CN)$ (**1**)		$RhI_3(dppm)(CH_3CN)$ (**2**)		$RhCl_3(dppm)(P\text{-}n\text{-}Bu_3)$ (**3**)	
Distances (Å)					
Rh(1)–Cl(1)	2.433(3)	Rh(1)–I(1)	2.755(1)	Rh(1)–Cl(1)	2.43(1)
Rh(1)–Cl(2)	2.302(3)	Rh(1)–I(2)	2.629(1)	Rh(1)–Cl(2)	2.36(1)
Rh(1)–Cl(3)	2.439(3)	Rh(1)–I(3)	2.727(1)	Rh(1)–Cl(3)	2.33(1)
Rh(1)–P(1)	2.267(3)	Rh(1)–P(1)	2.278(2)	Rh(1)–P(1)	2.28(1)
Rh(1)–P(2)	2.250(3)	Rh(1)–P(2)	2.302(2)	Rh(1)–P(2)	2.36(1)
Rh(1)–N(1)	2.003(8)	Rh(1)–N(1)	2.051(9)	Rh(1)–P(3)	2.35(1)
P(1)–C(1)	1.850(10)	P(1)–C(1)	1.842(10)	P(1)–C(1)	1.81(3)
P(1)–C(2)	1.812(9)	P(1)–C(2)	1.806(10)	P(1)–C(2)	1.84(3)
P(1)–C(8)	1.798(11)	P(1)–C(8)	1.808(9)	P(1)–C(8)	1.80(3)
P(2)–C(1)	1.865(10)	P(2)–C(1)	1.842(10)	P(2)–C(1)	1.83(3)
N(1)–C(26)	1.134(14)	N(1)–C(26)	1.107(15)	P(3)–C(26)	1.84(4)
C(2)–C(3)	1.34(2)	C(2)–C(3)	1.396(13)	P(3)–C(30)	1.91(5)
C(26)–C(27)	1.49(2)	C(26)–C(27)	1.51(2)	P(3)–C(34)	1.87(4)
Angles (°)					
Cl(1)–Rh(1)–Cl(2)	92.4(1)	I(1)–Rh(1)–I(2)	91.12(2)	Cl(1)–Rh(1)–Cl(2)	90.6(4)
Cl(1)–Rh(1)–Cl(3)	91.4(1)	I(1)–Rh(1)–I(3)	93.90(2)	Cl(1)–Rh(1)–Cl(3)	90.6(4)
Cl(1)–Rh(1)–P(1)	170.1(1)	I(1)–Rh(1)–P(1)	170.54(6)	Cl(1)–Rh(1)–P(1)	168.7(4)
Cl(1)–Rh(1)–P(2)	96.4(1)	I(1)–Rh(1)–P(2)	97.35(6)	Cl(1)–Rh(1)–P(2)	95.2(4)
Cl(1)–Rh(1)–N(1)	89.4(3)	I(1)–Rh(1)–N(1)	88.8(2)	Cl(1)–Rh(1)–P(3)	89.1(4)
Cl(2)–Rh(1)–Cl(3)	91.8(1)	I(2)–Rh(1)–I(3)	92.11(3)	Cl(2)–Rh(1)–Cl(3)	177.3(4)
Cl(2)–Rh(1)–P(1)	87.6(1)	I(2)–Rh(1)–P(1)	89.43(6)	Cl(2)–Rh(1)–P(1)	87.5(4)
Cl(2)–Rh(1)–P(2)	87.4(1)	I(2)–Rh(1)–P(2)	87.64(6)	Cl(2)–Rh(1)–P(2)	84.9(4)
Cl(2)–Rh(1)–N(1)	178.2(3)	I(2)–Rh(1)–N(1)	177.8(2)	Cl(2)–Rh(1)–P(3)	95.5(4)
Cl(3)–Rh(1)–P(1)	98.5(1)	I(3)–Rh(1)–P(1)	95.52(6)	Cl(3)–Rh(1)–P(1)	90.9(4)
Cl(3)–Rh(1)–P(2)	172.2(1)	I(3)–Rh(1)–P(2)	168.75(6)	Cl(3)–Rh(1)–P(2)	92.5(4)
Cl(3)–Rh(1)–N(1)	87.7(3)	I(3)–Rh(1)–N(1)	85.7(2)	Cl(3)–Rh(1)–P(3)	87.0(4)
P(1)–Rh(1)–P(2)	73.7(1)	P(1)–Rh(1)–P(2)	73.24(8)	P(1)–Rh(1)–P(2)	73.6(4)
P(1)–Rh(1)–N(1)	90.7(3)	P(1)–Rh(1)–N(1)	91.0(2)	P(1)–Rh(1)–P(3)	102.2(4)
P(2)–Rh(1)–N(1)	92.9(3)	P(2)–Rh(1)–N(1)	94.5(2)	P(2)–Rh(1)–P(3)	175.7(4)
Rh(1)–P(1)–C(1)	95.7(3)	Rh(1)–P(1)–C(1)	94.6(3)	Rh(1)–P(1)–C(1)	94(1)
Rh(1)–P(1)–C(2)	122.7(4)	Rh(1)–P(1)–C(2)	114.4(3)	Rh(1)–P(1)–C(2)	120(1)
Rh(1)–P(1)–C(8)	114.0(4)	Rh(1)–P(1)–C(8)	126.3(3)	Rh(1)–P(1)–C(8)	124(1)
C(1)–P(1)–C(2)	105.7(5)	C(1)–P(1)–C(2)	109.3(4)	C(1)–P(1)–C(2)	110(2)
Rh(1)–P(2)–C(1)	95.9(3)	Rh(1)–P(2)–C(1)	93.9(3)	Rh(1)–P(2)–C(1)	91(1)
C(1)–P(2)–C(14)	105.9(5)	C(1)–P(2)–C(14)	107.5(4)	C(1)–P(2)–C(14)	108(2)
Rh(1)–N(1)–C(26)	178.(1)	Rh(1)–N(1)–C(26)	177.3(9)	Rh(1)–P(3)–C(26)	115(1)
P(1)–C(1)–P(2)	93.7(5)	P(1)–C(1)–P(2)	95.7(4)	Rh(1)–P(3)–C(30)	113(1)
N(1)–C(26)–C(27)	173.(1)	N(1)–C(26)–C(27)	176.(1)	Rh(1)–P(3)–C(34)	122(1)
				C(26)–P(3)–C(30)	106(2)
				P(1)–C(1)–P(2)	99(2)

Numbers in parentheses are e.s.d.s in the least significant digits.

1.761 e Å^{-3} which was of no chemical significance. The last cycle did not shift any parameter by more than 0.13 times its estimated standard deviation.

$RhI_3(dppm)(CH_3CN)$ (2)

Data collection on a red prismatic crystal of **2** was carried out in a similar fashion to that for **1** (see above). A ω–2θ scan motion was employed in this case to scan a possible 2987 data points in the range $4 \leq 2\theta \leq 50°$. Analysis of the systematic absences led to *Cc* as the choice for the space group. Direct methods program was used to determine the atomic coordinates for the Rh atom and two of the I atoms. A series of alternating least-squares refinements and difference Fourier maps resulted in the identification of the remaining 31 non-hydrogen atoms. After isotropic refinement, an additional absorption correction DIFABS [7] was applied because of the presence of the strongly absorbing iodine atoms. The final anisotropic refinements included 34 atoms with 307 parameters being fitted to 2402 reflections. Final residuals were $R = 0.0276$, $R_w = 0.0351$ and quality-of-fit of 1.019. The final cycle did not shift any parameter by more than 0.16 times its estimated standard deviation and the final difference map contained no peaks higher than 0.838 e Å^{-3}. As the structure was solved in the acentric space group *Cc* with two possible enantiomorphs, we determined the absolute configuration by applying Hamilton's significance test. Independent refinements led to residuals of 0.02762 for enantiomorph I and 0.02871 for enantiomorph II. The ratio of the two residuals is 1.03986 which is larger than the 1% significance point; therefore the originally chosen enantiomorph (I) is established at a 99% confidence level. That the choice of the acentric space group *Cc* is correct is established not only by the successful, convergent refinement, but also by geometrical considerations. There are four molecules in the unit cell, i.e. one molecule per asymmetric unit in *Cc*. If the space group were *C2/c*, each molecule would have to sit on either a two-fold axis or an inversion center. The molecule possesses neither of these point symmetries, and our successful refinement clearly establishes the absence of disorder.

$RhCl_3$(dppm)(P-n-Bu_3) (3)

Data collection on a needle-like orange crystal of **3** was carried out in a similar fashion to that of **1** and **2** (see above). After indexing with 25 strong reflections the orthorhombic space group $P2_12_12_1$ was determined and then verified by axial photography. A possible 2269 data points were scanned using a ω–2θ scan motion in the range $4 \leqslant 2\theta \leqslant 45°$. The direct methods program in SHELXS-86 [8] was used to determine the position of the Rh atom. The remaining 43 non-hydrogen atoms were determined from a series of alternating difference Fourier maps and least-squares refinements. Anisotropic refinement on all atoms except the carbon atoms gave residuals of $R = 0.0553$ and $R_w = 0.0733$ and a quality-of-fit of 1.467 for 212 parameters being fitted to 2043 reflections. The final cycle did not shift any parameter by more than 0.080 times its estimated standard deviation and the final difference map contained no peaks higher than 0.540 e Å^{-3}.

Structural results

$RhCl_3$(dppm)(CH_3CN) (**1**) belongs to the body-centered tetragonal space group $I\bar{4}$, RhI_3(dppm)-(CH_3CN) (**2**) belongs to the monoclinic *Cc* space group while $RhCl_3$(dppm)(P-n-Bu_3) (**3**) crystallizes in the orthorhombic group $P2_12_12_1$. Each consists of discrete monomeric units of the molecule in the asymmetric unit. In the case of **1** and **2** the facial isomers are present, but for compound **3** the meridional isomer is formed. The structure of a closely related complex $RhCl_3(PPh_3)_2(CH_3CN)$ was reported some years ago by Walton and co-workers [9] in which the chlorine atoms are arranged in a meridional fashion and the PPh_3 ligands are *trans* to one another.

Labeled ORTEP diagrams for **1**, **2** and **3** are shown in Figs. 1, 2 and 3, respectively. Important distances and angles are listed in Table 5. The geometry of the molecules in **1**, **2** and **3** is that of a distorted octahedron. The chelating dppm ligands form strained four-membered rings with the Rh atom as evidenced by the angles P(1)–Rh(1)–P(2) of 73.7(1)° in **1**, 73.24(8)° in **2** and 73.64(4)° in **3**. The CH_3CN ligand is almost linear in compounds **1** and **2** with N(1)–C(26)–C(27) of 173(1)° in **1** and 176(1)° in **2**. In **1** and **2** the Rh–X bond distances *trans* to the P atoms are longer by *c*. 0.13 Å than the Rh–X bonds that are *trans* to the N atom of the CH_3CN ligands. For **3**, we see that the Rh–Cl(1) distance (*trans* to a P atom) is *c*. 0.087 Å larger than the Rh–Cl(2) and Rh–Cl(3) bonds which are *trans* to

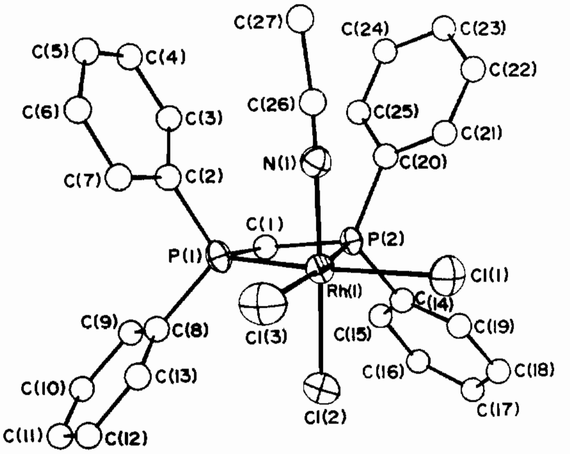

Fig. 1. ORTEP diagram of $RhCl_3$(dppm)(CH_3CN) (**1**) showing atoms as their 50% probability ellipsoids. Carbon atoms are drawn as spheres of arbitrary radii.

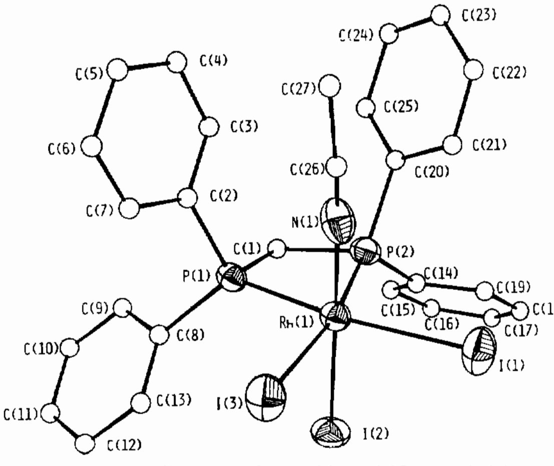

Fig. 2. ORTEP diagram of RhI_3(dppm)(CH_3CN) (**2**) showing atoms as their 50% probability ellipsoids. Carbon atoms are drawn as spheres of arbitrary radii.

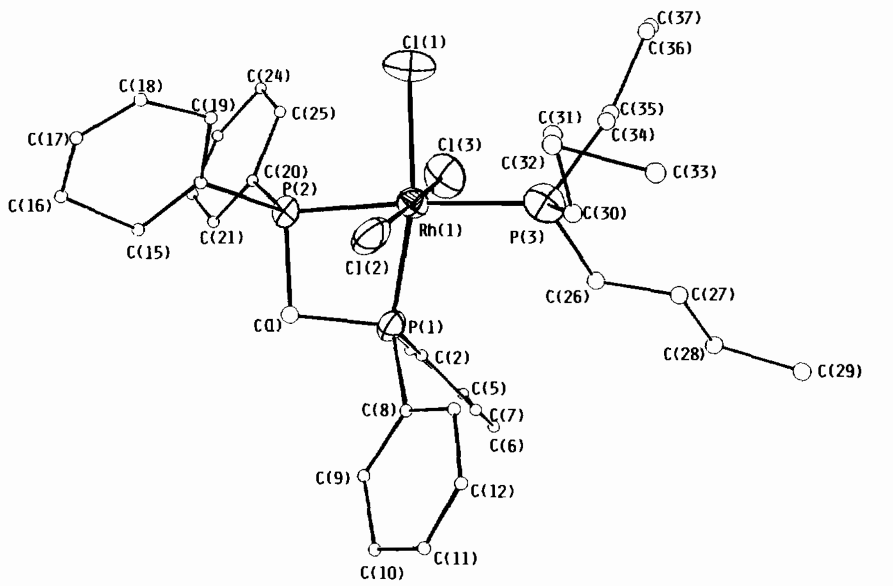

Fig. 3. ORTEP diagram of $RhCl_3(dppm)(P\text{-}n\text{-}Bu_3)$ (**3**) showing atoms as their 50% probability ellipsoids. Carbon atoms are drawn as spheres of arbitrary radii. For the sake of clarity, not all of the carbons atoms have been labeled.

one another. For the chelating dppm ligands, the average Rh–P bond distances are 2.258[3] Å for **1**, 2.290[2] Å for **2** and 2.31[1] Å for **3**. All other bond distances and angles are within expected ranges.

Discussion

As we have shown previously, the reaction of $Rh_2(O_2CCH_3)_4$ with dppm in the presence of Me_3SiCl leads to the dimer $Rh_2Cl_4(dppm)_2$ [1] in high yield. During the course of this investigation we were able to isolate a minor product, $RhCl_3(dppm)(CH_3CN)$ (**1**) when the crude product was crystallized from a mixture of dichloromethane and acetonitrile. The iodide derivative of **1**, i.e. $RhI_3(dppm)(CH_3CN)$ (**2**) was prepared in a similar fashion. In this case the source of halide is from Me_3SiI. We were unable to isolate $Rh_2I_4(dppm)_2$, which we initially thought was a second product. Instead, the monomeric salt $[RhI_2(dppm)_2]I_3$ (**4**) was formed. This latter complex was characterized by X-ray crystallography but, owing to a poor data set (the crystals did not diffract well), the large R values and quality-of-fit make this a structure which cannot be published in full form.*

The cation in compound **4** has a distorted octahedral structure in which the I atoms are *trans* with a mean Rh–I distance of 2.68 Å and a mean Rh–P distance of 2.37 Å. This is isostructural with *trans*-$RuCl_2(dppm)_2$ [10]. The I_3^- counter anion is unsymmetrical (I–I distances of 2.88 Å and 2.92 Å) and deviates from linearity by *c*. 2°.

Our strategy to synthesize compound **3** involved treating the dimer $Rh_2Cl_6(P\text{-}n\text{-}Bu_3)_4$ [2] with dppm in the hope that $Rh_2Cl_4(dppm)_2$ [1] or $Rh_2Cl_6(dppm)_2$ [11] would be formed by displacement of the P-n-Bu_3 ligands with dppm. As it turned out, Rh–Cl and Rh–P bond rupture resulted to give the monomer $RhCl_3(dppm)(P\text{-}n\text{-}Bu_3)$ (**3**) in high yield. With the knowledge that the Rh–(P-n-Bu_3) bond is fairly labile, we heated a sample of **3** to 150 °C *in vacuo* for several hours. The yellow monomer **3** turned orange–red and formed the dimer $Rh_2Cl_4(dppm)_2$ in good (70%) yield. The most likely fate of the P-n-Bu_3 ligand is the formation of a dichlorophosphine followed by decomposition

$$\underset{\mathbf{3}}{2\mathrm{RhCl_3(dppm)(PR_3)}} \xrightarrow{\Delta}$$

$$\mathrm{Rh_2Cl_4(dppm)_2 + PR_3Cl_2 + PR_3}$$

$$\searrow$$

$$\mathrm{R = Bu^n} \qquad \mathrm{PR_2Cl + RCl}$$

The mechanism for this dimerization must also involve at least one of the Rh–P bonds of the dppm ligands breaking and reforming since this bidentate

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*Crystal data for $[RhI_2(dppm)_2]I_3$ (**4**): triclinic space group $P\bar{1}$, $a = 21.098(8)$, $b = 22.099(10)$, $c = 12.068(4)$ Å, $\alpha = 100.16(3)$, $\beta = 92.55(3)$, $\gamma = 97.21(3)°$, $V = 5482(4)$ Å^3, $Z = 4$. Structure solution and refinement based on 4694 reflections with $F_o^2 > 3\sigma(F_o)^2$ (Mo Kα radiation, $\lambda = 0.71073$ Å) converged at $R = 0.0884$, $R_w = 0.1125$ with quality-of-fit = 2.01. See also 'Supplementary material'.

phosphine rearranges from a chelating mode in **3** to the bridging mode in $Rh_2Cl_4(dppm)_2$.

Dimerization of **1** to form $Rh_2Cl_4(dppm)_2$ (in very low yield) occurs thermally when **1** is refluxed in toluene for several hours. When **1** is heated *in vacuo* for several hours, an insoluble black solid forms which we were unable to characterize.

The thermolysis reaction, *in vacuo*, of $RhCl_3$(dppm)(P-n-Bu_3) (1) to form $Rh_2Cl_4(dppm)_2$ is a method which allows us to use an easily obtainable starting material to form a dimeric compound. The potential range of applications for such a methodology may be large. Compounds that are, so far, unobtainable through traditional synthetic techniques (i.e. $Rh_2Cl_4(dppe)_2$) may be accessible through this route.

Supplementary material

For all crystal structures, full tables of crystal parameters and details of data collection and refinement, bond distances, bond angles, and anisotropic displacement parameters and tables of observed and calculated structure factors are available upon request from author F.A.C.

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