New Preparations and Molecular Structures of *cis*-$MCl_2(Ph_2PCH_2PPh_2)_2$, M = Ru, Os and *trans*-$RuCl_2(Ph_2PCH_2PPh_2)_2$

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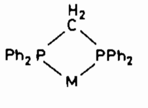
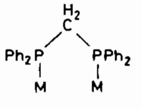
The title compounds were made by reacting bis(diphenylphosphino)methane (dppm) with reduced solutions of $OsCl_6^{4-}$ *and* $Ru_2OCl_{10}^{4-}$. *The crystal and molecular structures of these compounds have been determined from three-dimensional X-ray study. The* cis-*isomers crystallize with one* $CHCl_3$ *per molecule of the complex. All three compounds crystallize in the monoclinic space group* $P2_1/n$ *with unit cell dimensions as follows:* Cis-$OsCl_2(dppm)_2\cdot CHCl_3$: a = 13.415(4) Å, b = 22.859(4) Å, c = 16.693(3) Å, β = 105.77(3)°, V = 4926(3) Å^3, Z = 4. cis-$RuCl_2(dppm)_2\cdot CHCl_3$: a = 13.442(3) Å, b = 22.833(7) Å, c = 16.750(4) Å, β = 105.53(2)°, V = 4953(3) Å^3, Z = 4. trans-$RuCl_2(dppm)_2$: a = 11.368(7) Å, b = 10.656(6) Å, c = 18.832(12) Å; β = 103.90(6)°, V = 2213(7) Å^3; Z = 2. *The structures were refined to* R = 0.044 (R_w = 0.055) *for* cis-$OsCl_2(dppm)_2\cdot CHCl_3$; R = 0.065 ($R_w$ = 0.079) *for* cis-$RuCl_2(dppm)_2\cdot CHCl_3$ *and* R = 0.028 (R_w = 0.038) *for* trans-$RuCl_2(dppm)_2$. *The complexes are six coordinate with stable four-membered chelate rings. The P–M–P angle in the chelate rings is* ca. *71° in each case.*

Introduction

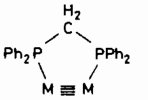
The ligand P,P,P′,P′-tetraphenyldiphosphinomethane, commonly called bis-(diphenylphosphino)methane and, based on this name, abbreviated as dppm, is stereochemically quite versatile. It can serve as a chelating bidentate ligand, *a*, as a bridging ligand across a pair of metal atoms that are not bonded to each other, *b*, as a bridging ligand across a pair of metal atoms that are strongly bonded to each other, *c*, and, perhaps most remarkably in situation *d*, where it spans a linear M–O–M group [1]. When it serves as a chelating ligand a four-membered ring is formed and because of the strain associated with this, chelation might be considered the least favored mode of coordination. Whether this is so or not, the fact is that examples of chelating dppm are not uncommon.



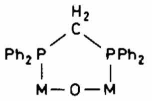
(a)



(b)



(c)



(d)

We previously reported [1] that the reaction of $OsCl_3$ with dppm in methanol afforded a fair yield (*ca.* 50%) of the oxo-bridged compound $Os_2(\mu\text{-}O)(\mu\text{-}dppm)_2Cl_6$. This product, though very interesting, was not the type of binuclear M–M bonded compound we were hoping for. We therefore tried again using $(NH_4)_2OsCl_6$ in the presence of Na/Hg in the hope of getting a dinuclear Os^{III} or Os^{II} complex with bridging dppm and an Os–Os bond. Again, however, we were disappointed: X-ray structural analysis of the yellow crystalline product showed it to be *cis*-$OsCl_2(dppm)_2$, a compound previously obtained by a different route (reduction of $OsCl_3$ by EtOH in presence of dppm) by Chatt and Hayter [2].

We then turned to the question of whether a ruthenium analog of the $Os_2(\mu\text{-}O)(\mu\text{-}dppm)_2Cl_6$ compound could be prepared, by treating K_4Ru_2-

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OCl_{10} with dppm. Our bad luck continued since neither of the two crystalline products obtained was the desired one. Rather, they were the *cis* and *trans* isomers of $RuCl_2(dppm)_2$. Both of these had also been reported by Chatt and Hayter [2].

We thus found ourselves, by pure misadventure, in the position of having the results of a fairly systematic structural investigation of the $MCl_2(dppm)_2$ molecules, in which we had varied M from Ru to Os and had examined both *cis* and *trans* isomers. Instead of writing a report in which this might have been described as a deliberate effort to carry out such a study, we decided to take the somewhat eccentric (but perhaps more refreshing and certainly more virtuous) course of describing exactly how it was that we have the results presented here.

Experimental

Materials

OsO_4 and RuO_4 were purchased from Sigma Chemical, Inc. and Alfa Chemical Co., respectively. $(NH_4)_2OsCl_6$ and $K_4Ru_2OCl_{10}$ were prepared by literature methods [3,4].

Preparations

All reactions were carried out in an argon atmosphere using Schlenk technique. The preparative methods devised in this work are detailed below. In addition, the osmium compound was made by Chatt and Hayter's method [2] and shown to be identical with our product.

Cis-*$OsCl_2(dppm)_2$*

Ammonium hexachloroosmate(IV) (110 mg, 0.25 mmol) was dissolved in 25 ml tetrahydrofuran (THF) and reduced at room temperature with 2 ml of sodium amalgam containing 13 mg (*ca.* 0.50 mmol) of sodium. The solution color became gray. To it 195 mg (0.50 mmol) of dppm was added. The mixture was stirred for 10 h. The color of the solution changed from grey to yellow. The solution was separated from mercury, evaporated to dryness in vacuum, and the residue was dissolved in $CHCl_3$. Yellow crystals were obtained by slow diffusion of hexane into the chloroform solution. Yield: *ca.* 50%.

Cis *and* Trans-*$Ru(dppm)_2Cl_2$*

240 mg (~0.33 mmol) of $K_4Ru_2OCl_{10}$ was stirred with 360 mg of dppm (~0.66 mmol) in 20 ml methanol for 24 h at room temperature. The solution was evaporated to dryness and the residue was dissolved in chloroform in a Schlenk tube. Yellow cubes and orange-red needles were obtained by slow diffusion (over a period of several days) of hexane into the chloroform solution. The solution was removed from the Schlenk tube and the crystals were kept under mineral oil before mounting on glass fibers.

The procedure just described can be modified as follows to provide much better yields. The K_4-Ru_2OCl_{10} (240 mg) is refluxed for several hours with a five-fold excess (650 mg) of dppm in ethanol (25 ml). Crystals were obtained by diffusion of hexane into the chloroform solution of the product after evaporation of the ethanol solvent. Orange-red needles and yellow cubes were obtained in *ca.* 50% and a 20% yield, respectively, based on K_4-Ru_2OCl_{10}.

X-ray Crystallographic Procedures

The structures of all three compounds were obtained by using the same general procedures as described elsewhere [5, 6]. The crystal parameters and basic information pertaining to data collection and structure refinement are summarized in Table I. Tables of structure factors are available from F.A.C. on request. A few details specific to each compound will now be given.

cis-*$OsCl_2(dppm)_2 \cdot CHCl_3$*

The crystal orientation matrix and unit-cell parameters were derived from a least-squares fit to the goniometer settings of 25 accurately located reflections in the range $21 < 2\theta < 37°$. Data scans, which employed an ω–2θ motion, were made for 9512 possible reflections in the range $5 \leqslant 2\theta \leqslant 50°$. Corrections were made for Lorentz and polarization effects. Three reflections, used as intensity standards, and re-measured after every hour of X-ray exposure time showed no significant change in intensity during the 78 hours of exposure. An empirical absorption correction was made, ($\mu(MoK\alpha) = 73.2$ cm^{-1}) based on azimuthal scans of 9 reflections with Eulerian angle χ near 90°. The position of the unique Os atom was found from a three-dimensional Patterson map. The remainder of the structure was located and refined by an alternating sequence of least-squares cycles and difference Fourier maps.

cis-*$RuCl_2(dppm)_2 \cdot CHCl_3$*

The lattice vectors were identified by application of the automatic indexing routine of the Syntex $P\bar{1}$ diffractometer to the positions of 15 reflections taken from a rotation photograph and located and centered by the diffractometer. Axial photography was used to verify the Laue class (2/m) and the unit-cell dimensions. The latter, along with the crystal orientation matrix were refined by a least-square fit to the goniometer positions of 15 accurately located reflections in the range $24 < 2\theta < 30°$. The ω–2θ scan technique was used to measure 8671 data in the range $4° \leqslant 2\theta \leqslant 50°$. Three standard reflections, remeasured after every 100 data scans, showed 36% loss in intensity over 314.8 hours of X-ray exposure

TABLE I. Crystallographic Data.

Formula	$OsCl_5P_4C_{51}H_{45}$	$RuCl_5P_4C_{51}H_{45}$	$RuCl_2P_4C_{50}H_{44}$
Compound	*cis*-$OsCl_2(dppm)_2CHCl_3$ (*1*)	*cis*-$RuCl_2(dppm)_2 \cdot CHCl_3$ (*2*)	*trans*-$RuCl_2(dppm)_2$ (*3*)
Formula weight	1149.29	1060.16	940.78
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
a, Å	13.415(4)	13.442(3)	11.368(7)
b, Å	22.859(4)	22.833(7)	10.656(6)
c, Å	16.693(3)	16.750(4)	18.832(12)
β, degrees	105.77(3)	105.53(2)	103.90(6)
V, Å^3	4926(3)	4953(3)	2213(7)
Z	4	4	2
d_{calc}, g/cm^3	1.550	1.422	1.412
Crystal size, mm	0.3 × 0.3 × 0.2	0.4 × 0.4 × 0.2	0.4 × 0.2 × 0.2
μ(MoKα), cm^{-1}	73.2	7.43	6.45
Data collection instrument	CAD-4	Syntex P$\bar{1}$	Syntex P$\bar{1}$
Radiation	Mo Kα	Mo Kα	Mo Kα
Scan method	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$
Data collection range, 2θ, dec.	4–50°	4–50°	4–50°
No. unique data,	6641	8671	2096
$F_o^2 \geq 3\sigma(F_o^2)$	5482	4403	2023
Number of parameters refined	530	550	319
R[a]	0.044	0.065	0.028
R_w[b]	0.055	0.079	0.038
Quality-of-fit indicator[c]	1.38	1.48	0.879
Largest shift/esd, final cycle	0.01	0.04	0.80

[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] Quality of fit $= [\Sigma w(|F_o| - |F_c|)^2/(N_{obs} - N_{parameters})]^{1/2}$.

time. The intensity data were corrected for Lorentz and polarization effects. The position of the Ru atom in the crystallographic asymmetric unit was derived from a three-dimensional Patterson map. Iterative application of least-squares refinement and difference Fourier maps led to the development of the entire structure.

trans-*$RuCl_2(dppm)_2$*

The lattice vectors were obtained by using the automatic indexing routine of the diffractometer with the 15 reflections taken from a rotation photograph. Laue class (2/m) and the unit-cell dimensions were verified from axial photography. Precise cell dimensions along with the crystal orientation matrix were obtained using least-square fits to the goniometer positions of 15 accurately located reflections in the range $22 < 2\theta < 32°$. Data collected in the range $4° < 2\theta < 50°$ using the $\omega-2\theta$ scan technique. There was no significant change in intensity during 66 h exposure time. Corrections were made for Lorentz and polarization effects. The position of the Ru atom in the crystallographic asymmetric unit was derived from the Patterson map and refined by least squares. Successive iterations of difference Fourier maps and least-squares cycles led to the development and convergent refinement of the remainder of the structure.

Results and Discussion

The rationale for the preparative reactions used in this work has already been explained. In our preparation of *cis*-$OsCl_2(dppm)_2$ the chemistry is more straightforward than that used previously [2] where it was first necessary to prepare $[Os_2Cl_3(PEt_2Ph)_6]Cl$ and then react this with dppm. Our procedure consists of reduction of $OsCl_6^{2-}$ with Na/Hg and reaction of the Os^{II} *in situ* with dppm (*i.e.*, it is a one-pot reaction using a commonly available starting material).

TABLE II. Positional Parameters and Their Estimated Standard Deviations in *cis*-$OsCl_2(dppm)_2 \cdot CHCl_3$ (*1*).

Atom	x	y	z	B (A2)
Os	0.16509(3)	0.09005(1)	0.29206(2)	2.792(6)
Cl(1)	0.0910(2)	0.1231(1)	0.4030(1)	4.00(5)
Cl(2)	0.0764(2)	0.1769(1)	0.2198(1)	4.11(6)
Cl(3)	0.3370(3)	0.2956(2)	0.9043(3)	9.6(1)*
Cl(4)	0.4853(4)	0.2059(2)	0.9385(3)	11.2(1)*
Cl(5)	0.3558(4)	0.2228(3)	0.7730(3)	13.2(2)*
P(1)	0.2821(2)	0.0284(1)	0.3791(2)	3.25(5)
P(2)	0.3209(2)	0.1406(1)	0.3433(2)	3.29(5)
P(3)	0.1844(2)	0.0495(1)	0.1713(1)	3.46(5)
P(4)	0.0256(2)	0.0270(1)	0.2383(1)	3.25(5)
C(1)	0.3988(7)	0.0755(4)	0.3904(6)	3.8(2)
C(2)	0.0783(7)	−0.0061(4)	0.1571(5)	3.6(2)
C(3)	0.427(1)	0.2592(6)	0.8624(8)	7.8(3)*
C(11)	0.3350(7)	0.1950(4)	0.4251(6)	3.7(2)
C(12)	0.2559(8)	0.2348(4)	0.4188(7)	4.9(3)
C(13)	0.2637(9)	0.2777(5)	0.4820(7)	6.1(3)
C(14)	0.3514(9)	0.2788(5)	0.5490(7)	5.6(3)
C(15)	0.4313(9)	0.2396(4)	0.5550(6)	5.7(3)
C(16)	0.4235(8)	0.1974(4)	0.4934(6)	4.7(3)
C(21)	0.2811(7)	0.0163(4)	0.4879(6)	4.0(2)
C(22)	0.2879(7)	0.0646(5)	0.5394(6)	4.2(2)
C(23)	0.2865(8)	0.0572(5)	0.6222(7)	5.5(3)
C(24)	0.2759(9)	0.0018(5)	0.6532(7)	5.6(3)
C(25)	0.729(1)	0.0462(6)	0.3975(7)	7.0(4)
C(26)	0.272(1)	−0.0397(5)	0.5183(7)	5.9(3)
C(31)	0.3921(8)	0.1760(4)	0.2767(6)	4.2(2)
C(32)	0.3343(8)	0.1965(4)	0.1995(6)	4.8(2)
C(33)	0.388(1)	0.2216(5)	0.1461(7)	6.5(3)
C(34)	0.493(1)	0.2260(6)	0.1701(8)	7.5(4)
C(35)	0.5485(9)	0.2057(6)	0.2482(9)	8.8(4)
C(36)	0.4994(8)	0.1803(5)	0.3027(8)	6.0(3)
C(41)	0.3180(8)	−0.0441(4)	0.3498(6)	4.1(2)
C(42)	0.4199(7)	−0.0603(4)	0.3552(6)	4.4(2)
C(43)	0.4428(9)	−0.1157(4)	0.3309(7)	5.2(3)
C(44)	0.3641(9)	−0.1571(5)	0.3040(7)	5.7(3)
C(45)	0.2622(9)	−0.1428(4)	0.3008(7)	5.2(3)
C(46)	0.2378(8)	−0.0857(4)	0.3251(7)	4.9(3)
C(51)	0.2987(7)	0.0103(4)	0.1626(6)	3.9(2)
C(52)	0.3938(7)	0.0396(5)	0.1826(6)	4.3(2)
C(53)	0.4840(8)	0.0104(5)	0.1755(7)	5.4(3)
C(54)	0.480(1)	−0.0477(5)	0.1473(8)	6.7(3)
C(55)	0.3844(9)	−0.0764(5)	0.1278(8)	6.1(3)
C(56)	0.2921(9)	−0.0485(5)	0.1338(6)	5.1(3)
C(61)	0.1495(8)	0.0910(4)	0.0738(5)	4.1(2)
C(62)	0.0465(9)	0.1074(5)	0.0416(6)	5.3(3)
C(63)	0.017(1)	0.1422(5)	−0.0344(6)	6.7(3)
C(64)	0.095(1)	0.1609(5)	−0.0707(6)	6.9(4)
C(65)	0.696(1)	0.3563(5)	0.4618(7)	7.1(4)
C(66)	0.2260(9)	0.1085(5)	0.0352(6)	5.4(3)
C(71)	−0.0055(7)	−0.0328(4)	0.2994(5)	3.5(2)
C(72)	−0.0545(8)	−0.0819(4)	0.2591(6)	4.8(3)
C(73)	−0.0796(9)	−0.1276(5)	0.3076(7)	5.9(3)
C(74)	−0.0480(9)	−0.1241(4)	0.3937(7)	5.4(3)
C(75)	−0.0018(8)	−0.0748(4)	0.4314(6)	4.9(3)
C(76)	0.0205(7)	−0.0284(4)	0.3846(6)	4.0(2)
C(81)	−0.1042(7)	0.0529(4)	0.1852(5)	3.8(2)
C(82)	−0.1668(8)	0.0239(5)	0.1148(7)	5.4(3)
C(83)	−0.2692(9)	0.0459(6)	0.0832(8)	7.0(3)
C(84)	−0.3068(9)	0.0911(6)	0.1156(8)	6.8(3)
C(85)	−0.2438(8)	0.1193(6)	0.1859(8)	6.3(3)
C(86)	−0.1415(8)	0.1001(5)	0.2210(7)	5.0(3)

Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: (4/3)* [a2*B(1,1) + b2*B(2,2) + c2*B(3,3) + ab(cos gamma)*B(1,2) + ac(cos beta)*B(1,3) + bc(cos alpha)*B(2,3)]

TABLE III. Positional Parameters and Their Estimated Standard Deviations in *cis*-$RuCl_2(dppm)_2 \cdot CHCl_3$ (*2*).

Atom	x	y	z	B (A2)
Ru	0.16613(6)	0.09048(3)	−0.20777(4)	1.89(1)
Cl1	0.0925(2)	0.1234(1)	−0.0970(1)	2.99(6)
Cl2	0.0791(2)	0.1769(1)	−0.2813(2)	3.09(6)
Cl3	0.3379(3)	0.2968(2)	0.4036(3)	8.2(1)
Cl4	0.4870(3)	0.2073(2)	0.4376(4)	9.6(1)
Cl5	0.3588(5)	0.2233(3)	0.2732(3)	11.6(2)
P1	0.1876(2)	0.0499(1)	−0.3279(2)	2.48(6)
P2	0.0270(2)	0.0277(1)	−0.2612(2)	2.39(5)
P3	0.2819(2)	0.0281(1)	−0.1204(2)	2.49(6)
P4	0.3213(2)	0.1412(1)	−0.1566(2)	2.28(5)
C1	0.0827(7)	−0.0053(4)	−0.3412(6)	2.8(2)
C2	0.3986(8)	0.0761(4)	−0.1103(6)	3.0(2)
C3	0.426(1)	0.2589(6)	0.3625(8)	6.0(4)
C11	−0.1010(7)	0.0541(5)	−0.3145(6)	2.9(2)
C12	−0.1410(8)	0.0995(5)	−0.2801(7)	4.0(3)
C13	−0.2429(9)	0.1190(6)	−0.3149(8)	5.0(3)
C14	−0.3026(8)	0.0897(6)	−0.3839(8)	5.6(3)
C15	−0.2646(9)	0.0432(7)	−0.4185(8)	6.1(4)
C16	0.3377(9)	0.4756(6)	0.1156(7)	4.6(3)
C21	−0.0055(8)	−0.0323(4)	−0.2009(6)	2.8(2)
C22	0.0193(8)	−0.0274(5)	−0.1156(6)	3.1(2)
C23	−0.0024(9)	−0.0737(5)	−0.0671(7)	4.0(3)
C24	−0.0505(9)	−0.1238(5)	−0.1075(7)	4.6(3)
C25	0.5776(9)	0.3719(5)	0.6926(7)	4.8(3)
C26	−0.0533(9)	−0.0826(5)	−0.2413(7)	4.2(3)
C31	0.3168(8)	−0.0445(4)	−0.1489(6)	2.8(2)
C32	0.2397(8)	−0.0865(5)	−0.1743(7)	3.7(3)
C33	0.264(1)	−0.1422(5)	−0.1973(7)	4.6(3)
C34	0.365(1)	−0.1578(5)	−0.1927(7)	4.8(3)
C35	0.4442(9)	−0.1162(5)	−0.1680(7)	4.3(3)
C36	0.4199(8)	−0.0593(4)	−0.1454(7)	3.5(3)
C41	0.3031(8)	0.0092(4)	0.6635(6)	3.0(2)
C42	0.3970(8)	0.0400(5)	−0.3165(6)	3.8(3)
C43	0.4873(9)	0.0096(6)	−0.3241(7)	4.9(3)
C44	0.481(1)	−0.0477(6)	−0.3518(8)	5.4(3)
C45	0.385(1)	−0.0771(5)	−0.3702(8)	5.5(3)
C46	0.7050(9)	0.0484(5)	0.3649(6)	3.8(3)
C51	0.3364(8)	0.1953(4)	−0.0757(6)	2.7(2)

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Table III. *(continued)*

Atom	x	y	z	B (A2)
C52	0.2575(9)	0.2365(5)	−0.0809(7)	4.0(3)
C53	0.765(1)	0.2207(5)	0.4816(8)	5.1(3)
C54	0.354(1)	0.2806(5)	0.0486(7)	4.7(3)
C55	0.4327(9)	0.2403(5)	0.0539(7)	4.3(3)
C56	0.4236(8)	0.1977(5)	−0.0072(6)	3.5(3)
C61	0.3922(8)	0.1754(4)	−0.2225(6)	3.1(2)
C62	0.336(1)	0.1972(4)	−0.3005(6)	4.3(3)
C63	0.393(1)	0.2218(6)	−0.3533(8)	6.0(4)
C64	0.501(1)	0.2245(6)	−0.3282(8)	6.2(4)
C65	0.553(1)	0.2043(6)	−0.2502(9)	5.9(4)
C66	0.5019(9)	0.1788(5)	−0.1955(7)	4.4(3)
C71	0.6540(8)	0.4081(4)	0.0731(6)	3.2(2)
C72	0.7291(9)	0.3918(5)	0.0346(7)	4.4(3)
C73	0.704(1)	0.3568(6)	0.9646(8)	6.0(4)
C74	0.599(1)	0.3392(5)	0.9308(7)	5.4(3)
C75	0.022(1)	0.1421(6)	−0.5328(7)	5.6(4)
C76	0.0503(9)	0.1071(5)	−0.4604(6)	4.0(3)
C81	0.7812(8)	0.4834(4)	0.4881(6)	2.9(2)
C82	0.2876(8)	0.0653(5)	0.0398(6)	3.6(3)
C83	0.2856(9)	0.0585(6)	0.1220(7)	4.7(3)
C84	0.7257(9)	−0.0026(6)	0.8469(7)	5.0(3)
C85	0.229(1)	0.4545(6)	0.3968(8)	6.3(4)
C86	0.227(1)	0.4610(5)	0.4803(6)	4.6(3)

Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: (4/3)* [a2*B(1,1) + b2*B(2,2) + c2*B(3,3) + ab(cos gamma)*B(1,2) + ac(cos beta)*B(1,3) + bc(cos alpha)*B(2,3)].

TABLE IV. Positional Parameters and Their Estimated Standard Deviations in *trans*-$RuCl_2(dppm)_2$ (*3*).

Atom	x	y	z	B (A2)
Ru	0.000	0.000	0.000	2.163(8)
Cl(1)	0.38414(9)	0.4276(1)	0.38164(6)	3.20(2)
P(1)	0.65614(9)	0.3712(1)	0.48053(6)	2.48(2)
P(2)	0.96158(9)	0.2085(1)	0.03150(6)	2.36(2)
C	0.4303(3)	0.7746(4)	0.5186(2)	2.53(9)
C(1)	0.8148(3)	0.2843(4)	−0.0040(2)	2.50(9)
C(2)	0.2106(4)	0.6386(4)	0.0647(3)	3.5(1)
C(3)	0.3232(4)	0.5814(5)	0.0871(3)	4.2(1)
C(4)	0.4099(4)	0.6008(5)	0.0501(3)	4.5(1)
C(5)	0.6122(4)	0.3228(5)	0.0095(3)	5.3(1)
C(6)	0.7251(4)	0.2668(5)	0.0335(3)	4.2(1)
C(7)	0.4891(3)	0.7862(4)	0.3794(2)	2.50(9)
C(8)	−0.0111(4)	0.4145(4)	0.1267(2)	3.7(1)
C(9)	0.0379(4)	0.4794(4)	0.1893(3)	4.0(1)
C(10)	0.1091(4)	0.4192(5)	0.2485(3)	4.3(1)
C(11)	0.1289(5)	0.2935(5)	0.2442(3)	4.7(1)
C(12)	0.0818(4)	0.2265(4)	0.1812(3)	3.9(1)
C(13)	0.2031(3)	0.6460(4)	0.4489(2)	2.55(8)
C(14)	0.1139(4)	0.5560(5)	0.4453(3)	3.6(1)
C(15)	0.0054(4)	0.5625(5)	0.3928(3)	4.1(1)
C(16)	−0.0132(4)	0.6566(5)	0.3423(3)	4.3(1)
C(17)	0.4270(5)	0.2452(5)	0.1555(3)	4.6(1)

TABLE IV. *(continued)*

Atom	x	y	z	B (A2)
C(18)	0.3180(4)	0.2406(4)	0.1022(3)	3.7(1)
C(19)	0.7086(3)	0.3627(4)	0.3961(2)	2.96(9)
C(20)	0.6655(4)	0.4463(5)	0.3392(3)	4.0(1)
C(21)	0.7036(5)	0.4375(6)	0.2758(3)	5.2(1)
C(22)	0.7876(5)	0.3479(6)	0.2687(3)	5.4(1)
C(23)	0.8311(5)	0.2662(6)	0.3238(3)	5.4(1)
C(24)	0.7925(4)	0.2736(5)	0.3878(3)	4.1(1)
H(1)	0.968(3)	0.710(3)	0.070(2)	1.8(7)*
H(2)	0.109(3)	0.354(3)	−0.001(2)	2.1(8)*
H(3)	0.158(3)	0.628(4)	0.089(2)	3.4(9)*
H(4)	0.333(3)	0.533(3)	0.127(2)	3.3(9)*
H(5)	0.486(3)	0.565(4)	0.067(2)	3.6(9)*
H(6)	0.553(4)	0.304(4)	0.033(2)	5(1)*
H(7)	0.764(3)	0.713(4)	0.432(2)	3.2(9)*
H(8)	0.944(3)	0.446(3)	0.091(2)	1.7(7)*
H(9)	0.023(4)	0.560(4)	0.193(2)	5(1)*
H(10)	0.148(4)	0.463(4)	0.292(2)	5(1)*
H(11)	0.318(4)	0.751(4)	0.218(2)	4(1)*
H(12)	0.406(3)	0.637(4)	0.324(2)	4(1)*
H(13)	0.876(4)	0.509(4)	0.524(2)	4(1)*
H(14)	0.952(4)	0.494(4)	0.393(2)	5(1)*
H(15)	0.922(3)	0.660(4)	0.314(2)	4(1)*
H(16)	0.436(4)	0.304(4)	0.187(2)	6(1)*
H(17)	0.254(3)	0.295(4)	0.103(2)	3.2(9)*
H(18)	0.611(3)	0.505(4)	0.349(2)	3.1(8)*
H(19)	0.674(4)	0.494(4)	0.245(2)	5(1)*
H(20)	0.816(4)	0.347(4)	0.229(2)	5(1)*
H(21)	0.613(4)	0.706(5)	0.177(3)	7(1)*
H(22)	0.678(4)	0.711(4)	0.071(2)	5(1)*

Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: (4/3)* [a2*B(1,1) + b2*B(2,2) + c2*B(3,3) + ab(cos gamma)*B(1,2) + ac(cos beta)*B(1,3) + bc(cos alpha)*B(2,3)].

The manner in which we obtain a mixture of *cis* and *trans*-$RuCl_2(dppm)_2$ is also straightforward but clearly has the disadvantage of producing a mixture of both isomers which then have to be separated. The reduction of the Ru^{IV} in $Ru_2OCl_{10}{}^{4-}$ to Ru^{II} is probably effected by the ethanol, but we cannot say with certainty that the excess dppm does not at least partially also function as a reductant. It is, of course, well known that alcohols can cause reduction of group VIII metals; for example, the Chatt and Hayter [2] preparation of *trans*-$MCl_2(diphos)_2$ species relies on this since the starting materials are the trihalides and no specific reducing agent is used.

The fact that no $Ru_2(\mu\text{-}O)(\mu\text{-}dppm)_2Cl_6$ product was obtained, even though the osmium analog exists is in keeping with the superior stability of the higher oxidation states for the heavier metal that is a general trend among the transition metals.

TABLE V. Some Bond Distances and Angles in *cis*-$OsCl_2(dppm)_2 \cdot CHCl_3$ (*1*) and *cis*-$RuCl_2(dppm)_2 \cdot CHCl_3$ (*2*).

	Bond Distances, Å	
	1	*2*
M–Cl(1)	2.448(2)	2.440(2)
M–Cl(2)	2.455(2)	2.451(13)
M–P(1)	2.306(2)	2.303(11)
M–P(2)	2.338(2)	2.335(10)
M–P(3)	2.297(2)	2.318(10)
M–P(4)	2.339(2)	2.338(11)
P(1)–C(1)	1.867(8)	1.860(5)
P(2)–C(1)	1.865(8)	1.861(5)
P(3)–C(2)	1.875(8)	1.884(5)
P(4)–C(2)	1.853(8)	1.859(4)
	Bond Angles, deg.	
Cl(1)–M–Cl(2)	83.08(7)	84.1(5)
Cl(1)–M–P(1)	93.37(7)	163.4(5)
Cl(1)–M–P(2)	94.42(7)	92.0(5)
Cl(1)–M–P(3)	162.56(7)	92.9(4)
Cl(1)–M–P(4)	91.91(7)	94.2(5)
Cl(2)–M–P(1)	163.56(7)	92.3(4)
Cl(2)–M–P(2)	92.65(7)	94.4(4)
Cl(2)–M–P(3)	92.88(7)	164.0(5)
Cl(2)–M–P(4)	94.51(7)	92.5(4)
P(1)–M–P(2)	71.56(7)	72.1(3)
P(1)–M–P(3)	94.99(8)	94.8(4)
P(1)–M–P(4)	101.67(7)	102.2(4)
P(2)–M–P(3)	102.58(8)	101.4(4)
P(2)–M–P(4)	170.97(8)	171.2(5)
P(3)–M–P(4)	71.58(8)	72.0(3)
P(1)–C(1)–P(2)	93.4(4)	94.4(2)
P(3)–C(2)–P(4)	93.3(4)	93.9(2)
M–P(1)–C(1)	96.9(3)	96.3(3)
M–P(2)–C(1)	95.9(3)	95.2(3)
M–P(3)–C(2)	97.0(3)	95.8(3)
M–P(4)–C(2)	96.2(3)	95.8(3)

The complexes crystallize in the monoclinic space group $P2_1/n$. Crystallographic data are presented in Table I. Both *cis*-isomers contain one $CHCl_3$ molecule as a solvent of crystallization. The unit cell dimensions of the *cis*-isomers are very similar, and the structures are isotypic, but they differ from that of the *trans*-isomer (Table I). The positional parameters of the compounds are given in Tables II, III and IV, along with the equivalent isotropic thermal parameters. The anisotropic vibrational parameters show no unusual features, as is apparent from the figures, but lists are available (from FAC) to anyone interested.

Important bond distances and bond angles of *cis*-$OsCl_2(dppm)_2 \cdot CHCl_3$ (*1*), *cis*-$RuCl_2(dppm)_2 \cdot CHCl_3$ (*2*) and *trans*-$RuCl_2(dppm)_2$ (*3*) are presented in Tables V and VI. Perspective views of the molecules are shown in Figs. 1, 2, and 3.

TABLE VI. Some Bond Distances and Angles in *trans*-$RuCl_2(dppm)_2$, (*3*).

Bond Distances, Å	
Ru–Cl(1)	2.426(1)
Ru–P(1)	2.340(1)
Ru–P(2)	2.367(1)
P(1)–C	1.840(5)
P(2)–C	1.858(5)
Bond Angles, Deg.	
Cl(1)–Ru–Cl(1)′	180.00(2)
Cl(1)–Ru–P(1)	86.19(4), 93.81(4)
Cl(1)–Ru–P(2)	80.77(4), 99.23(4)
P(1)–Ru–P(1)′	180.00(2)
P(1)–Ru–P(2)	71.39(4), 108.61(4)
P(2)–Ru–P(2)′	180.00(2)
P(1)–C–P(2)	95.9(2)
Ru–P(1)–C	93.9(2)
Ru–P(2)–C	92.6(2)

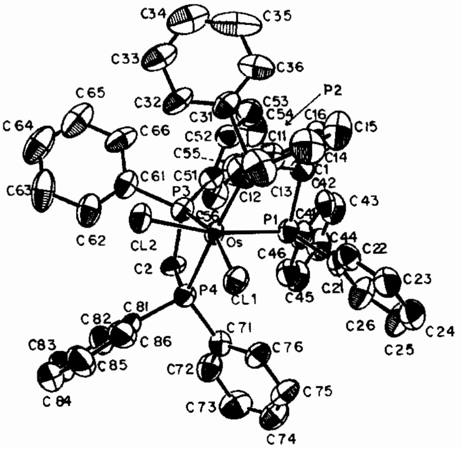

Fig. 1. An ORTEP drawing of the *cis*-$OsCl_2(dppm)_2$. Each atom is represented by its ellipsoid of thermal vibration scaled to give a 40% probability representation of the electron density.

In *1* and *2*, the Cl–M–Cl angles which are 83.08(7) and 84.1(5) are less than the ideal value of 90°. The angle between *cis* phosphorus atoms from different dppm ligands are considerably higher than 90°. The chelate ring is very much distorted as is evidenced from the P–Os–P angle which is *ca.* 72° The steric strain is also imposed on the C1, C2 and phosphorus atoms of the dppm ligands (Figs 1 and 2).

The complex *3* has a center of inversion (Fig. 3). *Trans* disposition of the ligands imposes less steric strain compared to that in *cis*-isomers. The P–Ru–P angle of the chelate ring is *ca.* 71° and the P(1)–C–

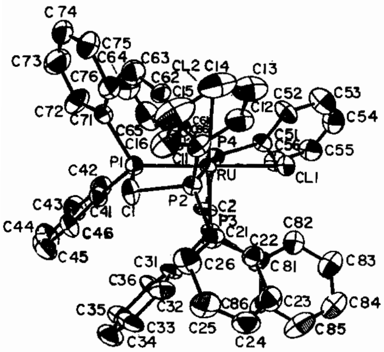

Fig. 2. Atom numbering scheme used for the *cis*-RuCl$_2$-(dppm)$_2$ with atoms represented by thermal vibration ellipsoids at the 40 % level.

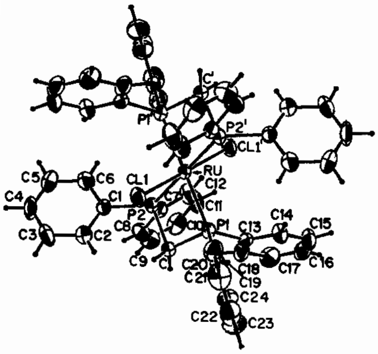

Fig. 3. An ORTEP drawing of the centrosymmetric molecule *trans*-RuCl$_2$(dppm)$_2$ with each atom represented by its ellipsoid of thermal vibration at the 40% level.

P(2) angle is *ca.* 96°. The angles Cl(1)–Ru–P(1) and Cl(1)–Ru–P(2) have two different values which means that the pseudoplane made by P(1)–P(2)–P(1)'–P(2)' is not perpendicular to the Cl(1)–Ru–Cl(1)' axis.

The bond lengths from metal to coordinated ligands are similar to those found in many other compounds [7–9]. Metal(II)–chlorine, phosphorus distances lie in the range 2.42–2.46 Å and 2.29–2.37 Å, respectively. Phosphine–carbon distances are *ca.* 1.86 Å. The metal–phosphorus distance is slightly higher in the *trans*-isomer than in the *cis* one. We may note that there is no significant difference in the apparent covalent radii of Ru^{II} and Os^{II} in the two *cis* compounds.

The structural results obtained for these three compounds can be compared with those available for some related ones, namely, *trans*-Ru(mph)$_2$(PPh$_3$)$_2$ [7], Ru(Ph$_2$Ppy)(CO)$_2$Cl$_2$ [8], Os$_2$N[S$_2$CN(CH$_3$)$_2$]$_5$ [10], Ru(CO)Cl(PPh$_3$)$_2$(PhCOO) [11], and Ru(PhNpy)$_2$(PPh$_3$)$_2$ [12] (where mhp = 6-methyl-2-pyridinolato, Ph$_2$PPy = 2-diphenylphosphinopyridine and PhNpy = anion of 2-anilinopyridine). The four-membered chelate rings are compressed considerably from the ideal value of 90° in all cases: O–Ru–N, 61.8°, P–Ru–N, 68.7°, S–Os–S, 74.2°, O–Ru–O, 61°; and N–Ru–N, 62.3°. The extent of compression is in the order PhCOO > mhp > PhNPy > Ph$_2$Ppy > dppm > S$_2$CN(CH$_3$)$_2$. Clearly, ligands with larger coordinating atoms, P, P or S, S, have larger bites, as would have been expected.

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