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Diosmium and Dirhodium Compounds Containing a Cisoid Arrangement of 2-Diphenylphosphinopyridine Bridges

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Abstract

Two new compounds with a novel cisoid arrangement of bridging 2-diphenylphosphinopyridine (Ph_2Ppy) have been synthesized. They have been prepared from the tetraacetate compounds and show varying degrees of substitution of the carboxylate ligands. $Os_2(O_2CCH_3)(Ph_2Ppy)_2Cl_4$ (**1**) has been isolated from the reaction of Ph_2Ppy with $Os_2(O_2CCH_3)_4Cl_2$. It has been obtained in two crystalline forms: as a dichloromethane adduct (**1a**) and as an acetone adduct (**1b**). Compound **1a** crystallizes in the monoclinic space group $P2_1/n$ with a = 10.496(3), b = 20.688(5), c = 18.440(5) Å, β = 91.62(2)°, V = 4003(3) Å^3 and Z = 4. Compound **1b** crystallizes in the monoclinic space group $P2_1/c$ with a = 18.977(5), b = 10.469(2), c = 20.737(6) Å, β = 92.36(2)°, V = 4116(3) Å^3 and Z = 4. The molecule of **1** contains a cisoid arrangement of the two Ph_2Ppy ligands arranged in a head-to-tail fashion, one bridging acetate ion and four chloride ions. The metal–metal distance is 2.395(1) Å in **1a** and 2.388(1) Å in **1b** and the formal bond order is 2.5. $Rh_2(O_2CCH_3)_2(Ph_2Ppy)_2Cl_2$ (**2**) has been isolated from the reaction of $Rh_2(O_2CCH_3)_4(MeOH)_2$ with Ph_2Ppy in toluene in the presence of LiCl. Compound **2** crystallizes in the tetragonal space group $P\bar{4}2_1c$ with $a = b$ = 22.203(3), c = 17.049(2) Å, V = 8404(2) Å^3 and Z = 8. The two Ph_2Ppy ligands are arranged in a cisoid fashion, along with two bridging acetate groups and two axial chloride ions. The rhodium–rhodium distance is 2.518(1) Å.

Introduction

Until relatively recently, the chemistry of compounds containing bonds between metal atoms of group 8, such as Os and Rh has shown little diversity, as compared to that of the earlier transition elements such as Mo, W and Re. To a large extent for Os and almost exclusively for Rh, the ligands occurring in Os_2^{n+} (n = 5, 6) and Rh_2^{4+} complexes have been carboxyl anions, or fairly homologous species such as amidato ions [1]. In this paper we present some results that contribute to broadening this chemistry. A preliminary report of some of these results has appeared [2].

More or less concurrently with the work reported here, in which the 2-diphenylphosphinopyridine ligand is employed, there have been some other studies in which other than carboxylate ligands have been introduced into diosmium chemistry [3–5] as well as into the chemistry of dirhodium [6]. Comparisons will be made in the 'Discussion'. It may be noted here that while the reactions we are about to describe display a number of similarities, they also reflect characteristic differences in the behavior of the Os_2^{6+} and Rh_2^{4+} units, wherein the former undergoes reduction to Os_2^{5+} concomitant with ligand substitution, whereas only ligand exchanges occur on Rh_2^{4+}.

Experimental

$Os_2(O_2CCH_3)_4Cl_2$ and $Rh_2(O_2CCH_3)_4(MeOH)_2$ were prepared by literature procedures [7, 8]. 2-Diphenylphosphinopyridine was prepared according to a modified procedure of Walton *et al.* [9] and was recrystallized from ethanol. Its purity was checked by ^{31}P NMR**. LiCl was dried in an oven at 110 °C for several hours and then handled under argon. Solvents were freshly distilled from the appropriate drying agents. All reactions were carried under an argon atmosphere unless otherwise stated.

Preparation of $Os_2(O_2CCH_3)(Ph_2Ppy)_2Cl_4$ *(1)*

This compound was originally prepared by the action of an excess of Ph_2Ppy on $Os_2(O_2CCH_3)_4Cl_2$ in toluene in the presence of an excess of Me_3SiCl. The yield of this reaction was low, *ca.* 30%, and we have now developed a method for the preparation

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**$^{31}P\{^1H\}$ NMR (in $CDCl_3$, referenced to 85% H_3PO_4 as an external standard) – 2.83 ppm.

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of **1** in better yield. $Os_2(O_2CCH_3)_4Cl_2$, 100 mg; LiCl, 0.6 g; Ph_2Ppy, 0.3 g and 10 ml of toluene were refluxed and stirred for 4 days. During that time the $Os_2(O_2CCH_3)_4Cl_2$ gradually disappeared and a brown product was deposited. The reaction mixture was cooled and filtered. Remaining solids were extracted with CH_2Cl_2 to give a red–brown solution. This solution was layered with hexane, and in a few days a crop of needle-shaped crystals of **1a** was deposited. These were filtered, washed with ether to remove any excess of Ph_2Ppy and dried. The yield was 0.125 g (75%). This compound has spectral and electrochemical properties identical to the authentic sample obtained from the original preparation [2].

X-ray quality crystals of **1b** were grown by slow evaporation of an acetone solution of **1**.

Preparation of $Rh_2(O_2CCH_3)_2(Ph_2Ppy)_2Cl_2$ *(2)*

$Rh_2(O_2CCH_3)_4(MeOH)_2$, 51 mg (0.1 mmol), Ph_2Ppy, 78 mg (0.3 mmol) and 0.4 g of LiCl were suspended in toluene. The reaction mixture was refluxed for 24 h, during which time the orange–pink precipitate of the product was formed. The reaction mixture was cooled and filtered. The solid residue was extracted with CH_2Cl_2 until the washings were colorless. The dichloromethane solution of the product containing an excess of the ligand was evaporated, and the residue was washed several times with ether to remove Ph_2Ppy. The yield was 72 mg (77%) of a pink, microcrystalline solid. UV (CH_2Cl_2 solution): λ_{max} = 503 nm (ϵ = 1050 M^{-1} cm^{-1}), λ_{max} = 310 nm (ϵ = 20 400 M^{-1} cm^{-1}). X-ray quality crystals were grown by the following method: a dichloromethane solution of **2** was placed in a 5 mm NMR tube, which was then placed inside a large test tube filled with ether. The large test tube was closed with a stopper. During a slow diffusion process (2–3 weeks) crystals of $Rh_2(O_2CCH_3)_2(Ph_2Ppy)_2Cl_2$ were deposited on the walls of the NMR tube.

X-ray Crystallographic Procedures

Single crystals were grown as described above. Cell dimensions and the Laue class were confirmed with axial photographs. The intensity data for **1a** and **1b** were collected with a CAD-4 autodiffractometer employing graphite-monochromated Mo Kα ($\bar{\lambda}$ = 0.71073 Å) radiation. The intensity data for **2** were collected with a Nicolet four-circle diffractometer employing Ni filtered Cu Kα ($\bar{\lambda}$ = 1.54184 Å) radiation. Data reduction was performed according to procedures routine in our laboratory. Calculations were done on a MicroVAXII with an SDP-plus package software. Crystallographic data are summarized in Table I.

$Os_2(O_2CCH_3)(Ph_2Ppy)_2Cl_4 \cdot 2CH_2Cl_2$ *(1a)*

The positions of the two Os atoms were obtained from the Patterson function, and the remaining non-hydrogen atoms were located in an alternating series of least-squares refinements and difference Fourier maps. An empirical absorption correction based on psi scans [10] was applied and in addition the structure was corrected for absorption with a program DIFABS [11]. The structure was refined using 2902 reflections with $F_o^2 > 3\sigma(F_o)^2$ to give residuals of $R = 0.0515$ and $R_w = 0.0566$. All of the non-hydrogen atoms were refined anisotropically with the exception of N(2), C(11), C(18) and C(27).

$Os_2(O_2CCH_3)(Ph_2Ppy)_2Cl_4 \cdot 2(CH_3)_2CO$ *(1b)*

The positions of the two Os atoms were located from the Patterson function, and the solution of the structure proceeded routinely. Empirical absorption corrections based on psi scans as well as the program DIFABS were applied to the data. Because of the more regular shape of the crystal, this structure did not suffer from absorption problems as much as did the structure of **1a**. In the final cycle of the refinement 5487 data with $F_o^2 > 3\sigma(F_o^2)$ were used to refine 449 parameters to give $R = 0.046$ and $R_w = 0.062$. The largest peak in a final difference Fourier map was 1.6 e/Å^3 and was a ghost of an Os atom.

$Rh_2(O_2CCH_3)_2(Ph_2Ppy)_2Cl_2$ *(2)*

The space group, $P\bar{4}2_1c$ (No. 114) is uniquely determined from the systematic absences. Positions of the two Rh atoms were obtained from the direct methods program, MULTAN. The rest of the non-hydrogen atoms were located by a series of alternating least-squares cycles and difference Fourier maps. At the end of the refinement the other enantimorph was also refined and the one giving lower residuals is reported here. In a final cycle 3264 reflections with $F_o^2 > 3\sigma(F_o^2)$ were used to refine 451 parameters to give $R = 0.0538$ and $R_w = 0.0712$. The largest peak in the final difference Fourier map was 1.2 e/Å^3.

Molecular Structures

$Os_2(O_2CCH_3)(Ph_2Ppy)_2Cl_4$ *(1)*

Two different crystals of **1** have been characterized, namely, **1a** and **1b**, which are dichloromethane and acetone solvates, respectively. In neither case does the solvent molecule make any close contacts with the osmium dimer, and close examination of bond distances and bond angles for **1a** and **1b** shows only minor differences in the dimensions of the Os_2^{5+} complex. Therefore only one structure, **1b**, will be discussed in detail. Molecules of **1b** reside on a general position in the unit cell. Atomic fractional coordinates are presented in Table II. Selected bond distances and angles for **1a** and **1b** are presented in Table III. Two cisoid Ph_2Ppy ligands are bonded in a head-to-tail fashion, presumably to relieve steric

TABLE I. Crystal Data for **1a**, **1b** and **2**

	1a	**1b**	**2**
Formula	$Os_2Cl_6P_2O_2N_2C_{37}H_{33}$	$Os_2Cl_4P_2O_3N_2C_{39}H_{37}$	$Rh_2Cl_2P_2N_2O_4C_{38}H_{34}$
Formula weight	1192.75	1165.90	921.37
Space group	$P2_1/n$	$P2_1/c$	$P\bar{4}2_1c$
Systematic absences	$0k0$: $k \neq 2n$	$0k0$: $k \neq 2n$	hhl: $l \neq 2n$
	$h0l$: $h + l \neq 2n$	$h0l$: $l \neq 2n$	$h00$: $h \neq 2n$, $00l$: $l \neq 2n$
a (Å)	10.496(3)	18.977(5)	22.203(3)
b (Å)	20.688(5)	10.469(2)	22.203(3)
c (Å)	18.440(5)	20.737(6)	17.049(2)
α (°)	90.0	90.0	90.0
β (°)	91.62(2)	92.36(2)	90.0
γ (°)	90.0	90.0	90.0
V (Å^3)	4003(3)	4116(3)	8404(2)
Z	4	4	8
D_{calc} (g/cm^3)	1.980	1.881	1.456
Crystal size (mm)	0.06 × 0.08 × 0.4	0.08 × 0.4 × 0.6	0.1 × 0.12 × 0.62
μ(Mo Kα) (cm^{-1})	68.73	65.53	87.456
Data collection instrument	CAD-4	CAD-4	P$\bar{1}$
Radiation (monochromated in incident beam)	Mo Kα (λ_α = 0.71073 Å)		Cu Kα (λ = 1.54184 Å)
Orientation reflections, number, range (2θ)	25, $14 < 2\theta < 27°$	25, $10 < 2\theta < 26$	15, $2\theta > 40°$
Temperature (°C)	22	22	20
Scan method	ω	$\omega-2\theta$	$\omega-2\theta$
Data collection range, 2θ (°)	4, 45	4, 50	3, 136.3
No. unique data, total with $F_o^2 > 3\sigma(F_o^2)$	5889, 2902	7178, 5487	4199, 3264
No. parameters refined	460	449	451
Trans. factors, max., min.	0.9941, 0.7929	0.9980, 0.2510	1.000, 0.391
R[a]	0.0515	0.046	0.0538
R_w[b]	0.0566	0.062	0.0712
Quality-of-fit indicator[c]	1.19	1.779	1.500
Largest shift/e.s.d., final cycle	0.34	0.41	0.05
Largest peak (e/Å^3)	1.23	1.6	1.2

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

TABLE II. Fractional Coordinates and Isotropic-equivalent Displacement Parameters for **1a** and **1b**[a]

Atom	x	y	z	B (Å^2)
Compound **1a**				
Os(1)	0.11845(8)	0.07775(4)	0.20967(5)	2.24(2)
Os(2)	0.26385(9)	0.16314(4)	0.24114(5)	2.42(2)
Cl(1)	−0.0171(5)	0.0114(3)	0.1309(3)	3.3(1)
Cl(2)	−0.0432(5)	0.0727(3)	0.2971(3)	3.7(1)
Cl(3)	0.3579(6)	0.2472(3)	0.3167(3)	4.0(1)
Cl(4)	0.2843(6)	0.2322(3)	0.1399(3)	3.7(1)
Cl(5)	0.6244(8)	0.3537(6)	0.2218(4)	8.6(3)
Cl(6)	0.860(1)	0.4249(5)	0.2239(7)	11.0(3)
P(1)	0.2659(5)	0.0629(3)	0.1192(3)	2.4(1)
P(2)	0.2805(6)	0.1024(3)	0.3475(3)	2.6(1)
O(1)	0.009(1)	0.1549(7)	0.1676(7)	2.6(3)
O(2)	0.096(1)	0.2164(7)	0.2552(8)	3.5(4)
N(1)	0.432(2)	0.1238(8)	0.207(1)	3.6(4)
N(2)	0.195(1)	−0.0002(8)	0.2682(8)	2.2(3)*
C(1)	0.427(2)	0.080(1)	0.151(1)	2.3(4)*
C(2)	0.538(2)	0.053(1)	0.125(1)	2.9(5)
C(3)	0.660(2)	0.074(1)	0.156(1)	4.4(6)
C(4)	0.663(2)	0.121(1)	0.209(1)	4.5(6)

(continued)

TABLE II. *(continued)*

Atom	x	y	z	B (Å^2)
C(5)	0.551(2)	0.146(1)	0.234(1)	3.5(5)
C(6)	0.246(2)	0.109(1)	0.035(1)	3.2(5)
C(7)	0.123(2)	0.127(1)	0.014(1)	4.2(6)
C(8)	0.100(2)	0.161(1)	−0.050(1)	4.8(6)
C(9)	0.202(2)	0.178(1)	−0.092(1)	4.5(7)
C(10)	0.328(3)	0.162(2)	−0.073(1)	6.7(8)
C(11)	0.347(3)	0.124(1)	−0.010(1)	5.6(7)
C(12)	0.282(2)	−0.0206(9)	0.090(1)	3.0(5)
C(13)	0.351(2)	−0.065(1)	0.133(1)	3.7(6)
C(14)	0.354(2)	−0.128(1)	0.115(1)	4.0(6)
C(15)	0.291(2)	−0.151(1)	0.052(1)	4.1(6)
C(16)	0.223(2)	−0.109(1)	0.007(1)	4.3(6)
C(17)	0.218(2)	−0.040(1)	0.026(1)	4.2(6)
C(18)	0.269(2)	0.016(1)	0.331(1)	3.2(5)*
C(19)	0.319(2)	−0.032(1)	0.375(1)	3.4(5)
C(20)	0.286(3)	−0.099(1)	0.355(1)	5.3(7)
C(21)	0.219(2)	−0.111(1)	0.294(1)	3.0(5)
C(22)	0.172(2)	−0.0599(9)	0.250(1)	2.9(5)
C(23)	0.167(2)	0.119(1)	0.423(1)	4.3(6)
C(24)	0.105(2)	0.1775(9)	0.423(1)	3.5(5)
C(25)	0.025(2)	0.190(1)	0.482(1)	5.3(7)
C(26)	0.014(2)	0.145(1)	0.537(1)	5.1(7)
C(27)	0.070(3)	0.086(1)	0.531(1)	5.8(7)*
C(28)	0.160(2)	0.073(1)	0.476(1)	5.9(7)
C(29)	0.434(2)	0.107(1)	0.395(1)	3.9(6)
C(30)	0.450(2)	0.156(1)	0.450(1)	4.6(5)
C(31)	0.578(2)	0.167(1)	0.480(1)	6.1(7)
C(32)	0.674(2)	0.126(2)	0.458(1)	7.3(8)
C(33)	0.661(2)	0.080(2)	0.403(1)	5.9(7)
C(34)	0.538(3)	0.069(1)	0.371(1)	6.0(7)
C(35)	0.705(3)	0.425(1)	0.253(2)	7.7(8)
C(36)	0.011(2)	0.205(1)	0.205(1)	3.4(5)
C(37)	−0.088(3)	0.255(1)	0.192(2)	6.4(8)
Compound **1b**				
Os(1)	0.27364(2)	0.13405(4)	0.10474(2)	2.353(7)
Os(2)	0.23553(2)	0.28920(4)	0.18020(2)	2.287(7)
Cl(1)	0.6470(2)	0.4862(3)	0.4466(1)	4.01(6)
Cl(2)	0.8143(2)	0.4757(3)	0.4095(1)	3.95(6)
Cl(3)	0.1548(2)	0.3956(3)	0.2508(1)	3.94(6)
Cl(4)	0.3255(2)	0.3138(3)	0.2620(1)	3.85(6)
P(1)	0.3678(1)	0.2764(2)	0.1001(1)	2.41(5)
P(2)	0.1410(1)	0.3004(3)	0.1044(1)	2.47(5)
O(1)	0.2997(4)	0.0307(7)	0.1889(3)	3.7(2)
O(2)	0.2077(4)	0.1266(7)	0.2336(3)	3.1(1)
O3	0.2584(7)	0.615(1)	−0.0489(6)	9.2(3)*
N(1)	0.2786(4)	0.4533(8)	0.1436(4)	2.5(2)
N(2)	0.2304(4)	0.2057(7)	0.0192(3)	2.2(1)
C(1)	0.3407(5)	0.442(1)	0.1128(5)	2.9(2)
C(2)	0.3777(6)	0.548(1)	0.0935(5)	3.7(2)
C(3)	0.3502(7)	0.671(1)	0.1050(5)	3.9(2)
C(4)	0.2886(7)	0.681(1)	0.1363(5)	4.1(2)
C(5)	0.2528(6)	0.5709(9)	0.1559(5)	3.1(2)
C(6)	0.4452(6)	0.252(1)	0.1545(5)	3.2(2)
C(7)	0.4871(7)	0.354(1)	0.1766(6)	5.0(3)
C(8)	0.5484(7)	0.329(2)	0.2162(6)	5.9(3)
C(9)	0.5683(7)	0.202(2)	0.2291(6)	5.9(3)
C(10)	0.5279(7)	0.105(1)	0.2077(6)	5.7(3)

(continued)

TABLE II. *(continued)*

Atom	x	y	z	B (Å^2)
C(11)	0.4643(7)	0.124(1)	0.1678(6)	5.1(3)
C(12)	0.4049(6)	0.285(1)	0.0193(5)	2.9(2)
C(13)	0.3722(6)	0.366(1)	−0.0272(5)	3.6(2)
C(14)	0.3981(7)	0.136(1)	0.4084(5)	4.7(3)
C(15)	0.4502(7)	0.221(1)	0.3924(5)	4.7(3)
C(16)	0.4819(7)	0.298(1)	0.4388(6)	4.5(3)
C(17)	0.4601(6)	0.204(1)	0.0048(5)	3.7(2)
C(18)	0.1692(6)	0.272(1)	0.0222(4)	3.4(2)
C(19)	0.1341(6)	0.323(1)	−0.0333(5)	3.1(2)
C(20)	0.1613(7)	0.289(1)	−0.0944(5)	4.4(3)
C(21)	0.2214(6)	0.215(1)	−0.0973(5)	3.7(2)
C(22)	0.2577(6)	0.175(1)	−0.0385(4)	3.6(2)
C(23)	0.0663(5)	0.193(1)	0.1131(4)	2.9(2)
C(24)	0.0205(6)	0.166(1)	0.0601(5)	4.2(3)
C(25)	−0.0377(7)	0.085(1)	0.0666(6)	4.5(3)
C(26)	−0.0519(6)	0.035(1)	0.1251(6)	4.8(3)
C(27)	−0.0058(7)	0.063(2)	0.1795(6)	5.7(3)
C(28)	0.0530(6)	0.143(1)	0.1737(5)	4.7(3)
C(29)	0.0999(6)	0.460(1)	0.0981(5)	3.2(2)
C(30)	0.1308(6)	0.552(1)	0.0598(5)	3.9(2)
C(31)	0.1034(8)	0.678(1)	0.0628(6)	5.8(3)
C(32)	0.0492(9)	0.708(1)	0.1018(7)	6.9(4)
C(33)	0.0187(7)	0.613(1)	0.1386(7)	6.1(3)
C(34)	0.0437(6)	0.488(1)	0.1370(5)	4.7(3)
C(36)	0.2537(6)	0.037(1)	0.2320(5)	3.7(2)
C(37)	0.2511(8)	−0.065(1)	0.2118(6)	6.0(3)
C(38)	0.282(1)	0.719(2)	−0.0668(8)	6.8(4)*
C(39)	0.355(1)	0.738(2)	−0.0714(9)	8.0(5)*
C(40)	0.224(1)	0.814(3)	−0.084(1)	11.7(7)*

[a] Numbers in parentheses are e.s.d.s. in the least significant digits. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)[a^{2}*B(1,1) + b^{2}*B(2,2) + c^{2}*B(3,3) + ab\cos\gamma B(1,2) + ac\cos\beta B(1,3) + bc\cos\alpha B(2,3)]$.

TABLE III. Selected Bond Distances (Å) and Bond Angles (°) for **1a** and **1b**[a]

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Atom 3	Angle
Compound **1a**						
Os(1)	Os(2)	2.395(1)	Os(2)	Os(1)	Cl(1)	156.9(1)
Os(1)	Cl(1)	2.428(6)	Os(2)	Os(1)	Cl(2)	109.3(1)
Os(1)	Cl(2)	2.377(6)	Os(2)	Os(1)	P(1)	80.7(1)
Os(1)	P(1)	2.329(5)	Os(2)	Os(1)	O(1)	82.5(4)
Os(1)	O(1)	2.10(1)	Os(2)	Os(1)	N(2)	102.1(4)
Os(1)	N(2)	2.09(2)	Cl(1)	Os(1)	Cl(2)	87.9(2)
Os(2)	Cl(3)	2.421(6)	Cl(1)	Os(1)	P(1)	83.6(2)
Os(2)	Cl(4)	2.365(6)	Cl(1)	Os(1)	O(1)	84.4(4)
Os(2)	P(2)	2.331(6)	Cl(1)	Os(1)	N(2)	94.9(4)
Os(2)	O(2)	2.10(1)	Cl(2)	Os(1)	P(1)	169.3(2)
Os(2)	N(1)	2.06(2)	Cl(2)	Os(1)	O(1)	83.7(4)
Cl(5)	C(35)	1.79(3)	Cl(2)	Os(1)	N(2)	83.6(4)
Cl(6)	C(35)	1.73(3)	P(1)	Os(1)	O(1)	101.7(4)
P(1)	C(1)	1.82(2)	P(1)	Os(1)	N(2)	90.8(4)
P(1)	C(6)	1.83(2)	O(1)	Os(1)	N(2)	167.3(5)
P(1)	C(12)	1.82(2)	Os(1)	Os(2)	Cl(3)	156.3(1)
P(2)	C(18)	1.81(2)	Os(1)	Os(2)	Cl(4)	109.0(1)

(continued)

TABLE III. *(continued)*

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Atom 3	Angle
P(2)	C(23)	1.89(2)	Os(1)	Os(2)	P(2)	80.7(1)
P(2)	C(29)	1.82(2)	Os(1)	Os(2)	O(2)	83.3(4)
O(1)	C(36)	1.25(3)	Os(1)	Os(2)	N(1)	100.4(5)
O(2)	C(36)	1.29(2)	Cl(3)	Os(2)	Cl(4)	88.6(2)
N(1)	C(1)	1.36(3)	Cl(3)	Os(2)	P(2)	83.3(2)
N(1)	C(5)	1.42(3)	Cl(3)	Os(2)	O(2)	83.3(4)
N(2)	C(18)	1.41(3)	Cl(3)	Os(2)	N(1)	97.0(5)
N(2)	C(22)	1.30(3)	Cl(4)	Os(2)	P(2)	169.4(2)
			Cl(4)	Os(2)	O(2)	82.9(4)
			Cl(4)	Os(2)	N(1)	84.1(5)
			P(2)	Os(2)	O(2)	102.8(4)
			P(2)	Os(2)	N(1)	90.2(5)
			O(2)	Os(2)	N(1)	166.9(6)
Compound **1b**						
Os(1)	Os(2)	2.388(1)	Os(2)	Os(1)	Cl(1)	158.16(6)
Os(1)	Cl(1)	2.436(2)	Os(2)	Os(1)	Cl(2)	109.12(6)
Os(1)	Cl(2)	2.362(2)	Os(2)	Os(1)	P(1)	81.12(5)
Os(1)	P(1)	2.332(2)	Os(2)	Os(1)	O(1)	82.7(2)
Os(1)	O(1)	2.096(5)	Os(2)	Os(1)	N(2)	101.3(2)
Os(1)	N(2)	2.066(6)	Cl(1)	Os(1)	Cl(2)	86.91(8)
Os(2)	Cl(3)	2.433(2)	Cl(1)	Os(1)	P(1)	84.23(8)
Os(2)	Cl(4)	2.371(2)	Cl(1)	Os(1)	O(1)	84.7(2)
Os(2)	P(2)	2.338(2)	Cl(1)	Os(1)	N(2)	95.0(2)
Os(2)	O(2)	2.110(5)	Cl(2)	Os(1)	P(1)	169.13(7)
Os(2)	N(1)	2.060(6)	Cl(2)	Os(1)	O(1)	83.3(2)
P(1)	C(1)	1.830(8)	Cl(2)	Os(1)	N(2)	83.9(2)
P(1)	C(6)	1.834(8)	P(1)	Os(1)	O(1)	102.1(2)
P(1)	C(12)	1.846(8)	P(1)	Os(1)	N(2)	90.6(2)
P(2)	C(18)	1.831(8)	O(1)	Os(1)	N(2)	167.2(2)
P(2)	C(23)	1.824(8)	Os(1)	Os(2)	Cl(3)	157.09(6)
P(2)	C(29)	1.844(8)	Os(1)	Os(2)	Cl(4)	108.32(6)
O(1)	C(36)	1.276(10)	Os(1)	Os(2)	P(2)	80.68(5)
O(2)	C(36)	1.284(10)	Os(1)	Os(2)	O(2)	83.3(2)
N(1)	C(1)	1.369(10)	Os(1)	Os(2)	N(1)	101.0(2)
N(1)	C(5)	1.352(9)	Cl(3)	Os(2)	Cl(4)	88.42(7)
N(2)	C(18)	1.356(11)	Cl(3)	Os(2)	P(2)	84.09(7)
N(2)	C(22)	1.362(9)	Cl(3)	Os(2)	O(2)	82.9(2)
			Cl(3)	Os(2)	N(1)	96.3(2)
			Cl(4)	Os(2)	P(2)	170.16(8)
			Cl(4)	Os(2)	O(2)	84.3(2)
			Cl(4)	Os(2)	N(1)	83.6(2)
			P(2)	Os(2)	O(2)	101.0(2)
			P(2)	Os(2)	N(1)	90.9(2)

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

interactions. There is one bridging acetate group, two *trans* equatorial chloride ions and two axial chloride ions. The diosmium unit together with the immediate coordination sphere has approximate C_2 symmetry. An ORTEP view of the molecule is presented in Fig. 1, which clearly illustrates the torsional twist. The Os–Os distance is 2.388(1) Å. This is one of the longest distances reported so far, for an Os_2^{5+} unit where the formal bond order is 2.5. The average osmium to axial chloride distance is 2.434(3) Å, while the equatorial Os–Cl bond lengths are 2.363(2) and 2.371(2) Å. Other important distances are: Os–P_{av} = 2.335[3], Os–N_{av} = 2.063[3], Os–O_{av} = 2.103[7] Å.

$Rh_2(O_2CCH_3)_2(Ph_2Ppy)_2Cl_2$ (2)

The molecule of **2** resides on a general position in a noncentrosymmetric space group $P42_1c$. The approximate molecular symmetry is C_2. Atomic fractional coordinates are given in Table IV. An

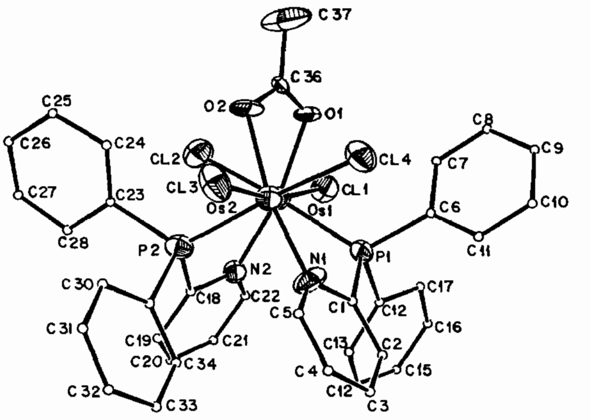


Fig. 1. An ORTEP drawing of $Os_2(O_2CCH_3)(Ph_2Ppy)_2Cl_4$ along Os–Os vector.

ORTEP drawing, presented in Fig. 2, shows that the molecule consists of a Rh_2^{4+} central core spanned by two cisoid Ph_2Ppy ligands, again in a head-to-tail relationship. Two acetate bridges and two axial chlorine atoms complete the coordination sphere. The geometry around each Rh atom is slightly distorted from octahedral. The molecule is twisted from the ideal eclipsed conformation with an average torsional angle of 15.5°. The two acetate bridges are twisted by 17.4°, the two Ph_2Ppy bridges are twisted by 13.86 and 13.51°. The Rh–Rh distance is 2.518(1) Å, much shorter than in corresponding $Rh_2(O_2CCH_3)_2(dppm)_2Cl_2$ [2.622(1) Å] but in a typical range for Rh(II) dimers. The average $Rh-Cl_{ax}$ distance is 2.538[1], $Rh-N_{av} = 2.061[2]$, $Rh-P_{av} =$

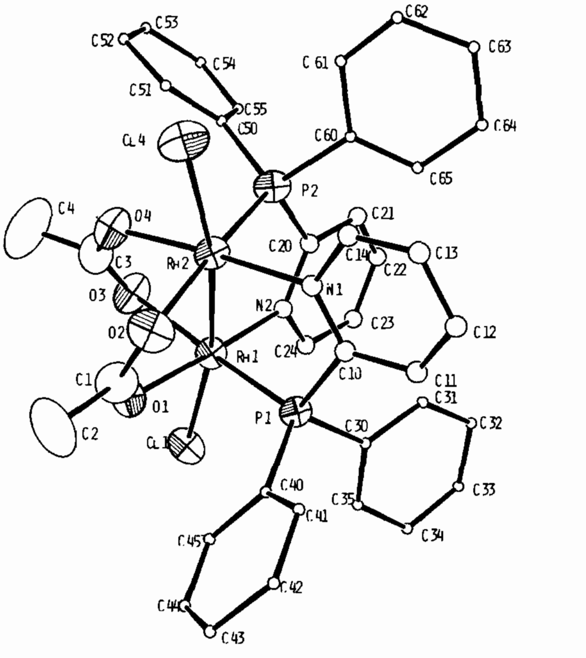


Fig. 2. An ORTEP drawing of $Rh_2(O_2CCH_3)_2(Ph_2Ppy)_2Cl_2$.

TABLE IV. Fractional Coordinates and Isotropic-equivalent Displacement Parameters for 2[a]

Atom	x	y	z	B (Å^2)
Rh(1)	0.30376(4)	0.10260(4)	0.69165(5)	2.12(1)
Rh(2)	0.24037(4)	0.16233(4)	0.78623(5)	2.27(1)
Cl(1)	0.3518(2)	0.0266(2)	0.5997(2)	3.24(6)
Cl(2)	0.1610(2)	0.2066(2)	0.8764(2)	4.03(7)
P(1)	0.3804(1)	0.1129(1)	0.7734(2)	2.13(5)
P(2)	0.2480(2)	0.2403(2)	0.7054(2)	2.63(6)
O(1)	0.2710(4)	0.0297(4)	0.7525(6)	2.9(2)
O(2)	0.2394(5)	0.0830(5)	0.8558(5)	3.5(2)
O(3)	0.2237(4)	0.0952(5)	0.6223(5)	3.2(2)
O(4)	0.1697(4)	0.1244(5)	0.7275(5)	3.2(2)
N(1)	0.3115(5)	0.1942(5)	0.8527(5)	2.5(2)
N(2)	0.3329(5)	0.1740(5)	0.6260(6)	2.3(2)
C(1)	0.2494(7)	0.0348(7)	0.8202(7)	3.0(3)
C(2)	0.232(1)	−0.0225(8)	0.862(1)	5.5(4)
C(3)	0.1758(7)	0.1004(7)	0.6590(8)	3.1(3)
C(4)	0.1192(9)	0.077(1)	0.621(1)	7.2(6)
C(10)	0.3673(5)	0.1741(6)	0.8453(7)	2.2(2)
C(11)	0.4137(6)	0.1973(7)	0.8909(8)	3.0(3)
C(12)	0.4029(7)	0.2391(7)	0.9471(8)	3.2(3)
C(13)	0.3436(7)	0.2603(7)	0.9549(7)	3.3(3)
C(14)	0.3007(7)	0.2382(7)	0.9064(8)	3.3(3)
C(20)	0.3110(6)	0.2318(7)	0.6354(8)	3.2(3)
C(21)	0.3320(7)	0.2810(6)	0.5934(8)	3.2(3)
C(22)	0.3771(7)	0.2718(7)	0.5351(9)	3.6(3)
C(23)	0.4000(7)	0.2148(7)	0.5263(8)	3.1(3)
C(24)	0.3766(6)	0.1659(6)	0.5737(7)	2.7(2)
C(30)	0.4505(6)	0.1331(6)	0.7257(7)	2.6(2)
C(31)	0.4662(6)	0.1921(6)	0.7141(7)	3.3(2)
C(32)	0.5191(8)	0.2089(9)	0.672(1)	4.7(4)
C(33)	0.5547(7)	0.162(1)	0.6424(9)	4.7(4)
C(34)	0.5427(8)	0.103(1)	0.655(1)	4.8(4)
C(35)	0.4865(8)	0.0900(7)	0.6975(8)	4.0(3)
C(40)	0.3960(6)	0.0489(6)	0.8353(7)	2.5(2)
C(41)	0.4117(7)	0.0574(8)	0.9146(9)	3.5(3)
C(42)	0.426(1)	0.0050(9)	0.9607(9)	5.2(4)
C(43)	0.4198(9)	−0.0560(8)	0.925(1)	4.7(4)
C(44)	0.4058(8)	−0.0609(8)	0.845(1)	4.3(3)
C(45)	0.3916(7)	−0.0108(7)	0.8029(9)	3.6(3)
C(50)	0.1824(7)	0.2564(7)	0.6431(8)	3.1(3)
C(51)	0.1256(7)	0.2436(9)	0.6743(9)	4.5(3)
C(52)	0.0737(8)	0.252(1)	0.627(1)	6.0(5)
C(53)	0.0808(8)	0.278(1)	0.552(1)	5.0(4)
C(54)	0.1375(8)	0.2919(9)	0.5252(9)	4.3(4)
C(55)	0.1895(8)	0.2807(8)	0.5667(8)	4.3(3)
C(60)	0.2659(7)	0.3109(7)	0.7527(8)	3.2(3)
C(61)	0.2167(7)	0.3469(6)	0.7806(8)	3.3(3)
C(62)	0.225(1)	0.3966(8)	0.823(1)	5.1(4)
C(63)	0.284(1)	0.4188(8)	0.838(1)	5.5(5)
C(64)	0.334(1)	0.3828(9)	0.813(1)	5.5(4)
C(65)	0.3226(9)	0.3274(8)	0.770(1)	4.5(4)

[a] Numbers in parentheses are e.s.d.s in the least significant digits. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)[a^2*B(1,1) + b^2*B(2,2) + c^2*B(3,3) + ab\cos\gamma B(1,2) + ac\cos\beta B(1,3) + bc\cos\alpha B(2,3)]$.

TABLE V. Selected Bond Distances (Å) and Bond Angles (°) for **2**[a]

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Atom 3	Angle
Rh(1)	Rh(2)	2.518(1)	Rh(2)	Rh(1)	Cl(1)	168.66(9)
Rh(1)	Cl(1)	2.538(3)	Rh(2)	Rh(1)	P(1)	88.40(7)
Rh(1)	P(1)	2.212(3)	Rh(2)	Rh(1)	O(1)	83.9(2)
Rh(1)	O(1)	2.055(8)	Rh(2)	Rh(1)	O(3)	86.0(2)
Rh(1)	O(3)	2.142(8)	Rh(2)	Rh(1)	N(2)	96.9(3)
Rh(1)	N(2)	2.046(10)	Cl(1)	Rh(1)	P(1)	97.8(1)
Rh(2)	Cl(2)	2.537(3)	Cl(1)	Rh(1)	O(1)	86.4(3)
Rh(2)	P(2)	2.220(3)	Cl(1)	Rh(1)	O(3)	87.5(2)
Rh(2)	O(2)	2.123(9)	Cl(1)	Rh(1)	N(2)	92.5(3)
Rh(2)	O(4)	2.043(9)	P(1)	Rh(1)	O(1)	92.0(3)
Rh(2)	N(1)	2.068(9)	P(1)	Rh(1)	O(3)	174.1(2)
P(1)	C(10)	1.853(11)	P(1)	Rh(1)	N(2)	91.2(3)
P(1)	C(30)	1.811(12)	O(1)	Rh(1)	O(3)	85.7(4)
P(1)	C(40)	1.802(11)	O(1)	Rh(1)	N(2)	176.7(4)
P(2)	C(20)	1.847(13)	O(3)	Rh(1)	N(2)	91.2(4)
P(2)	C(50)	1.838(12)	Rh(1)	Rh(2)	Cl(2)	168.7(1)
P(2)	C(60)	1.806(14)	Rh(1)	Rh(2)	P(2)	88.30(8)
O(1)	C(1)	1.255(14)	Rh(1)	Rh(2)	O(2)	85.8(2)
O(2)	C(1)	1.251(15)	Rh(1)	Rh(2)	O(4)	84.1(2)
O(3)	C(3)	1.239(15)	Rh(1)	Rh(2)	N(1)	96.0(3)
O(4)	C(3)	1.291(14)	Cl(2)	Rh(2)	P(2)	97.3(1)
N(1)	C(10)	1.323(14)	Cl(2)	Rh(2)	O(2)	88.6(3)
N(1)	C(14)	1.362(15)	Cl(2)	Rh(2)	O(4)	85.6(3)
N(2)	C(20)	1.38(2)	Cl(2)	Rh(2)	N(1)	93.8(3)
N(2)	C(24)	1.329(15)	P(2)	Rh(2)	O(2)	174.1(3)
C(1)	C(2)	1.51(2)	P(2)	Rh(2)	O(4)	94.4(3)
C(3)	C(4)	1.51(2)	P(2)	Rh(2)	N(1)	90.9(3)
			O(2)	Rh(2)	O(4)	85.6(4)
			O(2)	Rh(2)	N(1)	89.2(4)
			O(4)	Rh(2)	N(1)	174.8(4)
			Rh(1)	O(1)	C(1)	122.0(9)
			Rh(2)	O(2)	C(1)	116.0(7)
			Rh(1)	O(3)	C(3)	115.3(7)
			Rh(2)	O(4)	C(3)	122.3(8)
			Rh(2)	N(1)	C(10)	123.3(8)
			P(1)	C(10)	N(1)	117.2(9)
			P(2)	C(20)	N(2)	116.(1)

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

2.21[2] Å and Rh–O distances vary from 2.043(9) to 2.142(8) Å. Additional distances and angles are within expected ranges and require no further comment (see Table V).

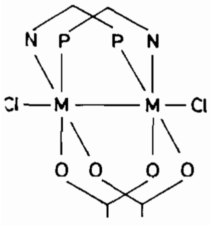
Discussion

In this report we describe two compounds formed from parent tetracarboxylates of osmium and rhodium in which different numbers of acetate ligands have been replaced.

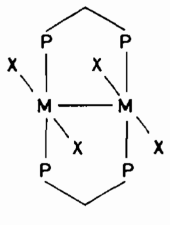
Compound **1**, $Os_2Cl_4(O_2CCH_3)(Ph_2Ppy)_2$, was initially prepared by the reaction of $Os_2(O_2CCH_3)_4Cl_2$ with 2-diphenylphosphinopyridine (Ph_2Ppy) in toluene in the presence of Me_3SiCl. The yield of this reaction was low (*ca.* 30%) and reaction times longer than 24 h led to extensive decomposition and even lower yields. Thus, as will be explained presently, a new preparative method was developed. The crystal structure determination of $Os_2(O_2CCH_3)(Ph_2Ppy)_2Cl_4 \cdot CH_2Cl_2$ (**1a**) was subject to severe absorption problems due to the acicular nature of the crystals. The formation of **1** entails substitution of three acetate bridging ligands with the concomitant reduction of the triple bond, giving a formal bond order in $Os_2(O_2CCH_3)(Ph_2Ppy)_2Cl_4$ of 2.5

We next turned our attention to the possibility of replacing the remaining acetate ligand. Prolonged reaction times and different stoichiometries were tried but only **1** was isolated in varying yields. We have recently successfully employed LiCl in substitution reactions [12]. Even when $Os_2(O_2CCH_3)_4Cl_2$ and Ph_2Ppy were reacted in toluene in the presence of a large excess of LiCl, only $Os_2(O_2CCH_3)(Ph_2Ppy)_2Cl_4$ was obtained, but in much better yield (*ca.* 70%). We have also obtained a different crystalline form of **1** containing acetone as a solvent of crystallization. A better molecular structure of **1** was obtained from these crystals and it is reported in this paper.

There have been some interesting parallels between diosmium and dirhodium chemistry in the past [13, 14]. At the time this investigation was undertaken there had not been any reports on Rh(II,II) dimers containing mixed phosphine and halide ligands. $Rh_2(O_2CCH_3)_2(Ph_2Ppy)_2Cl_2$ (**2**) was prepared by the reaction of $Rh_2(O_2CCH_3)_4(HOMe)_2$ with Ph_2Ppy in toluene in the presence of LiCl. IR evidence suggested the presence of a bridging acetate group and Ph_2Ppy ligands, but the exact molecular structure was elucidated only about one year later, when, after many frustrating attempts, we finally obtained single crystals of a size suitable for the X-ray structure determination. The molecule of **2** consists of two cisoid Ph_2Ppy ligands arranged in a head-to-tail fashion, two bridging acetate ligands and two axial chloride ions. The geometry is schematically depicted in **I** and may be contrasted with a typical $M_2X_4(LL)_2$ arrangement depicted as **II**.



I



II

Our attempts to force additional acetate substitution in **2** using either Me_3SiCl or LiCl have been unsuccessful; we do not have any evidence for the formation of $Rh_2Cl_4(Ph_2Ppy)_2$.

Two compounds related to the present work have been synthesized in our laboratory and reported recently [6]. $Rh_2(O_2CCH_3)_2(dppm)_2Cl_2$ has been obtained from $Rh_2(O_2CCH_3)_4$ and dppm in the presence of Me_3SiCl. It has a structure analogous to that of **2**, with two cisoid dppm groups. The replacement of dppm by Ph_2Ppy affects the molecular structures of the compounds. The Rh–Rh bonds in $Rh_2(O_2CCH_3)_2(Ph_2Ppy)_2Cl_2$ and $Rh_2(O_2CCH_3)_2(dppm)_2Cl_2$ are 2.518(1) and 2.622(1) Å, and the average Rh to axial chloride distances are 2.537[1] and 2.475[2] Å. These numbers clearly demonstrate the well known reciprocal relationship between axial bond strength and metal–metal bond strength. We believe that because the phosphinopyridine is a better electron donor, it creates a stronger metal–metal bond, which in turn forces axial chlorides into a weaker interaction. The electronic spectral properties of these two compounds are also different. The Ph_2Ppy complex exhibits a band at 503 nm (ϵ = 1050 M^{-1} cm^{-1}), while the dppm complex has a transition at 485 nm (ϵ = 800 M^{-1} cm^{-1}) with a shoulder at 520 nm. The assignment of these electronic transitions is not yet known.

A second interesting compound that has been recently reported is $Rh_2Cl_4(dppm)_2$, where all the acetate ligands have been replaced. However, this compound does not have the expected for the $M_2X_4(LL)_2$ species geometry. Instead the dppm ligands adopt a cisoid bridging configuration, while two chloride atoms serve as bridges, and the two remaining chlorine atoms serving as terminal ligands.

Supplementary Material

Full listing of bond distances, bond angles and anisotropic displacement parameters (17 pages), calculated and observed structure factors (59 pages) for **1a**, **1b** and **2** are available from author F.A.C.

Acknowledgement

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