

Metal–metal bond cleavage in the trinuclear clusters $M_3(CO)_{12-n}(Ph_2Ppy)_n$ ($M = Ru, n = 3; Os, n = 1;$ $Ph_2Ppy = 2-(diphenylphosphino)pyridine$) by Lewis acids

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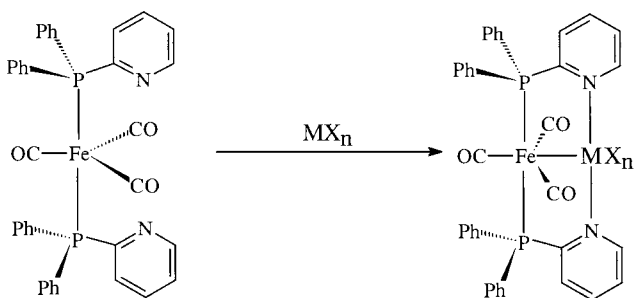
Abstract

Reaction of $M_3(CO)_{12-n}(Ph_2Ppy)_n$ ($M = Ru, n = 3; M = Os, n = 1$) with HgX_2 ($X = Br, Cl$) gave *cis*- $M(CO)_3(\mu-Ph_2Ppy)(HgX)_2$, ($M = Ru, \mathbf{1}; M = Os, \mathbf{2}$), and the reaction of $Ru_3(CO)_9(Ph_2Ppy)_3$ with CdI_2 resulted in the formation of $I(CO)_2Ru(\mu-Ph_2Ppy)_2Ru(CO)_2I, \mathbf{3}$, which demonstrate the cleavage of metal-metal bonds by Lewis acids. The crystal and molecular structures of $\mathbf{1}, \mathbf{2}$ and $\mathbf{3} \cdot 0.5MeOH \cdot H_2O$ have been determined by X-ray analysis. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Metal–metal bond; Cleavage; Ruthenium; Osmium; Lewis acid

1. Introduction

Recent work from our laboratories [1–6] has demonstrated that neutral 18-electron organometallic compounds typified by $Fe(CO)_3(Ph_2Ppy)_2$ can react with Lewis acids to form heterobinuclear complexes that are consolidated by a donor-acceptor metal–metal bond (Scheme 1).



Scheme 1.

In the ensuing study, we attempt to extend our investigation to the reaction of neutral transition metal trinuclear clusters with Lewis acids. Here we report new results on the reaction of trinuclear cluster derivatives $M_3(CO)_{12-n}(Ph_2Ppy)_n$ ($M = Ru, n = 3; M = Os, n = 1;$ $Ph_2Ppy = 2-(diphenylphosphino)pyridine$) with HgX_2 ($X = Cl, Br$) and CdI_2 , which demonstrate the cleavage of metal–metal bonds by Lewis acids.

2. Results and discussion

When 2 equiv. of $HgBr_2$ is reacted with 1 equiv. of $Ru_3(CO)_9(Ph_2Ppy)_3$ in dichloromethane at room temperature, *cis*- $Ru(CO)_3(\mu-Ph_2Ppy)(HgBr)_2$ $\mathbf{1}$ was obtained. Similarly, *cis*- $Os(CO)_3(\mu-Ph_2Ppy)(HgCl)_2$ $\mathbf{2}$ was isolated from the reaction of $HgCl_2$ with $Os_3(CO)_{11}(Ph_2Ppy)$. We propose that the products arise from successive oxidative addition of HgX_2 to two metal centers in the cluster, which results in cleavage of the metal–metal bonds.

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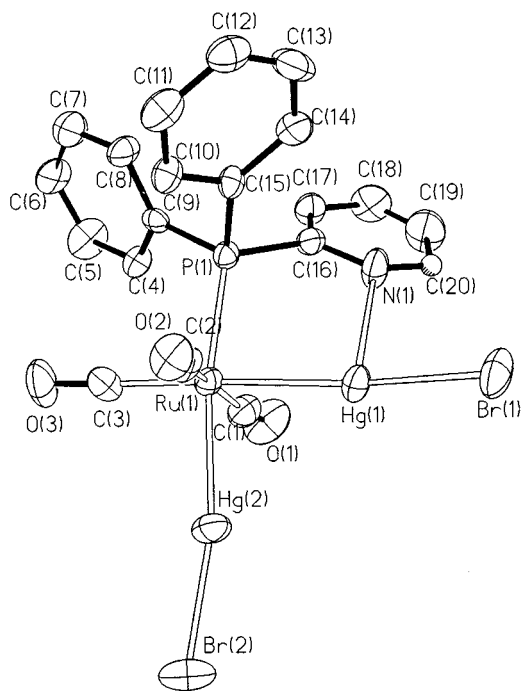


Fig. 1. Molecular structure of *cis*-Ru(CO)₃(μ -Ph₂Ppy)(HgBr)₂, **1**. The thermal ellipsoids are drawn at the 35% probability level. Selected bond lengths (Å) and angles (°): Ru(1)–Hg(1) 2.628(2), Ru(1)–Hg(2) 2.602(2), Hg(1)–Br(1) 2.540(3), Hg(2)–Br(2) 2.538(4); Hg(1)–Ru(1)–Hg(2) 84.5(1), Hg(1)–Ru(1)–P(1) 87.2(1), Ru(1)–Hg(2)–Br(2) 165.4(1), Ru(1)–Hg(1)–Br(1) 169.5(1).

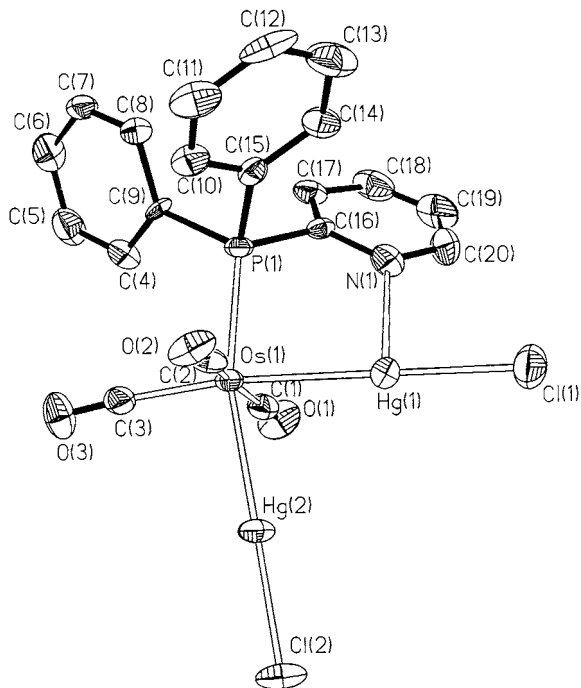


Fig. 2. Molecular structure of the *cis*-Os(CO)₃(μ -Ph₂Ppy)(HgCl)₂, **2**. The thermal ellipsoids are drawn at the 35% probability level. Selected bond lengths (Å) and angles (°): Os(1)–Hg(1) 2.651(1), Os(1)–Hg(2) 2.627(1), Hg(1)–Cl(1) 2.392(6), Hg(2)–Cl(2) 2.400(5); Hg(1)–Os(1)–Hg(2) 79.6(1), Hg(1)–Os(1)–P(1) 86.4(1), Os(1)–Hg(1)–Cl(1) 177.5(1), Os(1)–Hg(2)–Cl(2) 176.4(1).

The ³¹P{¹H}NMR spectra were triplets caused by coupling to ¹⁹⁹Hg (17% natural abundance). The ²J(³¹P–Fe–¹⁹⁹Hg) value is 432 Hz for **1** and 404 Hz for **2**. These ²J values are comparable to 419 Hz in ClFe(CO)₂(μ -Ph₂Ppy)₂HgCl [7] and larger than 190 Hz in Fe(CO)₃(μ -Ph₂Ppy)₂HgI₂ [2], but smaller than those found in [Ru₂(C₁₀H₈N₂)(CO)₄(P^{*i*}Pr₃)₂HgX₂): 1118 Hz, X = Cl; 1087 Hz, X = Br; 1004 Hz, X = I [8].

The X-ray structure of *cis*-Ru(CO)₃(μ -Ph₂Ppy)(HgBr)₂, **1**, is depicted in Fig. 1. The co-ordination geometry of the ruthenium center is a slightly distorted octahedron with one phosphine ligand, three carbonyl groups and two *cis*-HgBr fragments at its vertices. The Ru–Hg bond lengths are 2.602(2) and 2.628(2) Å, which are comparable to those (2.658(1), 2.655(1) Å) in *cis*-Ru(CO)₄[HgRu₃(CO)₉(μ -C₂-*t*-Bu)]₂ [9], but are much shorter than those (2.839(1), 2.859(1), 2.841(1), 2.842(1) Å) in [Ru₆(μ -Hg)₄(μ -ampy)₂(CO)₁₈] (ampy = 2-amino-6-methylpyridine) [10]. The Hg–Br bond distances are 2.538(4), 2.540(3) Å, which are shorter than that in [Ru₃(μ -HgBr)(μ_3 -ampy)(CO)₉] [10], 2.512(3) Å. The Hg(1)⋯Hg(2) distance, 3.518 Å, is out of the

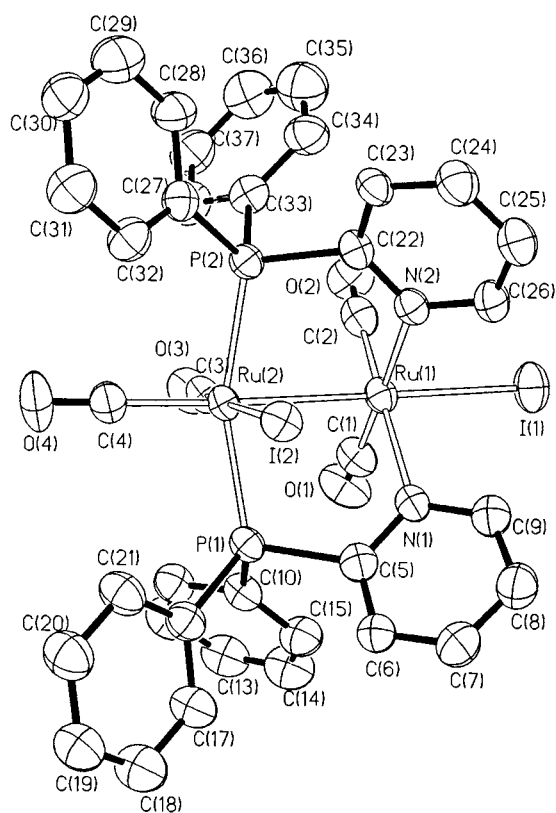


Fig. 3. Structure of the I(CO)₂Ru(μ -Ph₂Ppy)₂Ru(CO)₂I molecule, **3**, in 3·0.5MeOH·H₂O. The thermal ellipsoids are drawn at the 35% probability level. Selected bond lengths (Å) and angles (°): Ru(1)–Ru(2) 2.834(1), Ru(1)–I(1) 2.829(1), Ru(2)–I(2) 2.804(1); Ru(2)–Ru(1)–I(1) 177.3(1), Ru(1)–Ru(2)–C(4) 170.6(2), P(1)–Ru(2)–P(2) 159.5(1), N(1)–Ru(1)–N(2) 92.4(2), P(1)–Ru(2)–I(2) 81.6(1), P(2)–Ru(2)–I(2) 84.2(2), P(1)–Ru(2)–C(3) 78.6(2), P(2)–Ru(2)–C(3) 96.5(2).

Table 1
Crystal data and parameters for **1**, **2** and **3**·0.5MeOH·H₂O

Formula	C ₂₀ H ₁₄ Br ₂ Hg ₂ NO ₃ PRu 1	C ₂₀ H ₁₄ Cl ₂ Hg ₂ NO ₃ OsP 2	C ₃₈ H ₂₈ I ₂ N ₂ O ₄ P ₂ Ru ₂ ·0.5MeOH·H ₂ O 3 ·0.5MeOH·H ₂ O
Molecular weight	1009.4	1009.6	1128.4
Space group	P $\bar{1}$	P $\bar{1}$	P $\bar{1}$
Unit-cell dimensions			
<i>a</i> (Å)	9.540(2)	9.601(2)	10.771(2)
<i>b</i> (Å)	10.574(2)	10.530(2)	11.858(2)
<i>c</i> (Å)	12.524(3)	12.270(2)	18.674(4)
α (°)	102.16(3)	97.19(3)	95.28(3)
β (°)	92.21(3)	91.84(3)	101.03 (3)
γ (°)	91.49(3)	98.31(3)	108.31(3)
<i>V</i> (Å ³)	1233.3(6)	1216.2(6)	2192.7(11)
<i>Z</i>	2	2	2
<i>d</i> _{calcd} (g cm ⁻³)	2.718	2.757	1.703
Radiation	Mo–K α	Mo–K α	Mo–K α
Goodness-of-fit index	0.92	1.27	2.30
No. of unique reflections	4627	5512	8392
No. of observed reflection ($ F \geq 4\sigma(F)$)	2999	3380	7330
No. of variables, <i>p</i>	271	271	464
Weighting scheme $w^{-1} = \sigma^2(F) + gF^2$	0.005	0.0075	0.0004
<i>R</i> _F	0.072	0.062	0.0 53
<i>R</i> _{wF²}	0.089	0.136	0.061

bonding range though significantly shorter than that found in *cis*-Ru(CO)₄[HgRu₃(CO)₉(μ -C₂-*t*-Bu)]₂ [9], 3.55 Å. The shortness of this nonbonding Hg(1)···Hg(2) contact suggests that there may be significant interaction which led to the unusually small Hg(1)–Ru(1)–Hg(2) bond angle of 84.5(1)°.

Compound **2** (Fig. 2) is isostructural with **1** except for substitution of the metal center and the halide ligands. The Os, Hg and Cl atoms are almost collinear, with bond angles Os(1)–Hg(1)–Cl(1) = 176.4(1)° and Os(1)–Hg(2)–Cl(2) = 177.5(1)°. The Os–Hg bond distances of 2.627(1) and 2.651(1) Å are slightly longer than those of complex **1** and shorter than those found in [Os₃(CO)₉(C₂Ph₂)(μ -Cl)(μ -HgCl)]₂ [11], 2.830(1) Å. The Hg–Cl distances of 2.400(5) and 2.392(6) Å are comparable to those of [Os₃(CO)₉(C₂Ph₂)(μ -Cl)(μ -HgCl)]₂ [11], 2.387(8) Å, and ClW(CO)₃(bipy)HgCl [12], 2.36(2) Å. The Hg(1)···Hg(2) distance of 3.38 Å suggests a stronger interaction than that in complex **1**, and results in an even smaller Hg(1)–Os(1)–Hg(2) bond angle of 79.6(1)°. An even shorter Hg···Hg interaction of 3.17 Å has been found in *cis*-Fe(CO)₄(HgBr)₂ [13], which exists as a dimer in the solid state.

Reaction of Ru₃(CO)₉(Ph₂Ppy)₃ with CdI₂ resulted in the formation of I(CO)₂Ru(μ -Ph₂Ppy)₂Ru(CO)₂I, **3**, in low yield. The mechanism of this reaction is not clear, but it is certain that the terminal iodine ligands originate from CdI₂.

A singlet was observed in the ³¹P{¹H}NMR spectra of I(CO)₂Ru(μ -Ph₂Ppy)₂Ru(CO)₂I which indicates that the two P atoms are in equivalent environments. The molecular structure of I(CO)₂Ru(μ -Ph₂Ppy)₂Ru(CO)₂I,

3, is illustrated in Fig. 3. This binuclear Ru(I) complex contains two bridging Ph₂Ppy ligands that are disposed with respect to each other in a head-to-head fashion, so that the P and N donor atoms are attached to Ru(2) and Ru(1), respectively. The co-ordination geometries of Ru(1) and Ru(2) are both distorted octahedral. The two ruthenium atoms, two carbonyls bound to Ru(2), and two iodine atoms nearly lie in a plane, and I(1), Ru(1), Ru(2) and C(4) atoms are almost collinear. The Ru(1)–Ru(2) distance of 2.834(1) Å corresponds to a formal single bond and compares well with corresponding distances of 2.801(2) and 2.814(2) Å for [Ru₂(μ -CO)(CO)₄{ μ -(MeO)₂PN(Et)P(OMe)₂}₂] [14] and [Ru₂{ μ -OB(F)OH}(CO)₄{ μ -(PrⁱO)₂PN(Et)P(OPrⁱ)₂}₂](BF₄) [15], respectively. The bond angles P(1)–Ru(1)–P(2) = 159.5(1)° and N(1)–Ru(2)–N(2) = 92.4(2)° indicate the *trans* and *cis* configurations of pairs of P and N donor atoms, respectively.

3. Experimental

3.1. Synthesis

All reactions were carried out under nitrogen using Schlenk techniques. The solvents were purified by standard methods. Infrared spectra were recorded on a Perkin Elmer 1600 spectrometer as KBr discs. The ³¹P{¹H}NMR spectra were recorded on a Bruker ARX-500 spectrometer at 202.5 MHz using (PhO)₃P as the external standard and CDCl₃ as solvent. Ru₃(CO)₉(Ph₂Ppy)₃ [16] and Os₃(CO)₁₁(Ph₂Ppy) [17] were prepared by the published procedures.

3.1.1. Preparation of *cis*-Ru(CO)₃(μ-Ph₂Ppy)(HgBr)₂ **1**

HgBr₂ (0.072 g 0.2 mmol) was added to a solution of Ru₃(CO)₉(Ph₂Ppy)₃ (0.13 g 0.1 mmol) in dichloromethane (20 ml). The mixture was stirred at room temperature for 20 min and filtered. The filtrate was concentrated and diethyl ether was added to give a pale yellow precipitate. Pale yellow crystals were obtained from crystallization in dichloromethane/methanol. Yield: 58 mg (57.4%). Anal. Calc. for C₂₀H₁₄Br₂Hg₂NO₃PRu: C, 23.80; H, 1.40; N, 1.39. Found: C, 23.83; H, 1.65; N, 1.55. IR (νCO): 2024.7, 1990.0, 1948.9 cm⁻¹. ³¹P{¹H} NMR: δ = 53.83 ppm, ²J(P–Fe–¹⁹⁹Hg) = 432 Hz.

3.1.2. Preparation of *cis*-Os(CO)₃(μ-Ph₂Ppy)(HgCl)₂, **2**

The above procedure was repeated starting with HgCl₂ (0.055 g 0.2 mmol) and Os₃(CO)₁₁(Ph₂Ppy) (0.11 g, 0.1 mmol). Yield: Pale yellow crystals, 61 mg (60.5%). Anal. Calc. for C₂₀H₁₄Cl₂Hg₂NO₃POs: C, 23.79; H, 1.40; N, 1.39. Found: C, 24.06; H, 1.50; N,

Table 2

Atomic coordinates of complex **1** (×10⁵ for Hg and Ru; ×10⁴ for other atoms) and equivalent isotropic displacement coefficients (Å² × 10⁴ for Hg and Ru; Å² × 10³ for other atoms)

Atom	x	y	z	U _{eq}
Ru(1)	29269(13)	30529(13)	20252(12)	373(4)
Hg(1)	8869(7)	12991(7)	14247(7)	515(3)
Hg(2)	18499(8)	40990(8)	4910(7)	593(4)
Br(1)	-1292(2)	-186(3)	1158(2)	82(1)
Br(2)	1435(3)	5336(3)	-1017(2)	90(1)
P(1)	3712(4)	1821(4)	3268(4)	37(1)
C(1)	3957(18)	2033(17)	869(16)	61(2)
O(1)	4570(15)	1333(15)	224(13)	91(2)
C(2)	1553(14)	3979(14)	2946(14)	47(2)
O(2)	755(14)	4559(13)	3464(12)	69(2)
C(3)	4346(16)	4401(16)	2449(16)	55(2)
O(3)	5234(14)	5197(14)	2721(15)	91(2)
C(4)	6534(15)	2337(15)	3104(14)	48(2)
C(5)	7914(15)	2657(19)	3487(17)	70(2)
C(6)	8308(16)	2862(18)	4572(16)	64(2)
C(7)	7305(18)	2706(19)	5313(17)	68(2)
C(8)	5927(16)	2356(17)	4908(14)	55(2)
C(9)	5514(14)	2219(12)	3809(12)	36(2)
C(10)	2558(15)	3122(16)	5152(14)	46(2)
C(11)	1895(16)	3243(19)	6138(16)	63(2)
C(12)	1312(16)	2148(18)	6450(16)	61(2)
C(13)	1485(19)	951(19)	5794(17)	70(2)
C(14)	2150(17)	804(18)	4800(15)	60(2)
C(15)	2710(14)	1902(14)	4480(13)	37(2)
C(16)	3780(16)	86(14)	2658(13)	46(2)
C(17)	4964(16)	-671(15)	2712(15)	52(2)
C(18)	4881(18)	-1950(17)	2216(17)	73(2)
C(19)	3799(21)	-2411(20)	1656(20)	94(2)
C(20)	2607(19)	-1670(18)	1584(17)	74(2)
N(1)	2612(14)	-485(14)	2092(14)	61(2)

Equivalent isotropic *U* defined as one third of the trace of the orthogonalized *U*_{ij} tensor.

Table 3

Atomic coordinates of complex **2** (×10⁵ for Os and Hg; ×10⁴ for other atoms) and equivalent isotropic displacement coefficients (Å² × 10⁴ for Os and Hg; Å² × 10³ for other atoms)

Atom	x	y	z	U _{eq}
Os(1)	31722(8)	80582(5)	17048(5)	302(2)
Hg(1)	9239(9)	62414(6)	14492(6)	444(2)
Hg(2)	17485(9)	88560(6)	1245(6)	431(2)
Cl(1)	-1163(7)	4670(5)	1253(5)	75(1)
Cl(2)	553(6)	9538(5)	-1399(4)	62(1)
P(1)	3984(5)	6927(3)	3085(3)	31(1)
C(1)	3970(10)	6893(9)	580(9)	43(1)
O(1)	4442(10)	6245(9)	-40(8)	70(1)
C(2)	2117(10)	9092(9)	2691(9)	36(1)
O(2)	1517(10)	9737(8)	3266(8)	56(1)
C(3)	4733(10)	9435(9)	1702(9)	48(1)
O(3)	5614(9)	10229(8)	1645(9)	64(1)
C(4)	6862(10)	7656(9)	2813(9)	46(1)
C(5)	8335(11)	7934(10)	3139(10)	71(1)
C(6)	8746(10)	7870(10)	4240(10)	63(1)
C(7)	7683(10)	7577(10)	4954(9)	57(1)
C(8)	6286(10)	7312(9)	4656(9)	46(1)
C(9)	5860(10)	7350(9)	3549(8)	30(1)
C(10)	3081(10)	8258(9)	4990(9)	48(1)
C(11)	2385(10)	8437(10)	5944(9)	62(1)
C(12)	1703(11)	7332(10)	6313(10)	81(1)
C(13)	1628(11)	6125(10)	5731(10)	78(1)
C(14)	2325(10)	5972(9)	4746(9)	48(1)
C(15)	3055(10)	7045(9)	4371(9)	39(1)
C(16)	3806(10)	5167(9)	2681(9)	30(1)
C(17)	4939(10)	4480(9)	2807(9)	45(1)
C(18)	4597(11)	3145(9)	2445(10)	70(1)
C(19)	3389(11)	2577(9)	1966(10)	75(1)
C(20)	2384(11)	3319(9)	1862(10)	67(1)
N(1)	2552(10)	4624(9)	2158(9)	57(1)

Equivalent isotropic *U* defined as one third of the trace of the orthogonalized *U*_{ij} tensor.

1.36. IR(CO): 2063.3, 2003.2, 1982.5 cm⁻¹. ³¹P{¹H} NMR: δ = 55.67 ppm, ²J(P–Fe–¹⁹⁹Hg) = 404 Hz.

3.1.3. Preparation of I(CO)₂Ru(μ-Ph₂Ppy)₂Ru(CO)₂I **3**

CdI₂ (0.073 g 0.2 mmol) was added to a solution of Ru₃(CO)₉(Ph₂Ppy)₃ (0.13 g 0.1 mmol) in dichloromethane (20 ml). The mixture was stirred at room temperature for 24 h and filtered. The filtrate was concentrated and diethyl ether was added to give an orange precipitate. Orange crystals **3**·0.5MeOH·H₂O were obtained from crystallization in dichloromethane/methanol. Yield: 28 mg (24.8%). Anal. Calc. for C₃₈H₂₈I₂N₂O₄P₂Ru₂·0.5MeOH·H₂O: C, 40.97; H, 2.86; N, 2.48. Found: C, 40.58; H, 2.45; N, 2.87. IR (νCO): 2046.1, 1992.5, 1980.2 cm⁻¹. ³¹P{¹H} NMR: δ = 17.03 ppm.

3.2. X-ray crystallography

The intensity data of **1** and **3**·0.5MeOH·H₂O were collected at 294 K on a Rigaku RAXIS IIC imaging-

Table 4

Atomic coordinates of complex $3 \cdot 0.5\text{MeOH} \cdot \text{H}_2\text{O}$ ($\times 10^5$ for Ru and I; $\times 10^4$ for other atoms) and equivalent isotropic displacement coefficients ($\text{\AA}^2 \times 10^4$ for Ru and I; $\text{\AA}^2 \times 10^3$ for other atoms)

Atom	x	y	z	U_{eq}
Ru(1)	28535(5)	49488(4)	17160(2)	497(2)
Ru(2)	40313(4)	58507(4)	32378(2)	453(2)
I(1)	15815(6)	40941(6)	2038(3)	809(2)
I(2)	23045(4)	71589(4)	33799(2)	552(2)
P(1)	5177(2)	7574(1)	27	50(1)
			99(1)	
P(2)	2242(2)	4216(1)	33	48(1)
			89(1)	
N(1)	2983(5)	6842(4)	1618(3)	51(1)
N(2)	926(4)	4552(4)	2056(3)	49(1)
C(1)	4452(6)	5138(6)	1417(4)	65(1)
O(1)	5372(5)	5131(5)	1211(4)	92(1)
C(2)	2844(6)	3374(6)	1722(3)	63(1)
O(2)	2911(6)	2443(4)	1655(3)	83(1)
C(3)	5083(6)	4974(5)	3014(3)	58(1)
O(3)	5780(5)	4435(5)	2893(3)	79(1)
C(4)	4975(6)	6270(5)	4258(3)	61(1)
O(4)	5611(6)	6448(6)	4840(3)	102(1)
C(5)	3932(6)	7815(5)	2028(3)	55(1)
C(6)	4061(6)	8920(5)	1956(3)	60(1)
C(7)	3101(7)	9099(6)	1449(4)	80(1)
C(8)	2100(7)	8193(6)	1017(4)	75(1)
C(9)	2080(7)	7050(6)	1100(4)	66(1)
C(10)	6560(6)	7559(5)	2369(4)	60(1)
C(11)	7630(6)	7304(6)	2801(4)	68(1)
C(12)	8731(7)	7333(7)	2521(5)	83(1)
C(13)	8760(8)	7550(7)	1829(5)	87(1)
C(14)	7760(8)	7834(7)	1417(5)	93(1)
C(15)	6653(7)	7842(6)	1680(4)	73(1)
C(16)	5949(6)	9057(5)	3408(4)	58(1)
C(17)	6748(7)	10033(6)	3169(4)	75(1)
C(18)	7369(8)	11129(7)	3652(5)	92(1)
C(19)	7209(7)	11278(7)	4340(5)	83(1)
C(20)	6432(7)	10265(7)	4587(5)	84(1)
C(21)	5792(7)	9177(6)	4138(4)	69(1)
C(22)	724(5)	4206(5)	2715(3)	51(1)
C(23)	-434(5)	3896(5)	2908(3)	52(1)
C(24)	-1490(7)	3995(6)	2435(4)	70(1)
C(25)	-1390(6)	4376(6)	1778(4)	71(1)
C(26)	-173(6)	4611(5)	1588(4)	60(1)
C(27)	1768(6)	4226(5)	4279(3)	54(1)
C(28)	1013(7)	3156(7)	4473(4)	75(1)
C(29)	671(8)	3150(8)	5159(5)	99(1)
C(30)	1076(7)	4178(6)	5650(4)	75(1)
C(31)	1817(7)	5223(7)	5461(4)	76(1)
C(32)	2162(7)	5256(6)	4792(3)	65(1)
C(33)	2183(6)	2666(5)	3177(4)	62(1)
C(34)	1004(8)	1754(6)	2798(4)	75(1)
C(35)	979(9)	575(8)	2687(6)	111(1)
C(36)	2033(9)	269(8)	2924(6)	108(1)
C(37)	3273(8)	1176(7)	3304(5)	90(1)
C(38)	3352(7)	2406(6)	3451(4)	75(1)
O(5)	5339(12)	1795(11)	482(10)	217(1)
C(39)	5821(11)	2650(11)	125(9)	124(1)
O(1W)	8415(10)	1066(9)	998(7)	116(1)
O(2W)	10000	0	0	183(1)

Atoms O(5) to O(2w) belonging to the MeOH and two independent H₂O molecules all have half site occupancy.

plate diffractometer using Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) from a rotating-anode generator operating at 50 kV and 90 mA ($2\theta_{\text{min}} = 4^\circ$, $2\theta_{\text{max}} = 52^\circ$, 36° oscillation frames in the range of $0-180^\circ$, exposure 8 min. per frame) [18]. A self-consistent semi-empirical absorption correction based on Fourier coefficient fitting of symmetry-equivalent reflections was applied using the *ABSCOR* program [19]. Intensity data of **2** were collected in the variable ω -scan mode on a four-circle diffractometer (Siemens R3 m/V) using Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$, 50 kV, 25 mA, $2\theta_{\text{min}} = 3^\circ$, $2\theta_{\text{max}} = 55^\circ$) at 294 K.

The crystal structures were determined by direct methods which yielded the positions of all non-hydrogen atoms. All the non-hydrogen atoms were refined anisotropically on F data. Hydrogen atoms were all generated geometrically (C-H bond lengths fixed at 0.96 \AA), assigned appropriate isotropic thermal parameters and allowed to ride on their parent carbon atoms. All the H atoms were held stationary and included in the structure factor calculation in the final stage of full-matrix least-squares refinement on the F data.

All computation were performed on a IBM-compatible 486 PC with the *SHELXTL* program package [20]. Analytic expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated [21].

Information concerning X-ray data collection and structure refinement of all compounds is summarized in Table 1. Final atomic coordinates and equivalent isotropic thermal parameters for the non-hydrogen atoms are given in Tables 2–4.

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