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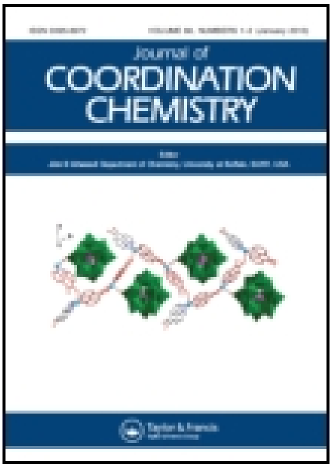

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Syntheses, characterization, and structures of three ruthenium complexes containing two monodentate dppm ligands

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Syntheses, characterization, and structures of three ruthenium complexes containing two monodentate dppm ligands

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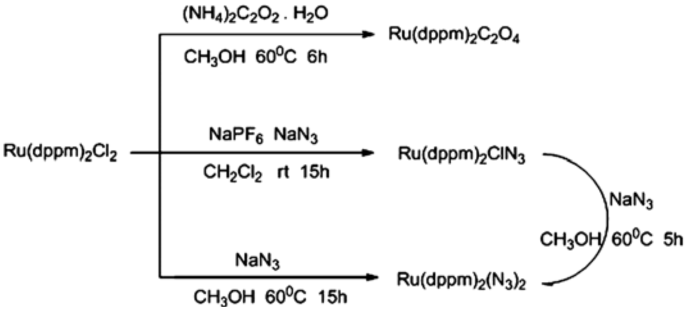

Three *cis*-Ru(dppm)$_2$XY complexes (XY = C_2O_4, **1**; X = Cl, Y = N_3, **2**; X = Y = N_3, **3**) were prepared by reactions of *cis*-Ru(dppm)$_2$Cl$_2$ with $(NH_4)_2C_2O_4$, a mixture of NaN_3 and $NaPF_6$, and only NaN_3, respectively, while **3** could also be obtained from further reaction of **2** with NaN_3 undergoing a facile chloride abstraction. All complexes have been characterized by IR, NMR, UV–vis, and luminescence spectroscopic analyses as well as X-ray diffraction studies. Of these structures, **1** shows oxalate coordinates to Ru as a chelating ligand, while **2** displays Ru and azide linear, and **3** gives two azide groups *cis* to each other, which are different from two substituting ligands commonly lying in *trans* positions in Ru(P–P)$_2$ complexes by using *cis*-Ru(dppm)$_2$Cl$_2$ as a precursor.

Keywords: Ruthenium; dppm; Syntheses; Structure

1. Introduction

Ruthenium diphosphine complexes have attracted much attention due to their structural diversities [1], extensive chemistry [2], and catalytic applications [3–5]. It is also well established that chloro ligands in *cis*-Ru(P–P)$_2$Cl$_2$ (P–P = dppm, dppe) could be readily abstracted by sodium salts, giving different ligand derivatives [6–8]. Since both the oxalate

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*Corresponding author. Email: luxiulian@cjlu.edu.cn and azide ligands have good electron transfer ability and versatile coordination [9, 10], we investigate the syntheses of dinuclear or multinuclear ruthenium complexes using *cis*-Ru(P–P)$_2$Cl$_2$ (P–P = dppm, dppe) as a precursor. Unfortunately, repeated efforts to prepare diruthenium or multinuclear ruthenium complexes bridged by oxalate or azide ligands were unsuccessful in this work.

We have a long-term interest in the syntheses, structures, and biological activities of ruthenium diphosphine complexes [2, 6, 11–13]. Herein, we report preparation and characterization of three Ru complexes containing two chelating dppm ligands and a comparison of X-ray structures of Ru(dppm)$_2$C$_2$O$_4$ (**1**), Ru(dppm)$_2$ClN$_3$ (**2**), and Ru(dppm)$_2$(N$_3$)$_2$ (**3**) (dppm = Ph$_2$P(CH$_2$)$_2$PPh$_2$). For comparison, similar reactions with *cis*-Ru(dppe)$_2$Cl$_2$ as a precursor were also examined. A portion of this work has been reported elsewhere [6].

2. Experimental

2.1. *General*

All reactions were performed under dry nitrogen using Schlenk techniques. Solvents were freshly distilled from standard drying agents. *cis*-Ru(dppm)$_2$Cl$_2$ was prepared according to literature procedures [14–16]. Infrared spectra in KBr disks were obtained on a Nicolet Nexus 670 FTIR spectrometer from 400 to 4000 cm^{-1}. ^{1}H and ^{31}P{^{1}H} NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer, ^{1}H shifts are reported relative to tetramethylsilane (TMS) and ^{31}P{^{1}H} shifts relative to 85% H$_3$PO$_4$. UV–vis spectra were measured on a TU1901 UV spectrophotometer and emission spectra were obtained on a Shimadzu RF-5301PC fluorophotometer with 1 cm quartz cell at room temperature. Elemental analyses were carried out with a Perkin-Elmer 2400II elemental analyzer.

2.1.1. Synthesis of Ru(dppm)$_2$C$_2$O$_4$ (1). To a solution of *cis*-Ru(dppm)$_2$Cl$_2$ (0.470 g, 0.5 mM) in CHCl$_3$ (15 mL) was added a solution of (NH$_4$)$_2$C$_2$O$_4$·H$_2$O (0.071 g, 0.5 mM) in CH$_3$OH (15 mL) and the mixture was refluxed at 60 °C for 6 h. The resultant solution was evacuated to dryness. The residue was extracted with CH$_2$Cl$_2$ (4 × 2 mL) to remove ammonium salts; concentration of the combined extracts to ca. 1 mL followed by addition of ether (2 mL) gave air-stable yellow solids of Ru(dppm)$_2$(C$_2$O$_4$) (**1**) (0.479 g, 79%). Anal. Calcd for C$_{52}$H$_{44}$O$_4$P$_4$Ru (%): C, 65.2; H, 4.63. Found: C, 65.31; H, 4.73. ^{1}H NMR (CDCl$_3$): δ 4.50–4.52 (m, 2H, CH$_2$), 4.92–5.01 (m, 2H, CH$_2$), 6.57 (t, 4H, dppm), 6.75 (t, 4H, dppm), 6.93 (t, 4H, dppm), 7.00 (m, 4H, dppm), 7.12–7.19 (m, 8H, dppm), 7.36–7.44 (m, 8H, dppm), 7.92 (d, 4H, dppm), 8.21 (m, 8H, dppm). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 1.87 (t), −17.29 (t). IR (KBr pellets, cm^{-1}): 3350 (ν_{PhH}), 3044(ν_{CH}), 1661 (ν_{as}COO), 1482 (ν_sCOO), 1434, 1375, 1175, 1066 (δ C–CH in the plane), 984, 780, 731 (δ C–C out of the plane), 696 (δ C–C in the plane), 547, 508, 475 (ν O/P–Ru).

2.1.2. Synthesis of Ru(dppm)$_2$ClN$_3$ (2). A mixture of *cis*-Ru(dppm)$_2$Cl$_2$ (0.470 g, 0.5 mM), NaPF$_6$ (0.186 g, 1 mM), and NaN$_3$ (0.033 g, 0.5 mM) was stirred in CH$_2$Cl$_2$ (30 mL) for 15 h at room temperature. The resultant suspension was filtered to give a filtrate, which was concentrated to ca. 1 mL, and then 3 mL of ether was added to afford air-stable yellow solids of Ru(dppm)$_2$ClN$_3$ (**2**) (0.289 g, 61%). Anal. Calcd for C$_{50}$H$_{44}$N$_3$ClP$_4$Ru (%): C, 63.39; H, 4.68;

N, 4.44. Found: C, 63.04; H, 4.85; N, 4.38. ^{1}H NMR (CD_2Cl_2): δ 4.12–4.16 (m, CH_2, 2H), 4.82–4.85 (m, CH_2, 2H), 6.53 (t, 6H, dppm), 6.88 (t, 4H, dppm), 7.04 (t, 4H, dppm), 7.17–7.41 (m, 18H, dppm), 7.53 (t, 4H, dppm), 7.88 (m, 4H, dppm). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 0.47(t), −18.39(t). IR (KBr pellets, cm^{-1}): 3202(ν_{PhH}), 3012(ν_{CH}), 2866, 2048 (terminal ν_{N3}), 1477($\nu_{C=C}$), 1389, 1334, 1094, 1072, 896, 757, 702, 633, 551 ($\nu_{N/P–Ru}$).

2.1.3. Synthesis of Ru(dppm)$_2$(N$_3$)$_2$ (3). To a solution of NaN_3 (0.067 g, 1 mM) in CH_3OH (15 mL) was added a solution of *cis*-Ru(dppm)$_2$Cl$_2$ (0.470 g, 0.5 mM) in CH_2Cl_2 (10 mL) and the mixture was refluxed at 60 °C for 15 h. The resultant solution was evacuated to dryness. The residue was extracted with CH_2Cl_2 (4 × 2 mL) to remove sodium salts; concentration of the combined extracts to ca. 1 mL followed by addition of ether (3 mL) gave air-stable yellow solids of Ru(dppm)$_2$(N$_3$)$_2$ (**3**) (0.334 g, 70%). Anal. Calcd for $C_{50}H_{44}N_6P_4Ru$ (%): C, 62.96; H, 4.65; N, 8.81. Found: C, 63.77; H, 4.44; N, 8.68. ^{1}H NMR (CD_2Cl_2): δ 4.50–4.52 (m, 2H, CH_2), 4.92–5.01 (m, 2H, CH_2), 6.55 (t, 4H, dppm), 6.70 (t, 4H, dppm), 6.94 (t, 4H, dppm), 7.06 (m, 6H, dppm), 7.11–7.29 (m, 6H, dppm), 7.36–7.40 (m, 6H, dppm), 7.60 (d, 6H, dppm), 7.78 (d, 2H, dppm), 8.11 (m, 2H, dppm). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 8.57(t), −11.35(t). IR (KBr pellets, cm^{-1}): 3400(ν_{PhH}), 2972 (ν_{CH}), 2036 (terminal ν_{N3}), 1574, 1189, 916, 878, 836, 808,741, 702, 675, 608, 543 (*ν*N/P–Ru).

2.2. *X-ray crystallographic study*

Yellow block crystals of Ru(dppm)$_2$C$_2$O$_4$ (**1**) and Ru(dppm)$_2$ClN$_3$ (**2**) were obtained by slow diffusion of hexane into CH_2Cl_2 solutions, while orange block crystals of Ru (dppm)$_2$(N$_3$)$_2$ (**3**) were obtained in CH_2Cl_2–hexane mixtures giving X-ray diffraction-quality crystals.

The crystals of **1**, **2,** and **3** were mounted on a fiber. X-ray diffraction measurements for **1** were performed on a *Rigaku Weissenbery IP diffractometer* using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 173(2) K and X-ray data for **2** and **3** were collected on a Siemens *SMART* diffractometer equipped with a CCD detector. The structures were solved with conventional direct methods using Mo Kα radiation at 173(2) K. Data were corrected for *Lorentz* and polarization effects with the *SMART* program [17] and for absorption effects with *SADABS* [18]. *SHELXTL-97* [19] was used to carry out the space group and the heavy atoms using the direct method or heavy atom method (*Patterson method*). All non-hydrogen atoms were assigned by difference *Fourier* method, amended by full-matrix least-square techniques.

3. Results and discussion

3.1. *Syntheses*

3.1.1. Reactions with (NH$_4$)$_2$C$_2$O$_4$. Treatment of *cis*-Ru(dppm)$_2$Cl$_2$ with equal equiv. of (NH$_4$)$_2$C$_2$O$_4$ under reflux resulted in air-stable Ru(dppm)$_2$C$_2$O$_4$ (**1**) as yellow solid in 79% yield (scheme 1). Initial attempts to synthesize dinuclear or multinuclear ruthenium complexes bridged by oxalate were unsuccessful, repeated efforts kept generating **1** when the molar ratio of *cis*-Ru(dppm)$_2$Cl$_2$ to (NH$_4$)$_2$C$_2$O$_4$ was changed from 2 : 1 or 1 : 2.

3.1.2. Reaction with NaN_3

3.1.2.1. *With NaN_3 and NH_4PF_6.* Treatment of *cis*-Ru(dppm)$_2$Cl$_2$ with one molar equiv. of NaN_3 in the presence of two molar equiv. of $NaPF_6$ gave one chloride loss to orange Ru(dppm)$_2$ClN$_3$ (**2**) in 61% yield. Although both **2** and Ru(dppm)$_2$(N$_3$)$_2$ (**3**) could be expected as main products, the $^{31}P\{^1H\}$ NMR spectral monitoring showed that **2** was mainly produced, together with minor amount of **3** and other unresolved Ru complexes with PF_6.

3.1.2.2. *With only NaN_3.* Ru(dppm)$_2$(N$_3$)$_2$ (**3**) was obtained in 70% yield by reaction of *cis*-Ru(dppm)$_2$Cl$_2$ with two molar equiv. of NaN_3 in $CHCl_3$ and CH_3OH under stirring for 15 h at room temperature. It could also be afforded when the molar ratio of *cis*-Ru(dppm)$_2$Cl$_2$ to NaN_3 was changed into 2 : 1. **3** could be isolated by undergoing further chloride substitution of **2**; the reaction of **2** with sodium azide was monitored by $^{31}P\{^1H\}$ NMR as well.

3.2. *Spectral characteristic*

^1H NMR spectra of **1** exhibit the protons of the benzene rings as multiplets at 7.95–6.88 ppm, and the proton signals at δ 5.1–4.0 ppm are assigned to CH_2 resonance of dppm, their peak integration ratio is about 10 : 1. $^{31}P\{^1H\}$ NMR spectra have two triplets at δ 1.87 and −17.29 ppm for **1**, δ 0.47 and −18.39 for **2**, and δ 8.57 and −11.35 ppm for **3**, due to coupling of four phosphorus of two dppm ligands, similar to that of the analogous *cis*-Ru(dppe)$_2$(C$_2$O$_4$) complex reported by our group [6].

IR spectra present the asymmetric and symmetric stretches of COO in oxalate of **1** with bands at 1661 and 1435 cm^{-1}, respectively, in contrast to those at 1642 and 1401 cm^{-1} for $(NH_4)_2C_2O_4$, indicating that the oxalate ligand coordinates to Ru. IR spectra show a strong and characteristic stretch for the terminal N_3 at 2048 cm^{-1} in **2** and 2036 cm^{-1} in **3**, comparing with 2136 cm^{-1} in NaN_3, due to azide terminally coordinated to Ru, similar to [((C$_6$Me$_6$)Ru(N$_3$)$_2$)$_2$(μ-diphosphine)] (diphosphine = dppm, dppe, dppp) ($\nu_{\text{terminal N3}}$, 2037 cm^{-1}) [10]. Decreasing frequencies of the terminal N_3 from 2048 cm^{-1} in **2** to 2036 cm^{-1} in **3** indicates the different electron density effect on Ru and N_3, consistent with their molecular structures.

UV–vis absorption spectra of the three complexes were measured in CH_2Cl_2. Electronic spectra for **1–3** exhibited two strong and broad bands in the ultraviolet region centered at $\lambda_{\max} = 224$ and 259 nm for **1**, $\lambda_{\max} = 201$ and 224 nm for **2**, and $\lambda_{\max} = 224$ and 259 nm for **3**, suggesting that all three complexes contain a conjugated double bond, in agreement with the results of their crystal structures (O1=C1–C1^{IV}=O1^{IV} in **1**, Ru1=N1=N2 in **2** and N1=N2=N3 in **3**). These two strong peaks are due to the $\pi \rightarrow \pi^*$ transition of $C_2O_4^{2-}$ and N_3^-. No strong bands in the visible region were detected for the complexes, indicating no Ru-ligand MLCT process, or ions of Ru^{2+} did not contribute to the absorption spectra of their complexes.

The emission spectra of **1–3** were measured in CH_2Cl_2 at room temperature. The spectra exhibited a strong and broad band at 428, 419, and 420 nm when excited at 509 nm for **1**, 498 nm for **2**, and 508 nm for **3**, respectively, attributed to $\pi \rightarrow \pi^*$ transitions, in agreement with the above absorption spectral results.

Table 1. Crystallographic data of $Ru(dppm)_2(C_2O_4)$ (**1**), $Ru(dppm)_2Cl(N_3)$ (**2**), and $Ru(dppm)_2(N_3)_2$ (**3**).

Compound	**1**	**2**	**3**
Formula	$C_{52}H_{44}O_4P_4Ru$	$C_{50}H_{44}P_4RuCl\ N_3$	$C_{50}H_{44}P_4RuN_6$
Formula weight (Mr)	958.30	948.19	976.85
Crystal dimensions (mm^3)	0.1 × 0.1 × 0.1	0.5 × 0.40 × 0.20	0.32 × 0.30 × 0.20
Crystal color	Yellow	Orange	Orange
Crystal system	Orthorhombic	Triclinic	Monoclinic
Space group	*P222₁*	*P-1*	*C2/c*
Unit cell dimensions	$a = 11.4053(8)$ Å,	$a = 11.198$ Å,	$a = 36.9402(19)$ Å,
	$\alpha = 90°$	$\alpha = 105.469(7)°$	$\alpha = 90°$
	$b = 24.6134(14)$ Å,	$b = 12.24840(10)$ Å,	$b = 11.3311(5)$ Å,
	$\beta = 90°$	$\beta = 93.130(10)°$	$\beta = 96.215(3)°$
	$c = 17.3529(9)$ Å,	$c = 21.44060(10)$ Å,	$c = 22.3979(10)$ Å,
	$\gamma = 90°$	$\gamma = 108.528(7)°$	$\gamma = 90°$
Volume (Å^3)	$V = 4871.4(5)$	$V = 2655.97(2)$	$V = 9320.1(8)$
Z	4	3	8
Calculated density (Mg m^{-3})	0.690	1.411	1.392
F (0 0 0)	1044	1150	4008
Absorption coefficient (mm^{-1})	0.252	0.558	0.519
θ for data collection (°)	1.65–27.48	2.04–27.48	2.07–27.48
Reflection collected	3095	20,629	35,259
Unique reflection (R(int))	3095 (R(int) = 0.032312)	12,005 (R(int) = 0.0223)	10,633 (R(int) = 0.0282)
Parameters	290	583	564
Goodness-of-fit on F^2	1.009	1.084	1.110
[a]R_1, wR_2 [$I > 2\sigma(I)$]	0.0447, 0.1345	0.0782, 0.2375	0.0577, 0.1659
[b]R_1, wR_2 (all data)	0.0489, 0.1415	0.0908, 0.2528	0.0667, 0.1733

[a] $R_1 = \sum||F_0| - |F_c||/\sum|F_0|$. [b] $wR_2 = \{\sum w|[(F_0{}^2 - F_c{}^2)^2]/\sum wF_0{}^4\}^{1/2}$; $\rho = [(F_0{}^2,\theta) + 2F_c{}^2]/3$.
Note: a indicates the length; b indicates the width.

3.3. *Crystallographic studies*

The crystallographic data of **1–3** are summarized in table 1, selected bond lengths and angles are listed in tables 2–4, and the molecular structures are illustrated in figures 1–3. Complex **1** crystallizes in the orthorhombic *P222₁* space group, **2** in the triclinic *P-1* space group, and **3** in the monoclinic *C2/c* space group, respectively.

The three structures of **1–3** are quite similar; the Ru is octahedrally coordinated by four phosphorus atoms of two monodentate dppm and O, Cl, or N donors. In the structure of **1**, ruthenium is coordinated by two oxygens of the chelating oxalate.

As expected, one of the bite angles of two diphosphine ligands (P(1)#1–Ru(1)–P(2): 70.54(4)°) is smaller than the chelated angle of the oxalate (O–Ru–O: 77.35(17)°); the other bite angles of the two diphosphine ligands are larger. Therefore, a regular octahedral structure cannot be achieved, giving distortion in the axial bonds. The Ru1–P1 distance is 2.3075 (11) Å, shorter than Ru–P2# (2.3477(11) Å), in which both P1 and P2# come from the same dppm ligand, attributed to the electron donation of the dianionic oxalate. The Ru–O bond length is 2.114(3) Å, which is slightly longer than that of $Ru(bpy)_2(ox)$ [20] and $[Ru(\eta^2\text{-}C_2O_4)(PPh_3)(\eta^6\text{-}p\text{-}Pr^IC_6H_4Me)]$ [21] (2.080(3)–2.093(6) Å), suggestive of the steric effect of the bulky diphosphine. The C1–O1 bond length (1.287(5) Å), slightly longer than common C=O double bond length (C1–O2, 1.216(5) Å), is indicative of partial double bond character. The sum of angles at C1 is 360.0° (O(2)–C(1)–O(1): 125.6(4)°, O(2)–C(1)–C(1)#1: 119.7(3)°, and O(1)–C(1)–C(1)#1: 114.8(2)°), suggesting that O1, C1, O2, and C1# are coplanar.

Similar to that of **1**, the Ru in **2** is octahedrally coordinated by four P from two dppm, one N from the terminal azide and one Cl in *cis* positions.

Table 2. Selected bond lengths (Å) and angles (°) for **1**.

Bond lengths (Å)			
Ru(1)–O(1)	2.114(3)	Ru(1)–O(1)#1	2.114(3)
Ru(1)–P(1)#1	2.3075(11)	Ru(1)–P(1)	2.3075(11)
Ru(1)–P(2)	2.3477(11)	Ru(1)–P(2)#1	2.3477(11)
O(1)–C(1)	1.287(5)	O(2)–C(1)	1.216(5)
P(1)–C(6)	1.843(5)	P(1)–P(2)#1	2.6883(15)
P(2)–C(6)#1	1.844(5)	P(2)–P(1)#1	2.6883(15)
C(1)–C(1)#1	1.556(8)	C(6)–P(2)#1	1.844(5)
P(2)–C(6)#1	1.844(5)		
Bond angles (°)			
O(1)–Ru(1)–O(1)#1	77.35(17)	O(1)–Ru(1)–P(1)#1	162.30(12)
O(1)#1–Ru(1)–P(1)#1	97.14(10)	O(1)–Ru(1)–P(1)	97.14(10)
O(1)#1–Ru(1)–P(1)	162.30(12)	P(1)#1–Ru(1)–P(1)	92.78(6)
O(1)–Ru(1)–P(2)	93.10(12)	O(1)#1–Ru(1)–P(2)	95.92(12)
P(1)#1–Ru(1)–P(2)	70.54(4)	P(1)–Ru(1)–P(2)	101.20(4)
O(1)–Ru(1)–P(2)#1	95.92(12)	O(1)#1–Ru(1)–P(2)#1	93.10(12)
P(1)#1–Ru(1)–P(2)#1	101.20(4)	P(1)#1–Ru(1)–P(2)#1	101.20(4)
P(2)–Ru(1)–P(2)#1	168.45(6)	C(1)–O(1)–Ru(1)	116.2(3)
C(6)–P(1)–Ru(1)	95.40(15)	C(6)–P(1)–P(2)#1	43.21(14)
Ru(1)–P(1)–P(2)#1	55.43(3)	C(6)#1–P(2)–Ru(1)	94.02(16)
C(6)#1–P(2)–P(1)#1	43.17(15)	Ru(1)–P(2)–P(1)#1	54.03(4)
O(2)–C(1)–O(1)	125.6(4)	O(2)–C(1)–C(1)#1	119.7(3)
O(1)–C(1)–C(1)#1	114.8(2)	C(9)–C(2)–C(20)	119.7(5)
P(1)–C(6)–P(2)#1	93.6(2)		

Note: Symmetry transformations used to generate equivalent atoms: #1 $-x, y, -z+3/2$.

Table 3. Selected bond lengths (Å) and angles (°) for **2**.

Bond lengths (Å)			
Ru1–N1	2.076(4)	Ru1–P4	2.3097(15)
Ru1–P2	2.3270(14)	Ru1–P3	2.3589(14)
Ru1–P1	2.3654(14)	Ru1–Cl1	2.4433(14)
P2–C13	1.832(6)	P4–C38	1.860(6)
N1–N2	1.134(9)	N2–N3	1.502(12)
P1–C13	1.857(6)	P3–C38	1.851(6)
Bond angles (°)			
N1–Ru1–P4	89.70(15)	N1–Ru1–P2	165.57(14)
P4–Ru1–P2	94.20(5)	N1–Ru1–P3	91.30(13)
P4–Ru1–P3	71.18(5)	P2–Ru1–P3	103.11(5)
N1–Ru1–P1	94.54(13)	P4–Ru1–P1	105.84(5)
P2–Ru1–P1	71.02(5)	P3–Ru1–P1	173.45(5)
N1–Ru1–Cl1	86.46(13)	P4–Ru1–Cl1	163.11(6)
P2–Ru1–Cl1	93.45(5)	P3–Ru1–Cl1	92.42(5)
P1–Ru1–Cl1	90.88(5)	C13–P2–Ru1	95.95(19)
C13–P2–C14	105.3(3)	C13–P2–C20	106.3(3)
C38–P4–Ru1	96.0(2)	C38–P3–Ru1	94.60(18)
N2–N1–Ru1	175.2(6)	N1–N2–N3	178.4(10)
P3–C38–P4	94.1(3)		

In **2**, Ru and three N atoms of azide ligand are almost linear (N2–N1–Ru1: 175.2(6)°, N1–N2–N3: 178.4(10)°). Since the nitrogen from azide generally adopts sp^2 hybridization, the bond angle of Ru–N–N is usually in the range of 110°–150° in ruthenium azide

Table 4. Selected bond lengths (Å) and angles (°) for **3**.

Bond lengths (Å)			
Ru1–N4	2.139(4)	Ru1–N1	2.163(4)
Ru1–P3	2.3096(11)	Ru1–P2	2.3097(10)
Ru1–P1	2.3467(10)	Ru1–P4	2.3496(10)
P1–C44	1.861(4)	P2–C44	1.866(4)
P3–C43	1.854(4)	P4–C43	1.858(4)
N1–N2	1.127(5)	N2–N3	1.164(6)
N4–N5	1.098(6)	N5–N6	1.174(7)
Bond angles (°)			
N4–Ru1–N1	86.37(16)	N4–Ru1–P3	93.06(13)
N1–Ru1–P3	164.06(11)	N4–Ru1–P2	167.04(12)
N1–Ru1–P2	88.60(11)	P3–Ru1–P2	95.03(4)
N4–Ru1–P1	96.58(11)	N1–Ru1–P1	94.82(12)
P3–Ru1–P1	101.06(4)	P2–Ru1–P1	71.94(4)
N4–Ru1–P4	90.58(12)	N1–Ru1–P4	92.10(11)
P3–Ru1–P4	71.97(4)	P2–Ru1–P4	101.55(4)
P1–Ru1–P4	170.33(4)	C44–P1–Ru1	95.39(13)
C44–P2–Ru1	96.47(13)	N2–N1–Ru1	129.8(3)
N5–N4–Ru1	139.7(4)	N4–N5–N6	179.2(8)
N1–N2–N3	175.8(6)		

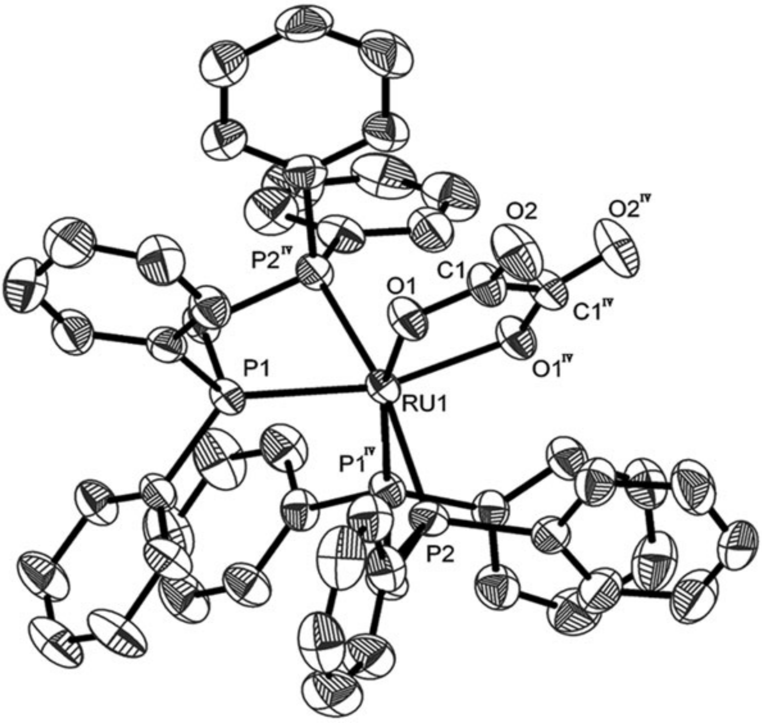


Figure 1. Molecular structure of Ru(dppm)$_2$C$_2$O$_4$ (**1**); hydrogens are omitted for clarity.

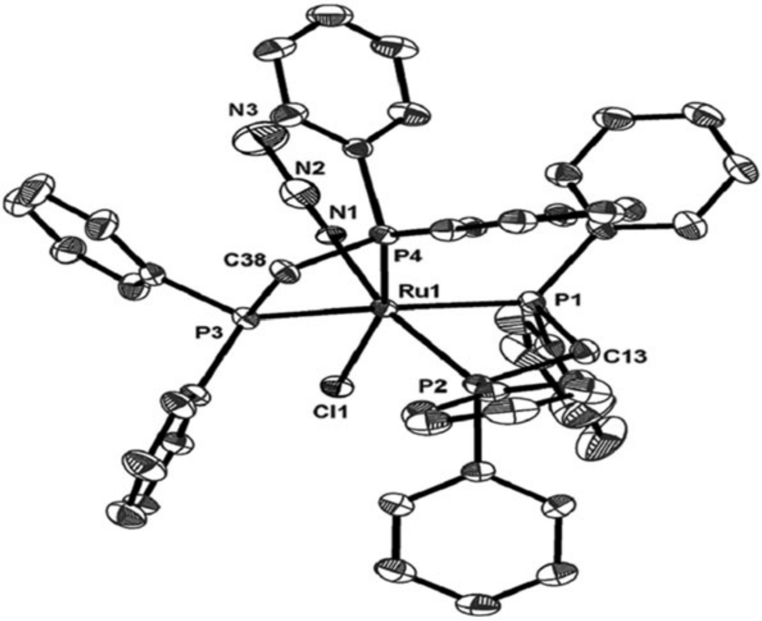


Figure 2. Molecular structure of Ru(dppm)$_2$ClN$_3$ (**2**); hydrogens are omitted for clarity.

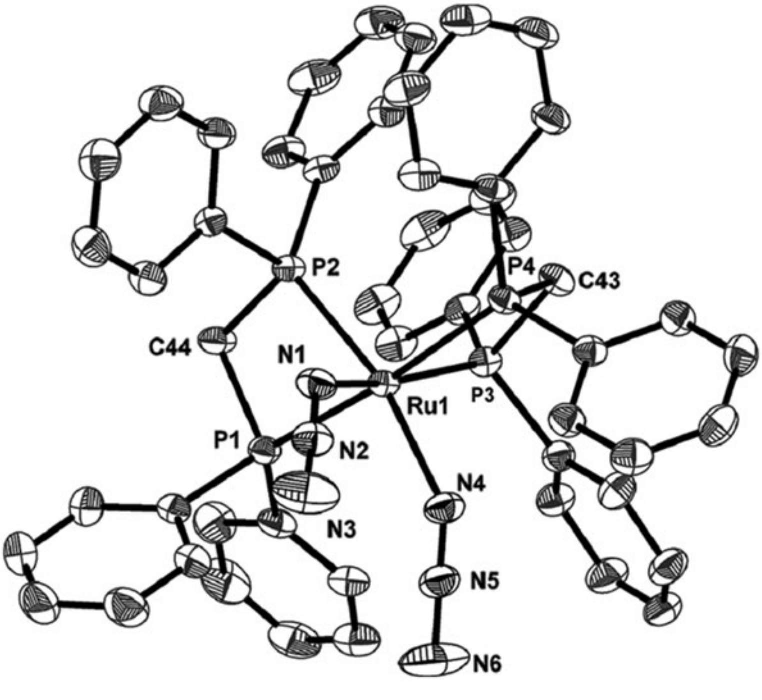
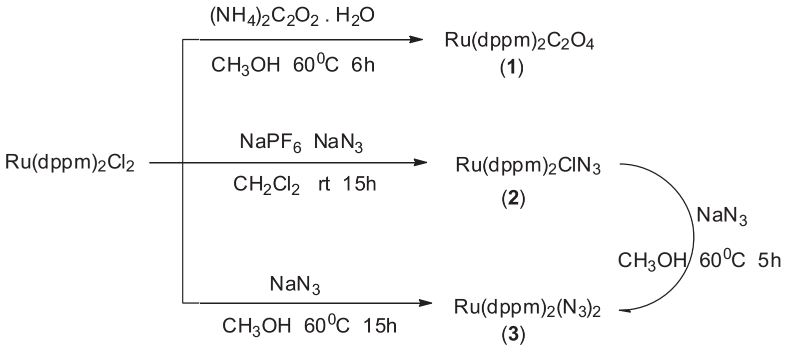


Figure 3. Molecular structure of Ru(dppm)$_2$(N$_3$)$_2$ (**3**); hydrogens are omitted for clarity.



Scheme 1. Syntheses of complexes **1**, **2**, and **3**.

complexes [10, 22–24]. Complex **2** is the first compound in which Ru ion and azide ligand nearly lie on a straight line.

The bond angle P1–Ru–P3 (173.45(5)°) shows that two P are *trans* to each other, the Ru1–P1 and Ru1–P3 bond distances are almost the same (2.3654(14) and 2.3589(14) Å), longer than Ru1–P2 and Ru1–P4 (2.3270(14) and 2.3097(15) Å), while P2 is *trans* to the N1 of the azide with bond angle of N1–Ru–P2 (165.57(14)°).

The Ru1–N1 bond length (2.076(4) Å) is significantly shorter than the common range of Ru–N bond lengths (2.10(3)–2.20(8) Å) in ruthenium azide complexes [10, 22–24], indicative of partial double bond character. Moreover, N1–N2 (1.134(9) Å) has significant double bond character while N2–N3 (1.502(12) Å) is typically a single bond, quite different from those having almost the same N–N double bond lengths in **3** (N1–N2: 1.127(5), N2–N3: 1.164(6), N4–N5: 1.098(6), N5–N6: 1.174(7) Å) and other related Ru phosphine complexes with terminal azide groups, such as $(C_6Me_6)Ru(PPh_3)(N_3)_2$ (N–N: 1.203 or 1.192–1.158 Å) [10]. The angle of N1–Ru1–Cl1 (86.46(13)°) is quite close to the Cl–Ru–Cl angle of the starting *cis*-$Ru(dppm)_2Cl_2$ (Cl–Ru–Cl (84.37(3)° [16] or 85.50(1)° [25, 26]), indicating that azide and chloride are *cis* to each other. The Ru–Cl bond length (2.4433(14) Å) is slightly shorter than for *trans*-$[Ru(P–P)_2Cl]^+$ complexes, e.g. *trans*-$[Ru(dppm)_2Cl(=C(CH_2)_3O)]PF_6$ (2.4740(14) Å) [16].

As in **1**, the bite angles of the chelating diphosphine in both **2** and **3** are the same and narrow, P1–Ru1–P2 (71.02(5)°) and P3–Ru1–P4 (71.18(5)°) for **2** and P1–Ru1–P2 (71.94(4)°) and P3–Ru1–P4 (71.97(4)°) for **3**, consistent with those of analogous $[Ru(dppm)_2]^{2+}$ complexes, due to strained phenyl rings.

In **3**, two azides are *cis* to each other, different from those substituted ligands always located *trans* in analogous complexes prepared from *cis*-$Ru(dppm)_2Cl_2$ [7, 8, 16, 27], because the *trans*-$[Ru(P–P)_2Cl]^+$ complexes may have more thermodynamic stability than those with *cis* structures [16]. In sharp contrast with **2**, two azide ligands (N1–N2–N3 and N4–N5–N5) and Ru in **3** are not linear (Ru1–N1–N2: 129.8(3), Ru1–N4–N5: 139.7(4)). The Ru–N bond lengths (Ru1–N1 (2.163(4) Å) and Ru1–N4 (2.139(4) Å)), in agreement with the normal range of Ru–N bond lengths (2.10(3)–2.20(8) Å), are significantly longer than that of **2** (Ru1–N1 (2.076(4) Å)) and other ruthenium azide complexes. In comparison with **2**, N–N bond lengths in **3** (N1–N2: 1.127(5) Å, N4–N5: 1.098(6) Å) are almost the same as those far away from Ru (N2–N3: 1.164(6) Å, N5–N6: 1.174(7) Å), suggesting N=N double bond, seldom found in the literature. These different Ru–N and N–N bond lengths in **2** and **3** explain the different electronic effect between Ru and N_3, consistent with the different stretching frequencies of $\nu_{\text{terminal N3}}$ in their IR spectra.

Likewise in **2**, the bond angle P1–Ru–P4 (170.33(4)°) in **3** shows that two P are also *trans* to each other; two pairs of Ru1–P1 and Ru1–P4 bond distances are almost the same (2.3467(10) and 2.3496(10) Å), but longer than Ru1–P2 and Ru1–P3 bond lengths (2.3097 (11) and 2.3096(10) Å), while P2 and P3 are *trans* to N4 and N1 of the azides with bond angles of P2–Ru1–N4 and P3–Ru1–N1 (164.06(11)° and 167.04(12)°), respectively. All the Ru–P bond lengths in **3** are shorter by about 0.02 Å than those in **2**. Three nitrogens of one azide are nearly linear (N4–N5–N6: 179.2(8)°), while those of the other azide are slightly bent (N1–N2–N3: 175.8(6)°), due to steric hindrance of phenyl rings of dppm.

4. Conclusion

We have synthesized and characterized three $Ru(dppm)_2$ complexes, $Ru(dppm)_2C_2O_4$ (**1**), $Ru(dppm)_2ClN_3$ (**2**), and $Ru(dppm)_2(N_3)_2$ (**3**). The remarkable feature of Ru and azide staying nearly on a straight line in the structure of **2**, is unprecedented for Ru(azide) complexes.

Supplementary material

Crystallographic data for $Ru(dppm)_2C_2O_4$ (**1**), $Ru(dppm)_2ClN_3$ (**2**), and $Ru(dppm)_2(N_3)_2$ (**3**) ($dppm = Ph_2PCH_2PPh_2$) have been deposited with the Cambridge Crystallographic Data Center as CCDC Nos. 961105, 961106, and 961107, respectively. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1233-336033, E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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