

## Short Communication

### Synthesis and crystal structure of a ruthenium complex containing two monodentate DPPM ligands (DPPM = bis(diphenylphosphino)methane)

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#### Abstract

The compounds *trans*-Ru(quin)<sub>2</sub>(dppm)<sub>2</sub> and *cis*- and *trans*-Ru(quin)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (quin = 2-quinaldinate anion; dppm = bis(diphenylphosphino)methane) have been prepared by the reaction of RuCl<sub>3</sub>·3H<sub>2</sub>O and Hquin, in basic alcoholic medium, in the presence of dppm and PPh<sub>3</sub>, respectively. The compounds are characterized by elemental analysis, IR, <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy. The structure of *trans*-Ru(quin)<sub>2</sub>(dppm)<sub>2</sub>·2MeOH has been determined by X-ray crystallography. The compound has two bidentate N,O-quinaldinate and two monodentate dppm ligands in a *trans*-N, *trans*-O, *trans*-P arrangement.

#### Introduction

Phosphine ligands have played an important role in the development of transition metal chemistry. Of these ligands, bis(diphenylphosphino)methane has been extensively used in numerous transition metal complexes [1–4]. In this ligand, three coordination modes are usually observed: (i) as bridge between two metal atoms; (ii) as chelate forming a four-membered ring; (iii) as monodentate. In the case of ruthenium, numerous examples of the bridging and chelate coordination modes have been described [5–18]; however, although some

examples of the monodentate coordination have been described [9, 13, 15, 19, 20], crystal structures of this coordination mode in ruthenium chemistry are very scarce [19, 20].

In this report, we describe the synthesis, characterization and crystal structure determination of *trans*-Ru(quin)<sub>2</sub>(dppm)<sub>2</sub>·2MeOH (quin = 2-quinaldinate anion), a new dppm-ruthenium complex, containing two dppm monodentate ligands. The similar *cis*- and *trans*-Ru(quin)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> compounds are also described.

#### Experimental

All reactions were carried out in an inert atmosphere, using standard Schlenk techniques. RuCl<sub>3</sub>·3H<sub>2</sub>O (Engelhard), Hquin (Fluka), dppm (Fluka), PPh<sub>3</sub> (Panreac) were purchased from commercial sources. Solvents (Panreac or sds) were used without previous purification.

<sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectra were recorded with a Varian VXR-300 spectrometer, using CDCl<sub>3</sub> as solvent. <sup>1</sup>H NMR chemical shifts are reported in ppm relative to TMS; <sup>31</sup>P NMR chemical shifts are reported in ppm relative to external 85% H<sub>3</sub>PO<sub>4</sub>. IR spectra were recorded, as KBr discs, on a Philips PU 9712 or on a Perkin-Elmer 1330 infrared spectrophotometer. Elemental analyses for C, H and N were performed in the Microanalytical Service of the Complutense University of Madrid.

#### Synthesis of *trans*-Ru(quin)<sub>2</sub>(dppm)<sub>2</sub>·2MeOH

To a solution of RuCl<sub>3</sub>·3H<sub>2</sub>O (0.15 g, 0.57 mmol) in methanol (20 ml) were added successively methanol solutions of Na<sub>2</sub>CO<sub>3</sub> (0.22 g, 1.71 mmol) (10 ml), dppm (0.66 g, 1.71 mmol) (10 ml) and 2-quinaldinic acid (0.30 g, 1.71 mmol) (10 ml). The reaction mixture was heated at reflux for 3 h to give a red solution. This solution was cooled to room temperature and the excess of dppm crystallized. The red solution was filtered, concentrated to vacuum and left to stand at room temperature, to give red crystals of *trans*-Ru(quin)<sub>2</sub>(dppm)<sub>2</sub>·2MeOH. *Anal.* Found: C, 67.31; H, 4.89; N, 2.33. *Calc.*: C, 67.65; H, 5.05; N, 2.19%.

#### Synthesis of *cis*- and *trans*-Ru(quin)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>·S (S = MeOH, Me<sub>2</sub>CO)

To a solution of RuCl<sub>3</sub>·3H<sub>2</sub>O (0.15 g, 0.57 mmol) in methanol (20 ml) was added KOH (0.09 g, 1.71 mmol) in methanol (10 ml), 0.45 g (1.71 mmol) of PPh<sub>3</sub> in methanol (10 ml) and 0.30 g (1.71 mmol) of 2-

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quinaldinic acid in 10 ml of methanol. The reaction was heated for 3 h giving a red solution. When the solution was allowed to stand at room temperature a brown solid *cis*-Ru(quin)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> was deposited. The solid was filtered and the red solution was concentrated to vacuum. Red crystals of *trans*-Ru(quin)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>·MeOH were formed in 24 h. The compound can be recrystallized from MeOH or acetone. *Anal.* for Ru(quin)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>·MeOH: Found: C, 68.36; H, 4.57; N, 2.71. Calc.: C, 68.32; H, 4.63; N, 2.80%. *Anal.* for Ru(quin)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>·Me<sub>2</sub>CO: Found: C, 68.54; H, 4.82; N, 2.56. Calc.: C, 68.93; H, 4.71; N, 2.72%.

#### X-ray structure determinations

A summary of the fundamental crystal data is given in Table 1. A red crystal of prismatic shape was resin epoxy coated and mounted in a kappa diffractometer. The cell dimensions were refined by least-squares fitting of the  $\theta$  values of 25 reflections. The intensities were corrected for Lorentz and polarization effects. Scattering factors for neutral atoms and anomalous dispersion corrections for Ru and P were taken from the International Tables for X-ray Crystallography [21]. The structure was solved by Patterson and Fourier methods. An empirical absorption correction [22] was applied at the end of the isotropic refinement. Some positional

TABLE 1. Crystal and refinement data for Ru(quin)<sub>2</sub>(dppm)<sub>2</sub>·2CH<sub>3</sub>OH

Formula	C <sub>70</sub> H <sub>56</sub> N <sub>2</sub> O <sub>4</sub> P <sub>4</sub> Ru·2CH <sub>3</sub> OH
M <sub>r</sub>	1278.3
Crystal system	monoclinic
Space group	P2 <sub>1</sub> /n
a (Å)	14.253(5)
b (Å)	15.240(4)
c (Å)	15.171(4)
$\beta$ (°)	107.46(3)
V (Å <sup>3</sup> )	3144(2)
Z	2
F(000)	1324
$\rho_{\text{calc}}$ (g cm <sup>-3</sup> )	1.35
Temperature (°C)	22
$\mu$ (cm <sup>-1</sup> )	3.962
Crystal Dimensions (mm)	0.4 × 0.2 × 0.2
Diffractometer	Enraf-Nonius CAD4
Radiation	graphite-monochromated Mo K $\alpha$ ( $\lambda = 0.71069$ Å)
Scan technique	$\Omega/2\theta$
$\theta$	1 < $\theta$ < 27
Data collected	(-18, 0, 0) to (18, 19, 19)
Reflections collected	7625
Unique data	6843
Unique data ( $I \geq 2\sigma(I)$ )	3469
R <sub>int</sub> (%)	10.6
Standard reflections	3/233
R <sub>F</sub> (%)	5.6
R <sub>wF</sub> (%)	6.3
Average shift/error	0.023

disorder was found around the MeOH molecule of crystallization; because of this the C36 and O3 have been refined only isotropically. No trend in  $\Delta F$  versus  $F_0$  or  $(\sin \theta/\lambda)$  was observed.

Hydrogen atoms were fixed at calculated positions, only those of MeOH were located in a final Fourier difference synthesis and their coordinates were subsequently refined. Final difference synthesis showed no significant electron density. Most of the calculations were carried out with the X-Ray 80 system [23].

Atomic coordinates for the non-hydrogen atoms are given in Table 2.

TABLE 2. Atomic parameters for C<sub>70</sub>H<sub>56</sub>N<sub>2</sub>O<sub>4</sub>P<sub>4</sub>Ru·2CH<sub>3</sub>OH

Atom	x/a	y/b	z/c
O3	0.6439(6)	0.4414(6)	0.2243(6)
C36	0.6449(9)	0.4051(9)	0.1499(9)
Ru	0.0000(0)	0.0000(0)	0.0000(0)
P1	0.1136(1)	0.0982(1)	0.0938(1)
P2	0.3208(1)	0.1801(1)	0.1061(1)
N	0.1059(4)	-0.0995(4)	0.0469(4)
O1	-0.0381(3)	-0.0545(3)	0.1101(3)
O2	0.0065(4)	-0.1479(4)	0.2276(4)
C1	0.0196(6)	-0.1121(5)	0.1590(5)
C2	0.1038(5)	-0.1373(5)	0.1244(5)
C3	0.1709(6)	-0.2008(6)	0.1728(6)
C4	0.2448(7)	-0.2248(6)	0.1389(7)
C5	0.2499(6)	-0.1894(6)	0.0558(6)
C6	0.1791(5)	-0.1266(4)	0.0099(5)
C7	0.1826(5)	-0.0929(5)	-0.0751(5)
C8	0.2552(6)	-0.1181(6)	-0.1119(6)
C9	0.3272(7)	-0.1777(7)	-0.0657(8)
C10	0.3254(7)	-0.2124(7)	0.0155(8)
C11	0.2219(5)	0.1006(5)	0.0537(5)
C12	0.0736(5)	0.2122(5)	0.0871(5)
C13	0.0733(7)	0.2622(5)	0.0112(6)
C14	0.0289(9)	0.3439(6)	-0.0037(8)
C15	-0.0106(9)	0.3786(6)	0.0587(9)
C16	-0.0109(8)	0.3322(7)	0.1353(8)
C17	0.0305(7)	0.2486(6)	0.1489(7)
C18	0.1577(5)	0.0693(5)	0.2149(5)
C19	0.2544(6)	0.0449(6)	0.2584(6)
C20	0.2838(7)	0.0177(8)	0.3479(7)
C21	0.2182(8)	0.0137(9)	0.3983(6)
C22	0.1221(7)	0.0379(7)	0.3571(6)
C23	0.0918(6)	0.0630(6)	0.2662(5)
C24	0.4289(5)	0.1083(5)	0.1434(5)
C25	0.5011(6)	0.1318(7)	0.2216(6)
C26	0.5837(7)	0.0776(9)	0.2559(7)
C27	0.5910(7)	0.0009(9)	0.2113(8)
C28	0.5196(7)	-0.0229(6)	0.1336(8)
C29	0.4395(6)	0.0308(6)	0.0990(6)
C30	0.3423(6)	0.2332(5)	0.0060(6)
C31	0.3129(8)	0.2049(7)	-0.0835(7)
C32	0.3317(9)	0.2520(8)	-0.1541(7)
C33	0.3829(8)	0.3288(8)	-0.1332(8)
C34	0.4094(10)	0.3604(8)	-0.0464(9)
C35	0.3908(8)	0.3123(7)	0.0230(7)

## Results and discussion

The reaction of  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  with Hquin (Hquin = 2-quinaldinic acid) and dppm in methanol in the presence of  $\text{Na}_2\text{CO}_3$  leads to the formation of *trans*- $\text{Ru}(\text{quin})_2(\text{dppm})_2$ . However, the similar reaction with  $\text{PPh}_3$  leads to the isolation of *cis*- and *trans*- $\text{Ru}(\text{quin})_2(\text{PPh}_3)_2$ . The compounds are stable, in the solid state, to air and moisture and can be manipulated in air without appreciable decomposition. They are soluble in common polar organic solvents, such as  $\text{CH}_2\text{Cl}_2$ , acetone, dmsO, etc. The *cis*- $\text{Ru}(\text{quin})_2(\text{PPh}_3)_2$  compound is unstable in solution, giving *trans*- $\text{Ru}(\text{quin})_2(\text{PPh}_3)_2$  in 48 h.

The IR spectrum (Table 3) of *trans*- $\text{Ru}(\text{quin})_2(\text{dppm})_2$  displays bands due to the presence of the 2-quinaldinate

TABLE 3. IR data ( $\text{cm}^{-1}$ ) of the compounds

Compound	$\nu_{\text{as}}(\text{COO})$	$\nu_{\text{s}}(\text{COO})$	$\Delta\nu$ ( $\text{cm}^{-1}$ )	$\text{C}_6\text{H}_5$
$\text{Ru}(\text{quin})_2(\text{dppm})_2 \cdot 2\text{MeOH}$	1640	1350	290	1480 1430 1090 700
$\text{Ru}(\text{quin})_2(\text{PPh}_3)_2 \cdot \text{MeOH}$	1625	1310	315	1480 1430 1090 700

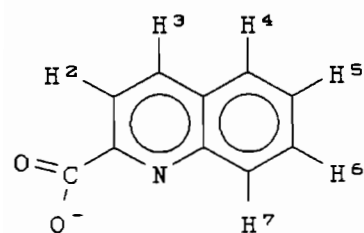


Fig. 1. 2-Quinaldinate anion.

and dppm ligands. The separation between the  $\nu_{\text{as}}(\text{COO})$  and  $\nu_{\text{s}}(\text{COO})$  ( $290 \text{ cm}^{-1}$ ) of the 2-quinaldinate ligand indicates that the carboxylate group is bonded only by one oxygen atom. Thus, if we presume a bidentate coordination via one oxygen atom of the COO group and the pyridinic nitrogen, then two dppm ligands are monodentated. In accordance with this, the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum (Table 4) shows two triplets centered at 26.82 and  $-28.83$  ppm with the same coupling constant (21.5 Hz); the first signal is due to the coordinated phosphorus atom and the second is due to the free phosphorus atom of dppm. The multiplicity observed could be explained with an AA'XX' system if  $J_{\text{AA}'} \gg J_{\text{AX}} = J_{\text{A}'\text{X}}$ . However, the intensities observed in both triplets (c. 1:2:1) are in better accordance if there are also coupling constants  $J_{\text{AX}'} = J_{\text{A}'\text{X}}$ . The spectrum can be simulated with  $J_{\text{AA}'} = 300$  Hz,  $J_{\text{AX}} = J_{\text{A}'\text{X}} = 21.5$  Hz and  $J_{\text{AX}'} = J_{\text{A}'\text{X}} = 14$  Hz. These coupling constants are in agreement with those described in the literature [24]. A similar system has been found in  $\text{Ru}(\text{TPP})(\text{dppm})_2$  (TPP = 5,10,15,20-tetraphenylporphyrinato) in which two monodentate dppm ligands are also present; in this compound, weak  $\text{Ru}\dots\text{P}_{\text{X}}$  and porphyrin $\dots\text{P}_{\text{X}}$  interactions in solution are supposed in order to explain the AA'XX' system [19]. In our compound, *trans*- $\text{Ru}(\text{quin})_2(\text{dppm})_2$ , some similar interactions in solution must be occurring which could explain the  $J_{\text{A}'\text{X}}$  and  $J_{\text{AX}'}$  values, although the coupling over four bonds,  $\text{P}_{\text{A}'}-\text{P}_{\text{X}'}$  and  $\text{P}_{\text{A}}-\text{P}_{\text{X}}$ , cannot be discarded. The  $^1\text{H}$  NMR spectrum (Table 4) shows the signals due to the  $\text{CH}_2$  protons of the dppm ligand at 2.66 ppm. The protons of the phenyl groups and 2-quinaldinate ligands are observed as several undistinguishable multiplets between 6.5 and 7.9 ppm. The only aromatic proton that can be assigned to 2-quinaldinate ligand is the  $\text{H}^2$  proton (Fig. 1), which is observed as a doublet at 9.50 ppm ( $J(\text{H}^2-\text{H}^3) = 9.0$  Hz).

TABLE 4.  $^1\text{H}$  and  $^{31}\text{P}$  NMR data (ppm) of the compounds

Compound	$^1\text{H}$ NMR			$^{31}\text{P}$ NMR
	quin $\text{H}^2$ ( $J(\text{H}^2-\text{H}^3)$ )	$\text{PPh}_3/\text{quin}$ ( $\text{H}^3-\text{H}^7$ )	Others	
<i>trans</i> - $\text{Ru}(\text{quin})_2(\text{dppm})_2 \cdot 2\text{MeOH}$	9.50d (9.00 Hz)	6.5–7.9m	2.66s, br ( $\text{CH}_2$ , dppm) 3.49s (Me) 5.30s (OH)	26.82t $-28.83\text{t}$ ( $J_{\text{AX}} = J_{\text{A}'\text{X}} = 21.5$ )
<i>trans</i> - $\text{Ru}(\text{quin})_2(\text{PPh}_3)_2 \cdot \text{MeOH}$	9.59d (8.70 Hz)	6.7–7.9m	3.50s (Me) 5.30s (OH)	29.46s
<i>cis</i> - $\text{Ru}(\text{quin})_2(\text{PPh}_3)_2 \cdot \text{MeOH}$	9.06d (9.00 Hz)	6.8–7.8m	3.50s (Me) 5.30s (OH)	43.02s

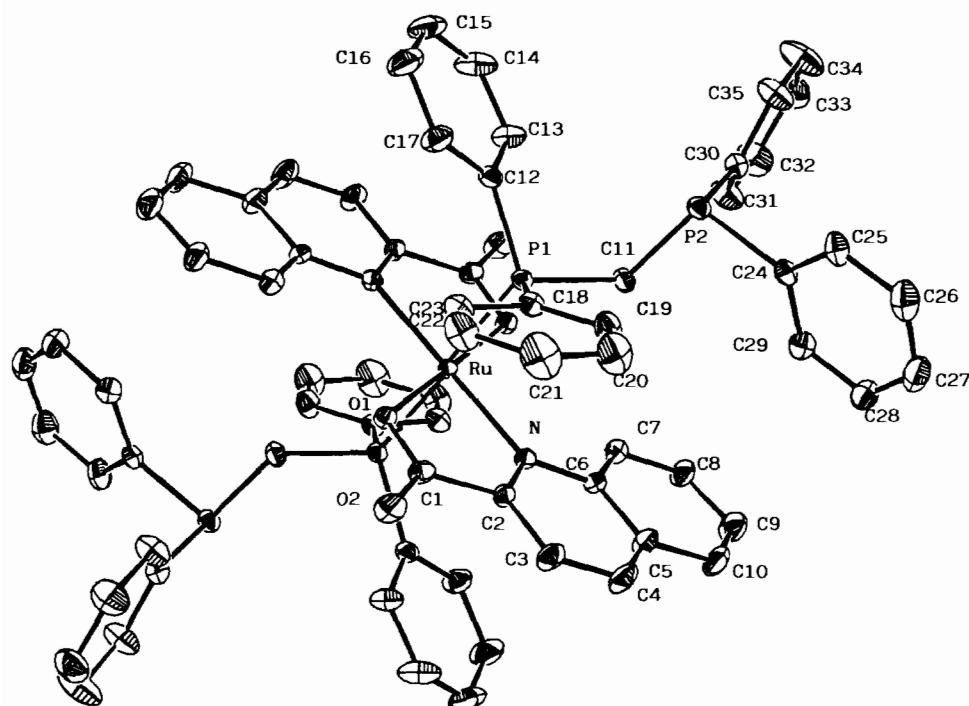


Fig. 2. ORTEP view of *trans*-Ru(quin)<sub>2</sub>(dppm)<sub>2</sub>·2MeOH. Solvent molecules and hydrogen atoms are omitted for clarity.

TABLE 5. Principal bond lengths (Å) and angles (°) in C<sub>70</sub>H<sub>56</sub>N<sub>2</sub>O<sub>4</sub>P<sub>4</sub>Ru·2CH<sub>3</sub>OH

Ru-P1	2.346(2)	O2-C1	1.238(10)
Ru-N	2.107(5)	C1-C2	1.497(12)
Ru-O1	2.078(5)	C2-C3	1.403(10)
P1-C11	1.821(9)	C3-C4	1.354(15)
P1-C12	1.822(7)	C4-C5	1.393(14)
P1-C18	1.809(7)	C5-C6	1.413(10)
P2-C11	1.848(7)	C5-C10	1.432(15)
P2-C24	1.835(8)	C6-C7	1.403(11)
P2-C30	1.826(9)	C7-C8	1.370(13)
N-C2	1.318(9)	C8-C9	1.392(13)
N-C6	1.388(10)	C9-C10	1.348(17)
O1-C1	1.277(8)		
N-Ru-O1	77.0(2)	O1-C1-C2	114.6(6)
P1-Ru-O1	93.8(1)	N-C2-C1	115.8(6)
P1-Ru-N	87.7(2)	C1-C2-C3	119.1(7)
Ru-P1-C18	115.3(2)	N-C2-C3	125.0(7)
Ru-P1-C12	115.3(3)	C2-C3-C4	118.2(8)
Ru-P1-C11	108.1(2)	C3-C4-C5	119.8(9)
C12-P1-C18	107.2(3)	C4-C5-C10	122.8(8)
C11-P1-C18	105.8(3)	C4-C5-C6	119.0(8)
C11-P1-C12	104.2(3)	C6-C5-C10	118.2(8)
C24-P2-C30	100.7(4)	N-C6-C5	121.0(7)
C11-P2-C30	103.3(4)	C5-C6-C7	118.9(7)
C11-P2-C24	101.7(4)	N-C6-C7	120.1(7)
Ru-N-C6	128.8(4)	C6-C7-C8	120.8(7)
Ru-N-C2	114.2(5)	C7-C8-C9	120.7(8)
C2-N-C6	116.9(6)	C8-C9-C10	120(1)
Ru-O1-C1	117.6(5)	C5-C10-C9	121(1)
O1-C1-O2	123.9(7)	P1-C11-P2	118.9(4)
O2-C1-C2	121.4(7)		

The <sup>1</sup>H NMR spectra of *cis*- and *trans*-Ru(quin)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> are very similar, showing multiplets between 6.7 and 7.9 ppm due to the phenyl and quin protons. Similarly to that observed in *trans*-Ru(quin)<sub>2</sub>(dppm)<sub>2</sub>, in *trans*-Ru(quin)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> one doublet at 9.59 (*J*(H<sup>2</sup>-H<sup>3</sup>) = 8.70 Hz) due to the H<sup>2</sup> proton of the quin ligand appears; however, in the *cis*- derivative, this signal is shifted to high field appearing at 9.06 ppm (*J*(H<sup>2</sup>-H<sup>3</sup>) = 9.00 Hz). The <sup>31</sup>P{<sup>1</sup>H} NMR spectra of these compounds show singlets at 43.02 and 29.46 ppm due to *cis*- and *trans*-Ru(quin)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, respectively, indicating the equivalence of the PPh<sub>3</sub> ligands in both complexes.

The X-ray crystal structure of *trans*-Ru(quin)<sub>2</sub>(dppm)<sub>2</sub>·2MeOH has been determined and an ORTEP view [25] is shown in Fig. 2. The Ru atom is situated in an inversion center. Because of this, the asymmetric unit consists of only one half molecule. Selected bond lengths and angles are presented in Table 5. The crystal structure of the complex consists of separated discrete molecular units and methanol molecules of solvation. The ruthenium atom has a distorted octahedral coordination geometry in which the equatorial positions are occupied by two bidentate N,O-quin aldinates; the apical positions are occupied by two monodentate dppm ligands. The distortion from octahedral coordination is evidenced especially by the Ru-P1 (2.346(2) Å), Ru-N (2.107(5) Å) and Ru-O1 (2.078(5) Å) distances; the distances and angles of the 2-quin aldinates

ligands are similar to those found in other 2-quinaldinate complexes [26, 27] and the analogous Ru(pyca)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (pyca = 2-pyridincarboxylate) [28]. The Ru–P of 2.346(2) Å is typical for *trans* P atoms on Ru [19, 28, 29]. The geometry of the compound and especially the distances and angles in the dppm ligands are closely similar to those observed in Ru(TPP)(dppm)<sub>2</sub> (TPP = 5,10,15,20-tetraphenylporphinato) [19].

### Supplementary material

Tables of hydrogen atom parameters, thermal parameters, structure factors, complete lists of bond lengths and angles and torsion angles are available on request from the authors.

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