NJC

Evidence of the unprecedented conversion of intermolecular proton- to water-bridging two phosphoryl ruthenium complexes

Rémy Sylvain,[a] LaureVendier,[a] Christian Bijani,[a] Antonio Santoro,[b] Fausto Punteriero,[b] Sebastiano Campagna,*[,b] Pierre Sutra[a] and Alain Igau*[,a]

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Experimental Section

General Information.

All reactions were conducted under an inert atmosphere of dry argon using standard Schlenk-line techniques. Solvents were dried, distilled, and degassed following conventional methods prior to use. Elemental analyses were carried out with a PerkinElmer 2400 Series II CHNS/O Elemental Analyzer. NMR spectra were recorded on a Bruker DPX 300, AV 300, AV 400 and on a Bruker AV 500 spectrometer. All the ^{1}H and ^{13}C signals were assigned on the basis of chemical shifts, spin-spin coupling constants, splitting patterns, and signal intensities and by using 2D experiments as ^{1}H-^{1}H COSY45 and ^{1}H-^{13}C HMQC experiments. Infrared spectra were recorded by using universal ATR sampling technology on a Perkin-Elmer spectrum 100 FT-IR. Mass spectra were recorded on a TSQ7000 instrument from ThermoElectron.

Data of compound **2** were collected at low temperature (180 K) on a Gemini Agilent diffractometer using a graphite-monochromated Cu-Kα Enhance radiation (λ = 1.54184 Å) and equipped with an Oxford Instrument Cooler Device. Indeed, it was really difficult to synthesise high diffracting crystals. In order to enhance the weak diffraction signal, we chose to record data under copper radiation.

Data of compound **3** were collected at low temperature (100 K) on a Bruker Kappa Apex II diffractometer using a graphite-monochromated Mo-Kα radiation (λ = 0.71073Å) and equipped with an Oxford Cryosystems Cryostream Cooler Device.

The final unit cell parameters have been obtained by means of a least-squares refinement. The structures have been solved by Direct Methods using SIR92,[1] and refined by means of least-squares procedures on a F^2 with the aid of the program SHELXL97[2] include in the softwares package WinGX version 1.63.[3] The Atomic Scattering Factors were taken from International tables for X-Ray Crystallography.[4] All hydrogens atoms were geometrically placed and refined by using a riding model.

All non-hydrogens atoms were anisotropically refined, and in the last cycles of refinement a weighting scheme was used, where weights are calculated from the following formula: $w=1/[\sigma^2(Fo^2)+(aP)^2+bP]$ where $P=(Fo^2+2Fc^2)/3$.

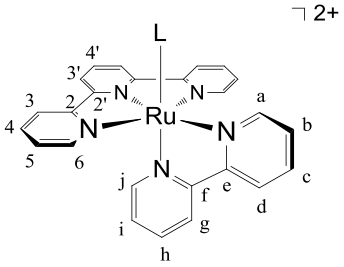
Drawing of molecule are performed with the program ORTEP32[5] with 30% probability displacement ellipsoids for non-hydrogen atoms.

The electrochemical measurements were obtained using an Autolab PGSTAT 100 potentiostat using tetrabutylammonium hexafluorophosphate as the supporting electrolyte in freshly distilled acetonitrile and a platinum working electrode.

Absorption spectra were recorded with a Jasco V-560 spectrophotometer. For steady-state luminescence measurements, a Jobin Yvon-Spex Fluoromax P spectrofluorimeter was used, equipped with a Hamamatsu R3896 photomultiplier. The spectra were corrected for photomultiplier response using a program purchased with the fluorimeter. For the luminescence lifetimes, an Edinburgh OB 900 time-correlated single-photon-counting spectrometer was used. As excitation sources, a Hamamatsu PLP 2 laser diode (59 ps pulse width at 408 nm) and/or the nitrogen discharge (pulse width 2 ns at 337 nm) were employed.

Electrospray mass spectrometry analyses were performed on a Perkin Elmer Sciex API-365 spectrometer in positive mode. Melting points were determined in capillaries using an Electrothermal melting point apparatus.

The ^{1}H and ^{13}C are numbered as shown below.



{[Ru(tpy)(bpy)(Ph$_2$PO)]$_2$H}[PF$_6$]$_3$ (2) : To a solution of [Ru(tpy)(bpy)(Ph$_2$PO)][PF$_6$] **1** (0.100 g, 0.012 mmol) in 5 mL acetonitrile was added HCl (1 eq.) in Et$_2$O and the mixture was stirred for 30 mn at room temperature. Addition of KPF$_6$ (1 eq) was followed and the cloudy mixture was filtered to remove the KCl salts. A large volume of ether (50 mL) was then added to the filtrate which was slowly reduced by two-thirds to give the product **2** as a red crystalline powder in 80% (81 mg) isolated yield, m. p. 168°C (dec).

NMR ^{31}P (121.5 MHz, CD_2Cl_2, 213K) : δ(ppm) = 112.2 (s), -144.2 (PF_6, $^{1}J_{PF}$=704.6 Hz).
NMR ^{1}H (500MHz, CD_2Cl_2, 298K) : δ(ppm) = 9.75 (d, 2H$_a$, ^{3}J=5Hz), 8.48 (d, 2H$_d$, ^{3}J=8Hz), 8.31 (d, 2H$_g$, ^{3}J=8Hz), 8.20 (t, 2H$_c$, ^{3}J=8Hz), 8.08-7.67 (m, 4H$_3$, 4H$_{3'}$, 2H$_{4'}$, 4H$_4$, 2H$_h$, 2H$_b$), 7.55 (d, 4H$_6$, ^{3}J=5Hz), 7.21-7.16 (m, 4H$_5$, 4H$_{para,}$ Ph, 2H$_i$), 6.94 (m, 8H$_{meta}$, Ph + 2Hj), 6.65 (dd, 8H$_{ortho}$, Ph, ^{3}J=7.7Hz , ^{3}J=8Hz). NMR ^{1}H (500MHz, CD_2Cl_2, 213K) : δ(ppm) = 10.06 (broad, H$^+$), 9.75 (2H$_a$), all the other signals are identicals to those observed at 298K.
NMR $^{13}C\{^{1}H\}$ (75 MHz, CD_2Cl_2, 213K) : δ(ppm) = 156.1 (C$_a$), 153.4 (C$_6$), 148.2 (C$_j$), 138.9 (C$_h$), 138.0 (C$_c$), 136.2 (C$_{4'}$), 133.1 (C$_{ipso}$, Ph), 130.4 (C$_{para}$, Ph), 128.9 (C$_{ortho}$, Ph), 128.6 (C$_{meta}$, Ph), 128.4 (C$_4$), 128.2 (C$_5$), 127.8 (C$_b$), 127.5 (C$_i$), 124.3 (C$_3$), 124.3 (C$_d$), 123.6 (C$_g$), 123.4 (C$_{3'}$), the ipso carbon atoms in the tpy (C$_2$ and C$_{2'}$) and bpy (C$_e$ and C$_f$) ligands have not been observed.
Mass (ES$^+$) : m/z = 692.1 [(2M-H$^+$-3PF$_6$)].

{[Ru(tpy)(bpy)(Ph$_2$PO)]$_2$H$_2$O}[PF$_6$]$_2$ (3) : In an acetonitrile solution (2 mL) of **2** (100 mg, 1.2 10-4 mol) was added water in excess followed by KPF$_6$ (0.221 mg, 1.2 10-3 mol). The reaction mixture was then stirred for 30 min. Complex **3** was isolated after filtration, washing with 3*10 mL of water then 3*10 mL of ether. The volatiles were evaporated and the product was isolated as a red solid in 91% (93 mg) yield, m. p. 142°C (dec).

RMN ^{31}P (121.5 MHz, CD_2Cl_2, 298K) : δ(ppm) = 95.3 (s), -144.4 (PF_6, $^{1}J_{PF}$=704.6 Hz).

RMN ^{1}H (300MHz, CD_2Cl_2, 298K) : δ(ppm) = 10.05 (d, 2H$_a$, ^{3}J=5Hz), 8.47 (d, 2H$_d$, ^{3}J=10Hz), 8.30 (d, 2H$_g$, ^{3}J=10Hz), 8.21 (t, 2H$_c$, ^{3}J=5Hz), 8.10-8.01 (m, 4H$_{3+}$4H$_{3'}$), 7.91 (t, 2H$_{4'}$, ^{3}J=5Hz), 7.86 (t, 2H$_h$, ^{3}J=5Hz), 7.60 (d, 4H$_6$, ^{3}J=5Hz), 7.53 (t, 2H$_b$, ^{3}J=5Hz), 7.28 (t, 4H$_5$, ^{3}J=10Hz), 7.20 (t, 4H$_4$, ^{3}J=5Hz), 7.16 (d, 2H$_j$, ^{3}J=5Hz), 7.01-6.95 (m, 18H, H$_i$+$_{meta, ortho,}$ Ph), 6.69 (t, 4H$_{para,}$ Ph, ^{3}J=10Hz).

NMR ^{1}H (500MHz, CD_2Cl_2, 183K) : δ(ppm) = 16.17 (t broad, H$_2$O).

RMN ^{13}C $\{^{1}H\}\{^{31}P\}$ (75 MHz, CD_2Cl_2, 298K) : δ (ppm) = 156.1 (C$_a$), 153.0 (C$_6$), 148,0 (C$_j$), 138.4 (C$_h$), 137.8 (C$_c$), 137.7 (C$_{4'}$), 135.4 (C$_{ipso}$, Ph), 129.8 (C$_4$), 128.8 (C$_{para}$, Ph), 128.7 (C$_{ortho,}$ Ph), 128.3 (C$_{meta}$, Ph), 127.9 (C$_b$), 127.2 (C$_i$), 127.1 (C$_i$), 123.9 (C$_3$), 123.7 (C$_d$), 123.2 (C$_g$), 123.0 (C$_{3'}$), the ipso carbon atoms in the tpy (C$_2$ and C$_{2'}$) and bpy (C$_e$ and C$_f$) ligands have not been observed.

Mass (ES+) : m/z = 692 ([2M-H$_2$O-2PF$_6$)].

Elemental analysis Calcd. for: $C_{74}H_{60}F_{12}N_{10}O_3P_4Ru_2$ (1692,17): C, 52.55; H, 3.58; N, 8.28. Found: C, 52.74; H, 3.79; N, 8.07.

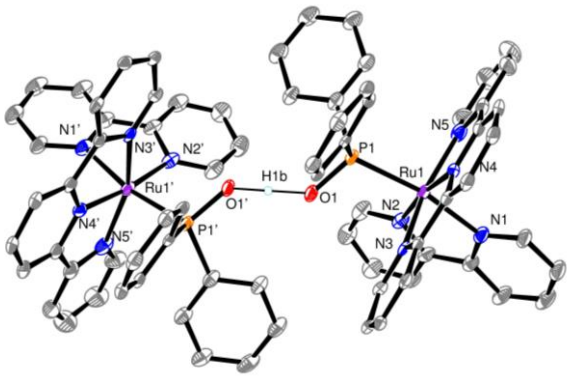


Figure S1. Molecular structure of complex **2**.

Table 1. Crystal data and structure refinement for complex **2**.

Identification code	remy240112
Empirical formula	C74 H59 N10 O2 P2 Ru2, 3(F6 P)
Formula weight	1819.30
Temperature	180(2) K
Wavelength	1.54180 A
Crystal system, space group	Monoclinic, C 1 2/c 1
Unit cell dimensions	a = 17.2568(6) A alpha = 90 deg. b = 29.2556(13) A beta = 100.457(3) deg. c = 15.1819(5) A gamma = 90 deg.
Volume	7537.4(5) A^3
Z, Calculated density	4, 1.603 Mg/m^3
Absorption coefficient	5.115 mm^-1
F(000)	3656
Crystal size	0.15 x 0.06 x 0.03 mm
Theta range for data collection	3.88 to 60.82 deg.
Limiting indices	-19<=h<=19, -32<=k<=29, -15<=l<=17
Reflections collected / unique	16962 / 5658 [R(int) = 0.0402]
Completeness to theta = 60.82	98.4 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8657 and 0.5714
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5658 / 0 / 513
Goodness-of-fit on F^2	1.051
Final R indices [I>2sigma(I)]	R1 = 0.0681, wR2 = 0.1900
R indices (all data)	R1 = 0.0866, wR2 = 0.2074
Largest diff. peak and hole	1.559 and -0.986 e.A^-3

Table 2. Atomic coordinates and equivalent isotropic displacement parameters for complex **2**.

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(11)	898(4)	779(3)	100(4)	31(2)
C(12)	516(4)	449(3)	-477(5)	33(2)
C(13)	823(4)	15(3)	-451(4)	30(2)
C(14)	1519(4)	-81(3)	126(4)	31(2)
C(15)	1888(4)	263(3)	675(4)	30(2)
C(16)	2657(4)	203(3)	1290(5)	32(2)
C(17)	3100(4)	-192(3)	1431(5)	42(2)
C(18)	3790(4)	-186(3)	2057(5)	44(2)
C(19)	4029(4)	211(3)	2502(5)	47(2)
C(20)	3585(4)	603(3)	2329(5)	39(2)
C(21)	3756(5)	1061(3)	2718(6)	47(2)
C(22)	4448(5)	1170(4)	3314(6)	61(3)
C(23)	4572(6)	1611(5)	3610(8)	83(4)
C(24)	4015(7)	1937(4)	3320(7)	73(3)
C(25)	3325(6)	1815(3)	2737(6)	58(2)
C(1)	3309(5)	1225(3)	148(6)	47(2)
C(2)	3522(5)	1386(4)	-630(6)	56(2)
C(3)	3082(6)	1719(3)	-1112(6)	61(3)
C(4)	2439(6)	1901(3)	-800(6)	52(2)
C(5)	2255(5)	1738(3)	-3(5)	41(2)
C(6)	1619(5)	1917(3)	411(5)	40(2)
C(7)	1114(6)	2264(3)	39(6)	53(2)
C(8)	546(6)	2424(3)	481(7)	59(2)
C(9)	487(6)	2243(3)	1300(6)	57(2)
C(10)	987(6)	1896(3)	1636(6)	52(2)
C(26)	1662(5)	1115(3)	3737(5)	39(2)
C(27)	1014(5)	1227(3)	4136(5)	41(2)
C(28)	1139(6)	1376(3)	5024(6)	53(2)
C(29)	1892(6)	1406(3)	5515(6)	56(2)
C(30)	2530(6)	1306(3)	5128(6)	51(2)
C(31)	2414(5)	1161(3)	4242(5)	44(2)
C(32)	1648(4)	271(3)	2833(4)	29(2)
C(33)	2330(4)	100(3)	3375(5)	34(2)
C(34)	2454(4)	-365(3)	3486(5)	38(2)
C(35)	1899(5)	-672(3)	3074(5)	41(2)
C(36)	1212(4)	-513(3)	2537(5)	36(2)
C(37)	1096(4)	-48(3)	2411(4)	31(2)
N(3)	1574(3)	690(2)	673(4)	29(1)
N(4)	2897(3)	591(2)	1734(4)	34(1)
N(5)	3190(4)	1385(2)	2441(4)	46(2)
N(1)	2689(4)	1401(2)	454(4)	42(2)
N(2)	1545(4)	1718(2)	1207(4)	39(2)
F(13)	4543(3)	337(2)	575(3)	61(1)
F(14)	5180(3)	-345(2)	827(3)	63(2)
F(15)	4193(3)	-262(2)	-370(3)	63(2)
P(1)	1495(1)	876(1)	2595(1)	31(1)
P(2)	0	1835(1)	7500	97(2)
P(3)	4686(3)	-1586(2)	2169(4)	69(2)
P(4)	5000	0	0	51(1)

Ru(1)	2226(1)	1137(1)	1557(1)	33(1)
F(1)	145(5)	1457(3)	8239(4)	110(3)
F(2A)	423(8)	2275(4)	7974(8)	95(2)
F(3A)	969(8)	1690(4)	7460(8)	95(2)
F(3B)	-233(11)	2080(6)	8498(11)	95(2)
F(2B)	759(11)	1995(6)	7772(11)	95(2)
F(7)	5111(10)	-1146(5)	2226(17)	166(8)
F(9)	5065(15)	-1647(5)	1612(18)	470(20)
F(8)	3945(12)	-1302(5)	2172(14)	298(12)
F(10)	4376(10)	-1979(6)	2406(19)	166(8)
O(1)	601(3)	926(2)	2200(3)	34(1)

Table 3. Bond lengths [A] and angles [deg] for complex **2**.

C(11)-N(3)	1.348(9)
C(11)-C(12)	1.388(10)
C(11)-H(11)	0.9500
C(12)-C(13)	1.373(10)
C(12)-H(12)	0.9500
C(13)-C(14)	1.381(10)
C(13)-H(13)	0.9500
C(14)-C(15)	1.385(10)
C(14)-H(14)	0.9500
C(15)-N(3)	1.359(9)
C(15)-C(16)	1.489(10)
C(16)-N(4)	1.347(9)
C(16)-C(17)	1.381(11)
C(17)-C(18)	1.382(11)
C(17)-H(17)	0.9500
C(18)-C(19)	1.368(12)
C(18)-H(18)	0.9500
C(19)-C(20)	1.381(12)
C(19)-H(19)	0.9500
C(20)-N(4)	1.355(9)
C(20)-C(21)	1.472(12)
C(21)-N(5)	1.370(11)
C(21)-C(22)	1.398(12)
C(22)-C(23)	1.368(15)
C(22)-H(22)	0.9500
C(23)-C(24)	1.369(17)
C(23)-H(23)	0.9500
C(24)-C(25)	1.396(14)
C(24)-H(24)	0.9500
C(25)-N(5)	1.344(11)
C(25)-H(25)	0.9500
C(1)-N(1)	1.344(11)
C(1)-C(2)	1.382(12)
C(1)-H(1)	0.9500
C(2)-C(3)	1.363(14)
C(2)-H(2)	0.9500
C(3)-C(4)	1.389(14)
C(3)-H(3)	0.9500
C(4)-C(5)	1.391(11)
C(4)-H(4)	0.9500
C(5)-N(1)	1.352(11)
C(5)-C(6)	1.457(11)
C(6)-N(2)	1.368(10)
C(6)-C(7)	1.390(12)
C(7)-C(8)	1.367(13)
C(7)-H(7)	0.9500
C(8)-C(9)	1.373(13)
C(8)-H(8)	0.9500
C(9)-C(10)	1.371(13)
C(9)-H(9)	0.9500
C(10)-N(2)	1.361(11)
C(10)-H(10)	0.9500
C(26)-C(31)	1.389(12)
C(26)-C(27)	1.405(11)
C(26)-P(1)	1.842(8)
C(27)-C(28)	1.397(11)
C(27)-H(27)	0.9500

C(28)-C(29)	1.378(13)
C(28)-H(28)	0.9500
C(29)-C(30)	1.370(13)
C(29)-H(29)	0.9500
C(30)-C(31)	1.389(11)
C(30)-H(30)	0.9500
C(31)-H(31)	0.9500
C(32)-C(33)	1.400(10)
C(32)-C(37)	1.402(10)
C(32)-P(1)	1.817(8)
C(33)-C(34)	1.382(11)
C(33)-H(33)	0.9500
C(34)-C(35)	1.379(11)
C(34)-H(34)	0.9500
C(35)-C(36)	1.392(11)
C(35)-H(35)	0.9500
C(36)-C(37)	1.381(11)
C(36)-H(36)	0.9500
C(37)-H(37)	0.9500
N(3)-Ru(1)	2.057(6)
N(4)-Ru(1)	1.963(6)
N(5)-Ru(1)	2.069(7)
N(1)-Ru(1)	2.126(6)
N(2)-Ru(1)	2.079(7)
F(13)-P(4)	1.614(5)
F(14)-P(4)	1.598(5)
F(15)-P(4)	1.599(5)
P(1)-O(1)	1.559(5)
P(1)-Ru(1)	2.3186(18)
P(2)-F(2B)	1.381(18)
P(2)-F(2B)#1	1.381(18)
P(2)-F(1)#1	1.563(8)
P(2)-F(1)	1.563(8)
P(2)-F(2A)#1	1.587(12)
P(2)-F(2A)	1.587(12)
P(2)-F(3A)#1	1.736(13)
P(2)-F(3A)	1.736(13)
P(2)-F(3B)#1	1.787(17)
P(2)-F(3B)	1.787(17)
P(3)-F(9)	1.173(9)
P(3)-P(3)#2	1.337(12)
P(3)-F(10)	1.342(16)
P(3)-F(7)	1.477(19)
P(3)-F(8)	1.526(14)
P(3)-F(7)#2	1.583(15)
P(3)-F(9)#2	1.83(3)
P(3)-F(10)#2	1.99(2)
P(4)-F(14)#3	1.598(5)
P(4)-F(15)#3	1.599(5)
P(4)-F(13)#3	1.614(5)
F(7)-F(7)#2	0.98(4)
F(7)-P(3)#2	1.583(15)
F(7)-F(9)	1.73(3)
F(7)-F(8)#2	1.78(3)
F(9)-P(3)#2	1.83(3)
F(8)-F(7)#2	1.78(3)
F(10)-P(3)#2	1.99(2)
O(1)-H(1B)	1.218(16)

N(3)-C(11)-C(12)	121.9(7)
N(3)-C(11)-H(11)	119.0

C(12)-C(11)-H(11)	119.0
C(13)-C(12)-C(11)	119.2(7)
C(13)-C(12)-H(12)	120.4
C(11)-C(12)-H(12)	120.4
C(12)-C(13)-C(14)	119.5(7)
C(12)-C(13)-H(13)	120.2
C(14)-C(13)-H(13)	120.2
C(13)-C(14)-C(15)	119.1(7)
C(13)-C(14)-H(14)	120.5
C(15)-C(14)-H(14)	120.5
N(3)-C(15)-C(14)	121.7(6)
N(3)-C(15)-C(16)	114.8(6)
C(14)-C(15)-C(16)	123.4(7)
N(4)-C(16)-C(17)	121.1(7)
N(4)-C(16)-C(15)	111.8(6)
C(17)-C(16)-C(15)	127.1(7)
C(16)-C(17)-C(18)	118.6(8)
C(16)-C(17)-H(17)	120.7
C(18)-C(17)-H(17)	120.7
C(19)-C(18)-C(17)	119.7(8)
C(19)-C(18)-H(18)	120.1
C(17)-C(18)-H(18)	120.1
C(18)-C(19)-C(20)	120.3(8)
C(18)-C(19)-H(19)	119.8
C(20)-C(19)-H(19)	119.8
N(4)-C(20)-C(19)	119.5(8)
N(4)-C(20)-C(21)	112.4(7)
C(19)-C(20)-C(21)	128.1(7)
N(5)-C(21)-C(22)	121.3(9)
N(5)-C(21)-C(20)	115.1(7)
C(22)-C(21)-C(20)	123.6(9)
C(23)-C(22)-C(21)	119.4(10)
C(23)-C(22)-H(22)	120.3
C(21)-C(22)-H(22)	120.3
C(22)-C(23)-C(24)	119.5(10)
C(22)-C(23)-H(23)	120.2
C(24)-C(23)-H(23)	120.2
C(23)-C(24)-C(25)	119.6(10)
C(23)-C(24)-H(24)	120.2
C(25)-C(24)-H(24)	120.2
N(5)-C(25)-C(24)	121.8(10)
N(5)-C(25)-H(25)	119.1
C(24)-C(25)-H(25)	119.1
N(1)-C(1)-C(2)	121.1(9)
N(1)-C(1)-H(1)	119.4
C(2)-C(1)-H(1)	119.4
C(3)-C(2)-C(1)	119.6(9)
C(3)-C(2)-H(2)	120.2
C(1)-C(2)-H(2)	120.2
C(2)-C(3)-C(4)	119.5(8)
C(2)-C(3)-H(3)	120.2
C(4)-C(3)-H(3)	120.2
C(3)-C(4)-C(5)	119.2(9)
C(3)-C(4)-H(4)	120.4
C(5)-C(4)-H(4)	120.4
N(1)-C(5)-C(4)	120.3(8)
N(1)-C(5)-C(6)	115.6(7)
C(4)-C(5)-C(6)	124.1(8)
N(2)-C(6)-C(7)	121.2(7)
N(2)-C(6)-C(5)	115.2(7)
C(7)-C(6)-C(5)	123.6(7)

C(8)-C(7)-C(6)	120.2(8)
C(8)-C(7)-H(7)	119.9
C(6)-C(7)-H(7)	119.9
C(7)-C(8)-C(9)	119.4(9)
C(7)-C(8)-H(8)	120.3
C(9)-C(8)-H(8)	120.3
C(10)-C(9)-C(8)	118.6(9)
C(10)-C(9)-H(9)	120.7
C(8)-C(9)-H(9)	120.7
N(2)-C(10)-C(9)	123.9(8)
N(2)-C(10)-H(10)	118.1
C(9)-C(10)-H(10)	118.1
C(31)-C(26)-C(27)	118.4(7)
C(31)-C(26)-P(1)	121.9(6)
C(27)-C(26)-P(1)	119.6(6)
C(28)-C(27)-C(26)	119.6(8)
C(28)-C(27)-H(27)	120.2
C(26)-C(27)-H(27)	120.2
C(29)-C(28)-C(27)	120.5(8)
C(29)-C(28)-H(28)	119.8
C(27)-C(28)-H(28)	119.8
C(30)-C(29)-C(28)	120.5(8)
C(30)-C(29)-H(29)	119.8
C(28)-C(29)-H(29)	119.8
C(29)-C(30)-C(31)	119.6(9)
C(29)-C(30)-H(30)	120.2
C(31)-C(30)-H(30)	120.2
C(26)-C(31)-C(30)	121.4(8)
C(26)-C(31)-H(31)	119.3
C(30)-C(31)-H(31)	119.3
C(33)-C(32)-C(37)	117.4(7)
C(33)-C(32)-P(1)	122.7(6)
C(37)-C(32)-P(1)	119.7(5)
C(34)-C(33)-C(32)	121.1(7)
C(34)-C(33)-H(33)	119.4
C(32)-C(33)-H(33)	119.4
C(35)-C(34)-C(33)	120.5(7)
C(35)-C(34)-H(34)	119.8
C(33)-C(34)-H(34)	119.8
C(34)-C(35)-C(36)	119.6(7)
C(34)-C(35)-H(35)	120.2
C(36)-C(35)-H(35)	120.2
C(37)-C(36)-C(35)	119.9(7)
C(37)-C(36)-H(36)	120.1
C(35)-C(36)-H(36)	120.1
C(36)-C(37)-C(32)	121.4(7)
C(36)-C(37)-H(37)	119.3
C(32)-C(37)-H(37)	119.3
C(11)-N(3)-C(15)	118.5(6)
C(11)-N(3)-Ru(1)	127.1(5)
C(15)-N(3)-Ru(1)	114.3(4)
C(16)-N(4)-C(20)	120.6(7)
C(16)-N(4)-Ru(1)	119.9(5)
C(20)-N(4)-Ru(1)	119.5(5)
C(25)-N(5)-C(21)	118.3(8)
C(25)-N(5)-Ru(1)	128.0(7)
C(21)-N(5)-Ru(1)	113.7(5)
C(1)-N(1)-C(5)	120.2(7)
C(1)-N(1)-Ru(1)	124.8(6)
C(5)-N(1)-Ru(1)	114.6(5)
C(10)-N(2)-C(6)	116.6(7)

C(10)-N(2)-Ru(1)	127.3(5)
C(6)-N(2)-Ru(1)	115.8(5)
O(1)-P(1)-C(32)	105.3(3)
O(1)-P(1)-C(26)	107.6(3)
C(32)-P(1)-C(26)	101.0(3)
O(1)-P(1)-Ru(1)	109.33(19)
C(32)-P(1)-Ru(1)	112.3(2)
C(26)-P(1)-Ru(1)	120.2(2)
F(2B)-P(2)-F(2B)#1	140.4(15)
F(2B)-P(2)-F(1)#1	118.3(8)
F(2B)#1-P(2)-F(1)#1	90.3(8)
F(2B)-P(2)-F(1)	90.3(8)
F(2B)#1-P(2)-F(1)	118.3(8)
F(1)#1-P(2)-F(1)	89.9(6)
F(2B)-P(2)-F(2A)#1	101.1(10)
F(2B)#1-P(2)-F(2A)#1	42.0(8)
F(1)#1-P(2)-F(2A)#1	104.3(5)
F(1)-P(2)-F(2A)#1	154.2(6)
F(2B)-P(2)-F(2A)	42.0(8)
F(2B)#1-P(2)-F(2A)	101.1(10)
F(1)#1-P(2)-F(2A)	154.2(6)
F(1)-P(2)-F(2A)	104.3(5)
F(2A)#1-P(2)-F(2A)	71.5(9)
F(2B)-P(2)-F(3A)#1	159.8(9)
F(2B)#1-P(2)-F(3A)#1	39.3(8)
F(1)#1-P(2)-F(3A)#1	79.8(5)
F(1)-P(2)-F(3A)#1	80.4(5)
F(2A)#1-P(2)-F(3A)#1	81.2(6)
F(2A)-P(2)-F(3A)#1	123.2(7)
F(2B)-P(2)-F(3A)	39.3(8)
F(2B)#1-P(2)-F(3A)	159.8(9)
F(1)#1-P(2)-F(3A)	80.4(5)
F(1)-P(2)-F(3A)	79.8(5)
F(2A)#1-P(2)-F(3A)	123.2(7)
F(2A)-P(2)-F(3A)	81.2(6)
F(3A)#1-P(2)-F(3A)	151.8(9)
F(2B)-P(2)-F(3B)#1	76.7(9)
F(2B)#1-P(2)-F(3B)#1	87.6(10)
F(1)#1-P(2)-F(3B)#1	73.0(6)
F(1)-P(2)-F(3B)#1	149.5(7)
F(2A)#1-P(2)-F(3B)#1	56.3(7)
F(2A)-P(2)-F(3B)#1	84.4(7)
F(3A)#1-P(2)-F(3B)#1	119.6(7)
F(3A)-P(2)-F(3B)#1	72.6(7)
F(2B)-P(2)-F(3B)	87.6(10)
F(2B)#1-P(2)-F(3B)	76.7(9)
F(1)#1-P(2)-F(3B)	149.5(7)
F(1)-P(2)-F(3B)	73.0(6)
F(2A)#1-P(2)-F(3B)	84.4(7)
F(2A)-P(2)-F(3B)	56.3(7)
F(3A)#1-P(2)-F(3B)	72.6(7)
F(3A)-P(2)-F(3B)	119.6(7)
F(3B)#1-P(2)-F(3B)	132.6(12)
F(9)-P(3)-P(3)#2	93.4(17)
F(9)-P(3)-F(10)	111.5(14)
P(3)#2-P(3)-F(10)	96.1(12)
F(9)-P(3)-F(7)	80.6(9)
P(3)#2-P(3)-F(7)	68.3(9)
F(10)-P(3)-F(7)	161.4(17)
F(9)-P(3)-F(8)	131.4(18)
P(3)#2-P(3)-F(8)	124.3(11)

F(10)-P(3)-F(8)	95.2(8)
F(7)-P(3)-F(8)	86.1(10)
F(9)-P(3)-F(7)#2	116.5(9)
P(3)#2-P(3)-F(7)#2	60.1(10)
F(10)-P(3)-F(7)#2	126.7(15)
F(7)-P(3)-F(7)#2	37.0(14)
F(8)-P(3)-F(7)#2	69.7(11)
F(9)-P(3)-F(9)#2	131.0(13)
P(3)#2-P(3)-F(9)#2	39.8(7)
F(10)-P(3)-F(9)#2	71.3(13)
F(7)-P(3)-F(9)#2	90.1(13)
F(8)-P(3)-F(9)#2	95.3(9)
F(7)#2-P(3)-F(9)#2	60.4(11)
F(9)-P(3)-F(10)#2	67.7(15)
P(3)#2-P(3)-F(10)#2	42.0(6)
F(10)-P(3)-F(10)#2	76.1(9)
F(7)-P(3)-F(10)#2	96.8(8)
F(8)-P(3)-F(10)#2	160.8(10)
F(7)#2-P(3)-F(10)#2	101.5(10)
F(9)#2-P(3)-F(10)#2	65.8(8)
F(14)#3-P(4)-F(14)	180.0(4)
F(14)#3-P(4)-F(15)#3	90.3(3)
F(14)-P(4)-F(15)#3	89.7(3)
F(14)#3-P(4)-F(15)	89.7(3)
F(14)-P(4)-F(15)	90.3(3)
F(15)#3-P(4)-F(15)	180.0(6)
F(14)#3-P(4)-F(13)	89.7(3)
F(14)-P(4)-F(13)	90.3(3)
F(15)#3-P(4)-F(13)	89.8(3)
F(15)-P(4)-F(13)	90.2(3)
F(14)#3-P(4)-F(13)#3	90.3(3)
F(14)-P(4)-F(13)#3	89.7(3)
F(15)#3-P(4)-F(13)#3	90.2(3)
F(15)-P(4)-F(13)#3	89.8(3)
F(13)-P(4)-F(13)#3	180.0(4)
N(4)-Ru(1)-N(3)	79.1(2)
N(4)-Ru(1)-N(5)	79.2(3)
N(3)-Ru(1)-N(5)	157.8(3)
N(4)-Ru(1)-N(2)	172.8(2)
N(3)-Ru(1)-N(2)	97.8(2)
N(5)-Ru(1)-N(2)	103.3(3)
N(4)-Ru(1)-N(1)	96.1(3)
N(3)-Ru(1)-N(1)	87.5(2)
N(5)-Ru(1)-N(1)	90.6(2)
N(2)-Ru(1)-N(1)	77.2(3)
N(4)-Ru(1)-P(1)	91.05(17)
N(3)-Ru(1)-P(1)	86.16(15)
N(5)-Ru(1)-P(1)	98.45(17)
N(2)-Ru(1)-P(1)	95.24(17)
N(1)-Ru(1)-P(1)	169.34(19)
F(7)#2-F(7)-P(3)	77.4(7)
F(7)#2-F(7)-P(3)#2	65.6(17)
P(3)-F(7)-P(3)#2	51.7(6)
F(7)#2-F(7)-F(9)	118.2(8)
P(3)-F(7)-F(9)	42.0(7)
P(3)#2-F(7)-F(9)	66.9(12)
F(7)#2-F(7)-F(8)#2	92(3)
P(3)-F(7)-F(8)#2	101.9(8)
P(3)#2-F(7)-F(8)#2	53.7(7)
F(9)-F(7)-F(8)#2	90.5(13)
P(3)-F(9)-F(7)	57.4(6)

P(3)-F(9)-P(3)#2	46.8(11)
F(7)-F(9)-P(3)#2	52.7(9)
P(3)-F(8)-F(7)#2	56.7(9)
P(3)-F(10)-P(3)#2	41.8(8)
P(1)-O(1)-H(1B)	133.9(14)

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

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for complex **2**.

The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(11)	38(4)	36(4)	23(4)	1(3)	13(3)	0(3)
C(12)	31(4)	50(5)	21(3)	2(3)	12(3)	-1(3)
C(13)	28(4)	43(4)	22(3)	-3(3)	9(3)	-11(3)
C(14)	36(4)	36(4)	26(4)	-2(3)	20(3)	-6(3)
C(15)	30(4)	40(4)	22(3)	-2(3)	15(3)	-5(3)
C(16)	30(4)	47(4)	24(3)	0(3)	15(3)	-3(3)
C(17)	36(4)	62(5)	32(4)	0(4)	19(3)	7(4)
C(18)	32(4)	70(6)	35(4)	1(4)	19(3)	11(4)
C(19)	27(4)	83(7)	35(4)	0(4)	19(3)	-3(4)
C(20)	29(4)	63(5)	30(4)	-5(4)	17(3)	-9(4)
C(21)	37(4)	68(6)	41(5)	-2(4)	21(4)	-12(4)
C(22)	34(5)	98(8)	49(5)	-20(5)	7(4)	-19(5)
C(23)	52(6)	110(10)	81(8)	-21(7)	-1(6)	-34(7)
C(24)	73(7)	76(7)	68(7)	-21(6)	6(6)	-40(6)
C(25)	70(6)	61(6)	45(5)	-2(5)	12(5)	-20(5)
C(1)	45(5)	61(6)	39(5)	-10(4)	21(4)	-21(4)
C(2)	54(5)	72(7)	50(5)	-9(5)	29(5)	-26(5)
C(3)	84(7)	65(6)	41(5)	0(5)	31(5)	-34(6)
C(4)	78(6)	46(5)	38(5)	2(4)	25(4)	-25(5)
C(5)	51(5)	39(4)	35(4)	-3(4)	14(4)	-20(4)
C(6)	58(5)	36(4)	28(4)	-5(3)	13(4)	-15(4)
C(7)	75(6)	43(5)	43(5)	5(4)	18(5)	-10(5)
C(8)	73(6)	45(5)	60(6)	7(5)	16(5)	0(5)
C(9)	71(6)	43(5)	62(6)	-1(4)	27(5)	6(5)
C(10)	75(6)	39(5)	46(5)	0(4)	26(5)	-2(4)
C(26)	51(5)	36(4)	34(4)	-1(3)	19(4)	-8(3)
C(27)	53(5)	38(4)	37(4)	-4(3)	21(4)	-3(4)
C(28)	75(6)	50(5)	41(5)	-19(4)	28(5)	-7(5)
C(29)	87(7)	47(5)	36(5)	-18(4)	20(5)	-23(5)
C(30)	69(6)	51(5)	36(5)	-8(4)	16(4)	-19(4)
C(31)	53(5)	48(5)	35(4)	-6(4)	17(4)	-15(4)
C(32)	30(4)	45(4)	18(3)	1(3)	15(3)	-1(3)
C(33)	28(4)	53(5)	24(4)	-6(3)	15(3)	-1(3)
C(34)	31(4)	58(5)	29(4)	4(4)	14(3)	9(4)
C(35)	49(5)	41(4)	37(4)	4(4)	22(4)	5(4)
C(36)	39(4)	42(5)	30(4)	-1(3)	15(3)	-1(3)
C(37)	31(4)	45(4)	21(3)	-1(3)	13(3)	-6(3)
N(3)	32(3)	40(3)	20(3)	1(3)	17(2)	-2(3)
N(4)	25(3)	54(4)	24(3)	-2(3)	10(2)	-9(3)
N(5)	51(4)	53(4)	38(4)	-10(3)	20(3)	-27(4)

N(1)	44(4)	53(4)	32(3)	-4(3)	16(3)	-22(3)
N(2)	54(4)	37(4)	29(3)	-4(3)	14(3)	-12(3)
F(13)	43(3)	104(4)	41(3)	-2(3)	19(2)	11(3)
F(14)	52(3)	104(4)	35(3)	14(3)	15(2)	8(3)
F(15)	36(2)	112(4)	42(3)	3(3)	13(2)	3(3)
P(1)	33(1)	39(1)	24(1)	-3(1)	14(1)	-5(1)
P(2)	123(4)	44(2)	97(3)	0	-54(3)	0
P(3)	84(4)	63(3)	76(4)	24(3)	60(3)	27(3)
P(4)	31(2)	96(3)	30(2)	7(2)	13(1)	9(2)
Ru(1)	37(1)	41(1)	25(1)	-3(1)	15(1)	-10(1)
F(1)	150(7)	129(6)	53(4)	17(4)	26(4)	2(5)
F(2A)	117(6)	81(5)	79(5)	-19(4)	-6(4)	12(4)
F(3A)	117(6)	81(5)	79(5)	-19(4)	-6(4)	12(4)
F(3B)	117(6)	81(5)	79(5)	-19(4)	-6(4)	12(4)
F(2B)	117(6)	81(5)	79(5)	-19(4)	-6(4)	12(4)
F(7)	110(8)	105(8)	330(20)	131(11)	175(12)	74(7)
F(9)	730(40)	188(13)	700(40)	-255(19)	700(40)	-242(19)
F(8)	400(20)	202(13)	390(20)	146(15)	320(20)	157(15)
F(10)	110(8)	105(8)	330(20)	131(11)	175(12)	74(7)
O(1)	33(3)	41(3)	30(3)	0(2)	17(2)	2(2)

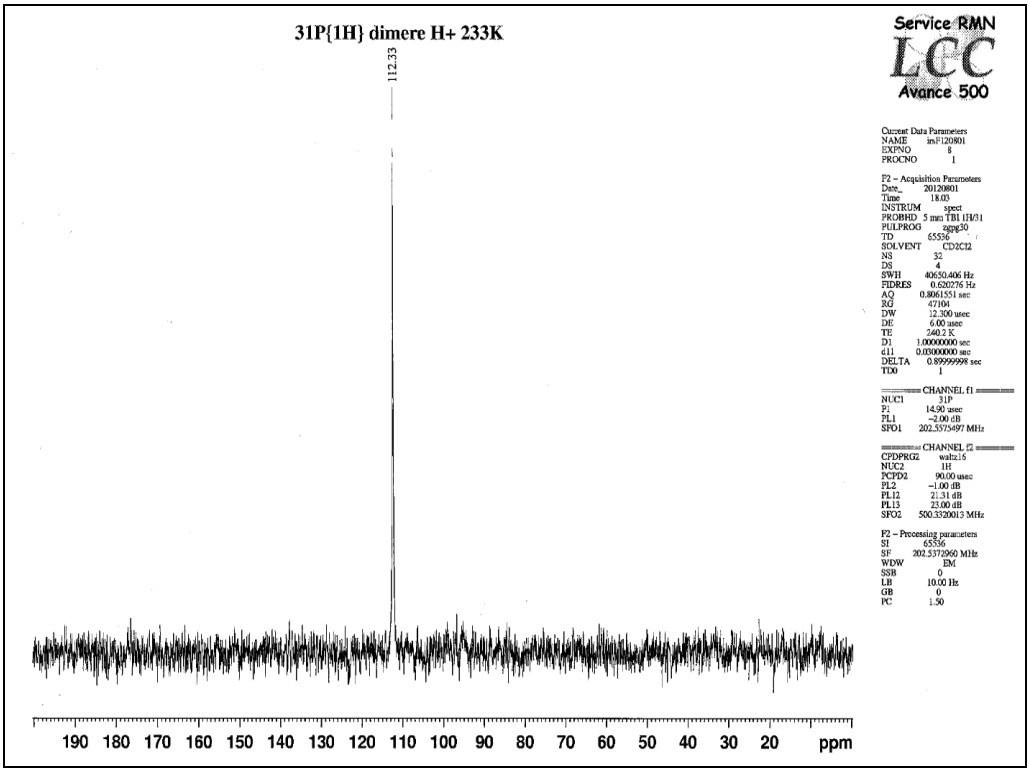


Figure S2 : $^{31}P\{^{1}H\}$ NMR spectra of complex **2** in CD_2Cl_2 at 233K.

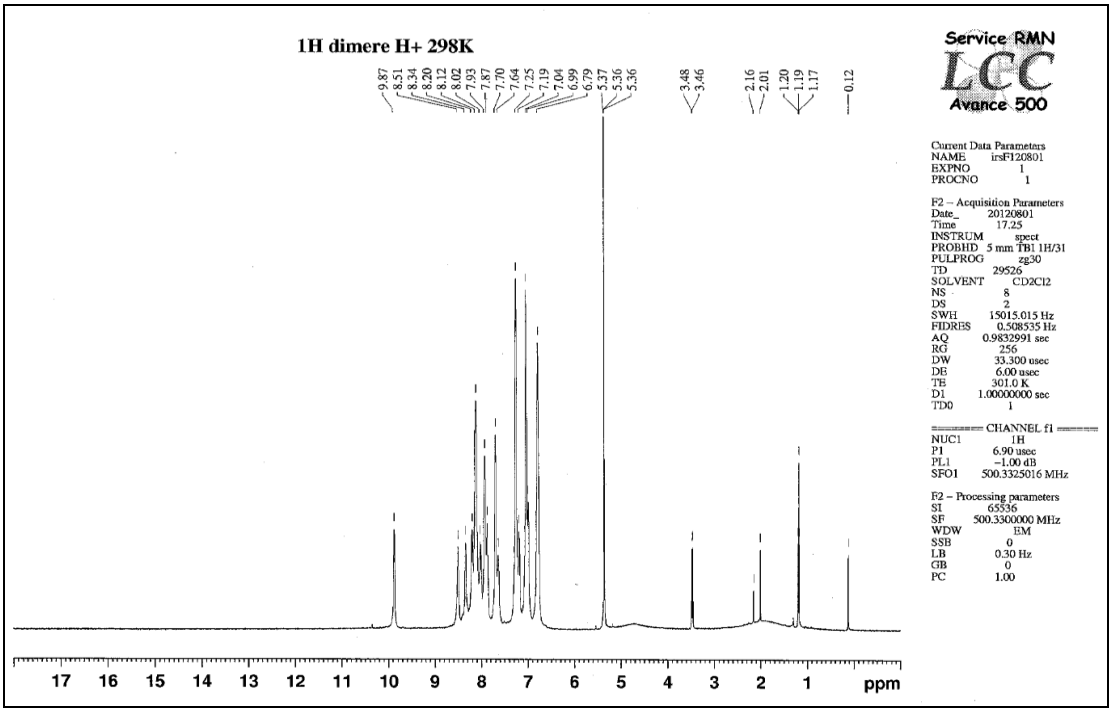


Figure S3 : ^{1}H NMR spectra of complex **2** in CD_2Cl_2 at 298K.

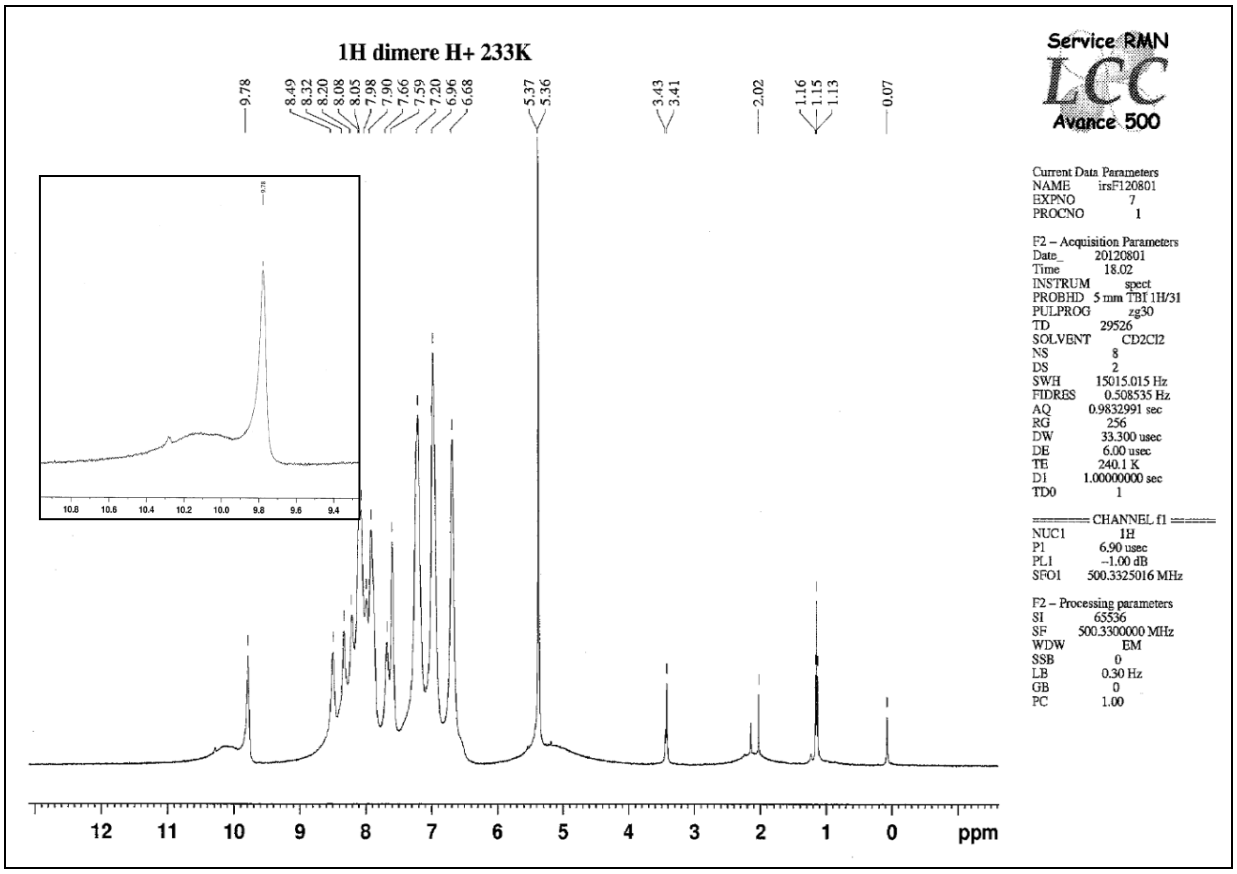


Figure S4 : ^{1}H NMR spectra of complex **2** in CD_2Cl_2 at 233K.

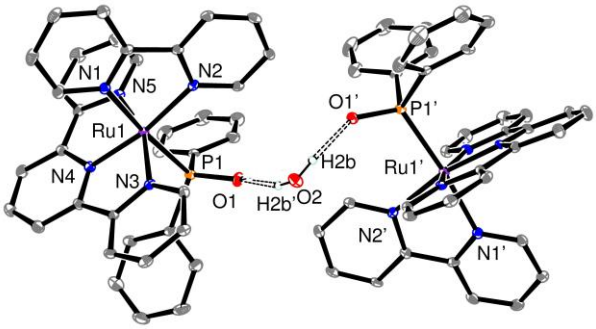


Figure S5. Molecular structure of complex **3**.

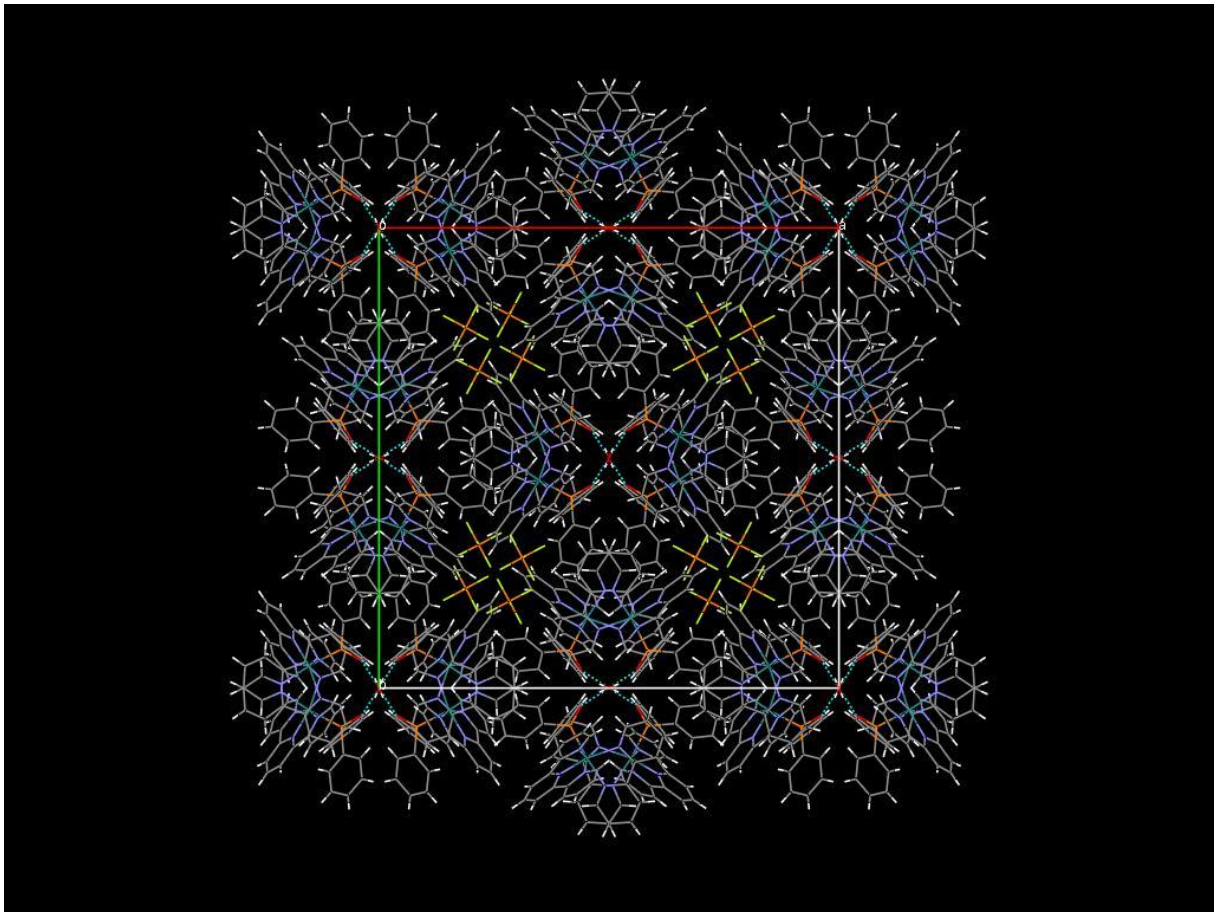


Figure S6. Packing of the molecular structure of complex **3** viewed along the C axis.

Table 5. Crystal data and structure refinement for complex **3**.

Identification code	rsi070212
Empirical formula	2(C37 H29 N5 O P Ru), 2(F6 P), H2 O
Formula weight	1691.34
Temperature	100(2) K
Wavelength	0.71073 A
Crystal system, space group	Tetragonal, I 41 c d
Unit cell dimensions	a = 28.4278(6) A alpha = 90 deg. b = 28.4278(6) A beta = 90 deg. c = 17.0604(4) A gamma = 90 deg.
Volume	13787.2(5) A^3
Z, Calculated density	8, 1.630 Mg/m^3
Absorption coefficient	0.622 mm^-1
F(000)	6832
Crystal size	0.15 x 0.03 x 0.02 mm
Theta range for data collection	2.00 to 21.70 deg.
Limiting indices	-29<=h<=29, -29<=k<=28, -17<=l<=17
Reflections collected / unique	98325 / 4063 [R(int) = 0.0583]
Completeness to theta = 21.70	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.989 and 0.812
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4063 / 1 / 477
Goodness-of-fit on F^2	1.056
Final R indices [I>2sigma(I)]	R1 = 0.0163, wR2 = 0.0349
R indices (all data)	R1 = 0.0195, wR2 = 0.0360
Absolute structure parameter	-0.032(16)
Largest diff. peak and hole	0.150 and -0.147 e.A^-3

Table 6. Atomic coordinates and equivalent isotropic displacement parameters for complex **3**.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(1)	10267(1)	7546(1)	11067(2)	22(1)
C(3)	9521(1)	7914(1)	11132(2)	30(1)
C(2)	9998(1)	7945(1)	10989(2)	30(1)
C(4)	9325(1)	7485(1)	11321(2)	25(1)
C(5)	9616(1)	7090(1)	11378(2)	17(1)
C(6)	9439(1)	6615(1)	11551(2)	16(1)
C(7)	8966(1)	6503(1)	11560(2)	20(1)
C(8)	8823(1)	6049(1)	11724(2)	21(1)
C(9)	9161(1)	5715(1)	11890(2)	19(1)
C(10)	9631(1)	5843(1)	11870(2)	17(1)
C(11)	10421(1)	6048(1)	9997(2)	18(1)
C(12)	10567(1)	5966(1)	9236(2)	19(1)
C(13)	10968(1)	6187(1)	8965(2)	21(1)
C(14)	11217(1)	6479(1)	9465(2)	20(1)
C(15)	11056(1)	6551(1)	10223(2)	16(1)
C(16)	11289(1)	6861(1)	10797(2)	18(1)
C(17)	11681(1)	7142(1)	10673(2)	25(1)
C(18)	11837(1)	7429(1)	11277(2)	29(1)
C(19)	11596(1)	7444(1)	11982(2)	26(1)
C(20)	11205(1)	7159(1)	12091(2)	19(1)
C(21)	10905(1)	7130(1)	12784(2)	20(1)
C(22)	10988(1)	7367(1)	13479(2)	28(1)
C(23)	10695(1)	7302(1)	14106(2)	34(1)
C(24)	10320(1)	7003(1)	14039(2)	31(1)
C(25)	10245(1)	6771(1)	13341(2)	23(1)
C(26)	10925(1)	5766(1)	13064(2)	19(1)
C(27)	11204(1)	6063(1)	13519(2)	26(1)
C(29)	10964(1)	5663(1)	14687(2)	43(1)
C(30)	10688(1)	5365(1)	14249(2)	41(1)
C(31)	10668(1)	5416(1)	13441(2)	30(1)
C(32)	11447(1)	5772(1)	11614(2)	18(1)
C(33)	11816(1)	6081(1)	11793(2)	23(1)
C(34)	12250(1)	6035(1)	11444(2)	31(1)
C(35)	12335(1)	5681(1)	10922(2)	40(1)
C(36)	11978(1)	5369(1)	10737(2)	42(1)
C(37)	11534(1)	5413(1)	11079(2)	28(1)
N(1)	10084(1)	7125(1)	11268(1)	17(1)
N(2)	9779(1)	6281(1)	11704(1)	14(1)
N(3)	10651(1)	6336(1)	10488(1)	14(1)
N(4)	11067(1)	6868(1)	11499(1)	16(1)
N(5)	10530(1)	6830(1)	12716(1)	18(1)
O(1)	10594(1)	5376(1)	11741(1)	23(1)
F(1)	12430(1)	7375(1)	17605(1)	28(1)
F(2)	12192(1)	6953(1)	18662(1)	44(1)
F(3)	11903(1)	6392(1)	17860(1)	42(1)
F(4)	12666(1)	6624(1)	17745(1)	35(1)
F(5)	11668(1)	7145(1)	17720(1)	35(1)
F(6)	12134(1)	6814(1)	16806(1)	27(1)
P(1)	10844(1)	5822(1)	11999(1)	16(1)
P(2)	12166(1)	6888(1)	17735(1)	23(1)
Ru(1)	10481(1)	6521(1)	11625(1)	14(1)
C(28)	11224(1)	6008(1)	14323(2)	35(1)
O(2)	10000	5000	10634(2)	25(1)

Table 7. Bond lengths [A] and angles [deg] for complex **3**.

C(1)-N(1)	1.349(4)
C(1)-C(2)	1.376(4)
C(1)-H(1)	0.9500
C(3)-C(2)	1.378(4)
C(3)-C(4)	1.380(4)
C(3)-H(3)	0.9500
C(2)-H(2)	0.9500
C(4)-C(5)	1.397(4)
C(4)-H(4)	0.9500
C(5)-N(1)	1.348(4)
C(5)-C(6)	1.471(4)
C(6)-N(2)	1.380(3)
C(6)-C(7)	1.382(4)
C(7)-C(8)	1.382(4)
C(7)-H(7)	0.9500
C(8)-C(9)	1.381(4)
C(8)-H(8)	0.9500
C(9)-C(10)	1.383(4)
C(9)-H(9)	0.9500
C(10)-N(2)	1.343(3)
C(10)-H(10)	0.9500
C(11)-N(3)	1.341(4)
C(11)-C(12)	1.383(4)
C(11)-H(11)	0.9500
C(12)-C(13)	1.383(4)
C(12)-H(12)	0.9500
C(13)-C(14)	1.386(4)
C(13)-H(13)	0.9500
C(14)-C(15)	1.386(4)
C(14)-H(14)	0.9500
C(15)-N(3)	1.379(4)
C(15)-C(16)	1.475(4)
C(16)-N(4)	1.355(4)
C(16)-C(17)	1.388(4)
C(17)-C(18)	1.387(4)
C(17)-H(17)	0.9500
C(18)-C(19)	1.384(4)
C(18)-H(18)	0.9500
C(19)-C(20)	1.391(4)
C(19)-H(19)	0.9500
C(20)-N(4)	1.362(4)
C(20)-C(21)	1.459(4)
C(21)-N(5)	1.370(4)
C(21)-C(22)	1.384(4)
C(22)-C(23)	1.368(5)
C(22)-H(22)	0.9500
C(23)-C(24)	1.369(4)
C(23)-H(23)	0.9500
C(24)-C(25)	1.378(4)
C(24)-H(24)	0.9500
C(25)-N(5)	1.348(4)
C(25)-H(25)	0.9500
C(26)-C(31)	1.392(4)
C(26)-C(27)	1.394(4)
C(26)-P(1)	1.838(3)
C(27)-C(28)	1.383(5)
C(27)-H(27)	0.9500

C(29)-C(30)	1.373(5)
C(29)-C(28)	1.377(5)
C(29)-H(29)	0.9500
C(30)-C(31)	1.388(5)
C(30)-H(30)	0.9500
C(31)-H(31)	0.9500
C(32)-C(37)	1.391(4)
C(32)-C(33)	1.401(4)
C(32)-P(1)	1.843(3)
C(33)-C(34)	1.376(4)
C(33)-H(33)	0.9500
C(34)-C(35)	1.366(5)
C(34)-H(34)	0.9500
C(35)-C(36)	1.384(5)
C(35)-H(35)	0.9500
C(36)-C(37)	1.394(5)
C(36)-H(36)	0.9500
C(37)-H(37)	0.9500
N(1)-Ru(1)	2.142(2)
N(2)-Ru(1)	2.112(2)
N(3)-Ru(1)	2.067(2)
N(4)-Ru(1)	1.949(2)
N(5)-Ru(1)	2.063(2)
O(1)-P(1)	1.5199(19)
F(1)-P(2)	1.5918(18)
F(2)-P(2)	1.5928(19)
F(3)-P(2)	1.6084(19)
F(4)-P(2)	1.6061(18)
F(5)-P(2)	1.594(2)
F(6)-P(2)	1.6020(17)
P(1)-Ru(1)	2.3260(8)
C(28)-H(28)	0.9500
O(2)-H(2B)	0.79(3)

N(1)-C(1)-C(2)	122.8(3)
N(1)-C(1)-H(1)	118.6
C(2)-C(1)-H(1)	118.6
C(2)-C(3)-C(4)	119.6(3)
C(2)-C(3)-H(3)	120.2
C(4)-C(3)-H(3)	120.2
C(1)-C(2)-C(3)	118.5(3)
C(1)-C(2)-H(2)	120.7
C(3)-C(2)-H(2)	120.7
C(3)-C(4)-C(5)	119.1(3)
C(3)-C(4)-H(4)	120.4
C(5)-C(4)-H(4)	120.4
N(1)-C(5)-C(4)	121.2(3)
N(1)-C(5)-C(6)	115.5(2)
C(4)-C(5)-C(6)	123.3(3)
N(2)-C(6)-C(7)	121.3(2)
N(2)-C(6)-C(5)	115.5(2)
C(7)-C(6)-C(5)	123.1(2)
C(6)-C(7)-C(8)	120.3(3)
C(6)-C(7)-H(7)	119.9
C(8)-C(7)-H(7)	119.9
C(9)-C(8)-C(7)	118.6(3)
C(9)-C(8)-H(8)	120.7
C(7)-C(8)-H(8)	120.7
C(8)-C(9)-C(10)	119.0(3)
C(8)-C(9)-H(9)	120.5
C(10)-C(9)-H(9)	120.5

N(2)-C(10)-C(9)	123.6(3)
N(2)-C(10)-H(10)	118.2
C(9)-C(10)-H(10)	118.2
N(3)-C(11)-C(12)	123.0(3)
N(3)-C(11)-H(11)	118.5
C(12)-C(11)-H(11)	118.5
C(13)-C(12)-C(11)	118.9(3)
C(13)-C(12)-H(12)	120.6
C(11)-C(12)-H(12)	120.6
C(12)-C(13)-C(14)	119.3(3)
C(12)-C(13)-H(13)	120.4
C(14)-C(13)-H(13)	120.4
C(13)-C(14)-C(15)	119.6(3)
C(13)-C(14)-H(14)	120.2
C(15)-C(14)-H(14)	120.2
N(3)-C(15)-C(14)	121.1(3)
N(3)-C(15)-C(16)	114.9(2)
C(14)-C(15)-C(16)	123.9(3)
N(4)-C(16)-C(17)	120.1(3)
N(4)-C(16)-C(15)	112.7(2)
C(17)-C(16)-C(15)	127.2(3)
C(18)-C(17)-C(16)	118.8(3)
C(18)-C(17)-H(17)	120.6
C(16)-C(17)-H(17)	120.6
C(19)-C(18)-C(17)	120.4(3)
C(19)-C(18)-H(18)	119.8
C(17)-C(18)-H(18)	119.8
C(18)-C(19)-C(20)	119.7(3)
C(18)-C(19)-H(19)	120.2
C(20)-C(19)-H(19)	120.2
N(4)-C(20)-C(19)	118.9(3)
N(4)-C(20)-C(21)	113.5(2)
C(19)-C(20)-C(21)	127.5(3)
N(5)-C(21)-C(22)	120.5(3)
N(5)-C(21)-C(20)	114.9(2)
C(22)-C(21)-C(20)	124.6(3)
C(23)-C(22)-C(21)	120.1(3)
C(23)-C(22)-H(22)	120.0
C(21)-C(22)-H(22)	120.0
C(22)-C(23)-C(24)	119.4(3)
C(22)-C(23)-H(23)	120.3
C(24)-C(23)-H(23)	120.3
C(23)-C(24)-C(25)	119.3(3)
C(23)-C(24)-H(24)	120.3
C(25)-C(24)-H(24)	120.3
N(5)-C(25)-C(24)	122.1(3)
N(5)-C(25)-H(25)	118.9
C(24)-C(25)-H(25)	118.9
C(31)-C(26)-C(27)	118.2(3)
C(31)-C(26)-P(1)	117.0(2)
C(27)-C(26)-P(1)	124.7(2)
C(28)-C(27)-C(26)	120.5(3)
C(28)-C(27)-H(27)	119.7
C(26)-C(27)-H(27)	119.7
C(30)-C(29)-C(28)	120.0(3)
C(30)-C(29)-H(29)	120.0
C(28)-C(29)-H(29)	120.0
C(29)-C(30)-C(31)	119.9(3)
C(29)-C(30)-H(30)	120.0
C(31)-C(30)-H(30)	120.0
C(30)-C(31)-C(26)	120.9(3)

C(30)-C(31)-H(31)	119.6
C(26)-C(31)-H(31)	119.6
C(37)-C(32)-C(33)	118.1(3)
C(37)-C(32)-P(1)	117.2(2)
C(33)-C(32)-P(1)	124.7(2)
C(34)-C(33)-C(32)	121.0(3)
C(34)-C(33)-H(33)	119.5
C(32)-C(33)-H(33)	119.5
C(35)-C(34)-C(33)	120.8(3)
C(35)-C(34)-H(34)	119.6
C(33)-C(34)-H(34)	119.6
C(34)-C(35)-C(36)	119.3(3)
C(34)-C(35)-H(35)	120.4
C(36)-C(35)-H(35)	120.4
C(35)-C(36)-C(37)	120.8(3)
C(35)-C(36)-H(36)	119.6
C(37)-C(36)-H(36)	119.6
C(32)-C(37)-C(36)	120.0(3)
C(32)-C(37)-H(37)	120.0
C(36)-C(37)-H(37)	120.0
C(5)-N(1)-C(1)	118.7(2)
C(5)-N(1)-Ru(1)	115.00(18)
C(1)-N(1)-Ru(1)	125.5(2)
C(10)-N(2)-C(6)	117.2(2)
C(10)-N(2)-Ru(1)	127.54(18)
C(6)-N(2)-Ru(1)	115.26(17)
C(11)-N(3)-C(15)	118.2(2)
C(11)-N(3)-Ru(1)	128.77(19)
C(15)-N(3)-Ru(1)	113.05(18)
C(16)-N(4)-C(20)	122.1(2)
C(16)-N(4)-Ru(1)	119.27(19)
C(20)-N(4)-Ru(1)	118.08(19)
C(25)-N(5)-C(21)	118.5(2)
C(25)-N(5)-Ru(1)	128.28(19)
C(21)-N(5)-Ru(1)	113.24(19)
O(1)-P(1)-C(26)	105.78(13)
O(1)-P(1)-C(32)	105.45(12)
C(26)-P(1)-C(32)	103.22(14)
O(1)-P(1)-Ru(1)	115.26(8)
C(26)-P(1)-Ru(1)	113.61(9)
C(32)-P(1)-Ru(1)	112.45(9)
F(1)-P(2)-F(2)	90.86(10)
F(1)-P(2)-F(5)	90.98(10)
F(2)-P(2)-F(5)	90.21(10)
F(1)-P(2)-F(6)	90.18(9)
F(2)-P(2)-F(6)	178.95(12)
F(5)-P(2)-F(6)	89.63(10)
F(1)-P(2)-F(4)	89.48(10)
F(2)-P(2)-F(4)	90.18(10)
F(5)-P(2)-F(4)	179.39(11)
F(6)-P(2)-F(4)	89.98(10)
F(1)-P(2)-F(3)	179.35(12)
F(2)-P(2)-F(3)	89.55(11)
F(5)-P(2)-F(3)	89.51(10)
F(6)-P(2)-F(3)	89.41(10)
F(4)-P(2)-F(3)	90.02(10)
N(4)-Ru(1)-N(5)	79.95(10)
N(4)-Ru(1)-N(3)	79.88(9)
N(5)-Ru(1)-N(3)	159.84(9)
N(4)-Ru(1)-N(2)	167.95(8)
N(5)-Ru(1)-N(2)	98.27(9)

N(3)-Ru(1)-N(2)	101.50(9)
N(4)-Ru(1)-N(1)	90.69(9)
N(5)-Ru(1)-N(1)	87.11(8)
N(3)-Ru(1)-N(1)	93.41(9)
N(2)-Ru(1)-N(1)	77.29(9)
N(4)-Ru(1)-P(1)	94.80(7)
N(5)-Ru(1)-P(1)	95.01(7)
N(3)-Ru(1)-P(1)	86.40(7)
N(2)-Ru(1)-P(1)	97.23(6)
N(1)-Ru(1)-P(1)	174.38(7)
C(29)-C(28)-C(27)	120.4(3)
C(29)-C(28)-H(28)	119.8
C(27)-C(28)-H(28)	119.8

Table 8. Anisotropic displacement parameters (A^2 x 10^3) for complex **3**.

The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
C(1)	21(2)	21(2)	25(2)	-3(2)	-4(1)	-3(2)
C(3)	31(2)	18(2)	42(2)	-4(2)	-13(2)	7(2)
C(2)	30(2)	18(2)	42(2)	4(2)	-13(2)	0(2)
C(4)	20(2)	27(2)	27(2)	-7(2)	-6(1)	-1(2)
C(5)	19(2)	21(2)	12(2)	-4(1)	-2(1)	5(1)
C(6)	18(2)	21(2)	10(2)	-5(2)	1(2)	1(1)
C(7)	13(2)	25(2)	21(2)	-6(2)	-6(2)	5(1)
C(8)	13(2)	34(2)	18(2)	-3(2)	0(2)	0(1)
C(9)	20(2)	23(2)	13(2)	-3(1)	4(1)	-6(1)
C(10)	18(2)	21(2)	13(2)	-5(1)	0(1)	2(1)
C(11)	15(2)	17(2)	21(2)	4(2)	-3(1)	0(1)
C(12)	21(2)	22(2)	15(2)	-3(1)	-5(2)	4(1)
C(13)	30(2)	23(2)	11(2)	-2(1)	-1(1)	6(2)
C(14)	18(2)	20(2)	23(2)	5(1)	6(2)	5(1)
C(15)	12(2)	15(2)	21(2)	1(1)	1(1)	4(1)
C(16)	17(2)	19(2)	19(2)	4(1)	1(1)	1(1)
C(17)	23(2)	27(2)	24(2)	-1(2)	4(2)	-3(2)
C(18)	19(2)	28(2)	39(2)	-3(2)	2(2)	-7(2)
C(19)	20(2)	22(2)	36(2)	-9(2)	-5(2)	-4(2)
C(20)	15(2)	19(2)	24(2)	-2(2)	-5(1)	3(1)
C(21)	19(2)	19(2)	21(2)	-6(1)	-10(2)	1(1)
C(22)	30(2)	25(2)	28(2)	-7(2)	-5(2)	-4(2)
C(23)	41(2)	41(2)	19(2)	-10(2)	-5(2)	0(2)
C(24)	35(2)	38(2)	20(2)	-2(2)	4(2)	0(2)
C(25)	25(2)	25(2)	18(2)	-5(2)	-1(2)	0(1)
C(26)	19(2)	21(2)	16(2)	2(2)	4(1)	7(1)
C(27)	28(2)	29(2)	21(2)	5(2)	-4(2)	1(2)
C(29)	71(3)	42(2)	15(2)	4(2)	4(2)	16(2)
C(30)	63(2)	32(2)	27(2)	10(2)	24(2)	4(2)
C(31)	32(2)	30(2)	29(2)	1(2)	11(2)	3(2)
C(32)	23(2)	19(2)	13(2)	2(2)	1(2)	9(1)
C(33)	17(2)	27(2)	24(2)	2(1)	-2(1)	6(1)

C(34)	23(2)	41(2)	29(2)	12(2)	-2(2)	2(2)
C(35)	28(2)	44(2)	47(2)	10(2)	17(2)	8(2)
C(36)	56(3)	37(2)	33(2)	-3(2)	21(2)	16(2)
C(37)	38(2)	23(2)	23(2)	3(2)	6(2)	3(2)
N(1)	18(2)	16(2)	16(1)	-2(1)	-1(1)	-1(1)
N(2)	20(1)	14(1)	8(1)	-2(1)	-1(1)	1(1)
N(3)	15(1)	14(1)	14(1)	-1(1)	-3(1)	3(1)
N(4)	12(1)	18(1)	17(2)	-1(1)	-5(1)	1(1)
N(5)	19(1)	21(2)	14(1)	-1(1)	-4(1)	3(1)
O(1)	22(1)	17(1)	29(1)	-3(1)	-8(1)	-1(1)
F(1)	31(1)	20(1)	33(1)	-1(1)	4(1)	-3(1)
F(2)	37(1)	74(2)	19(1)	0(1)	-1(1)	-22(1)
F(3)	42(1)	35(1)	48(1)	14(1)	-15(1)	-21(1)
F(4)	26(1)	28(1)	50(1)	2(1)	-8(1)	4(1)
F(5)	23(1)	50(1)	33(1)	-13(1)	4(1)	5(1)
F(6)	31(1)	31(1)	20(1)	-7(1)	2(1)	6(1)
P(1)	15(1)	19(1)	15(1)	0(1)	-2(1)	1(1)
P(2)	22(1)	26(1)	22(1)	1(1)	0(1)	-4(1)
Ru(1)	13(1)	16(1)	13(1)	-1(1)	-2(1)	0(1)
C(28)	47(2)	35(2)	23(2)	-4(2)	-9(2)	9(2)
O(2)	23(2)	36(2)	15(2)	0	0	-5(2)

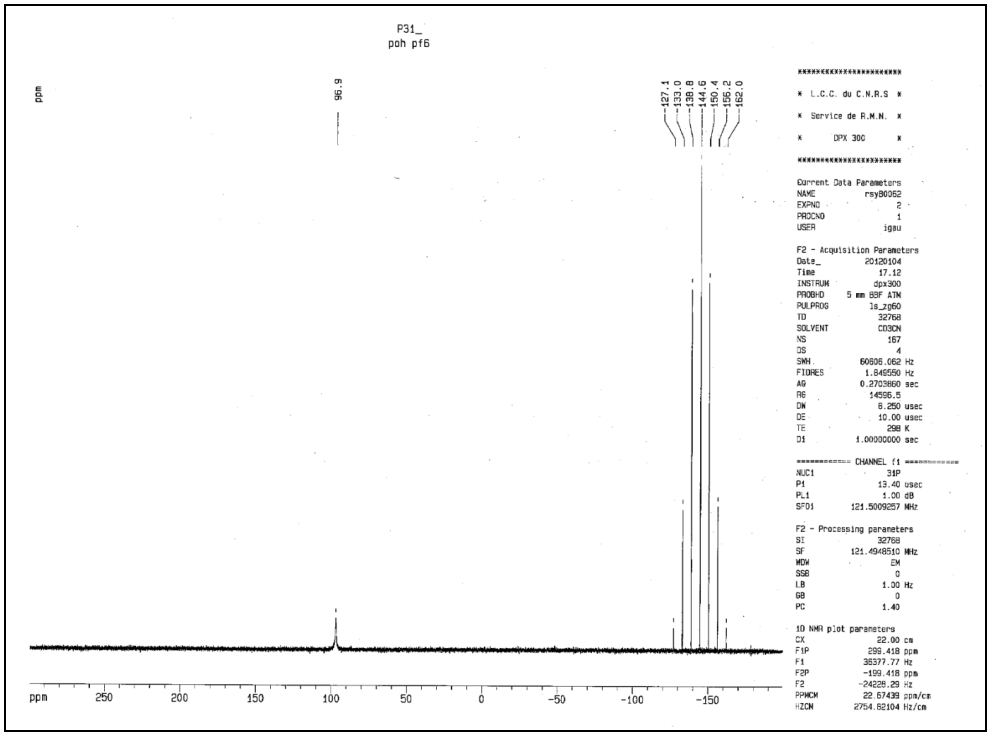


Figure S7 : ^{31}P NMR spectra of complex **3** in CD_3CN at 298K.

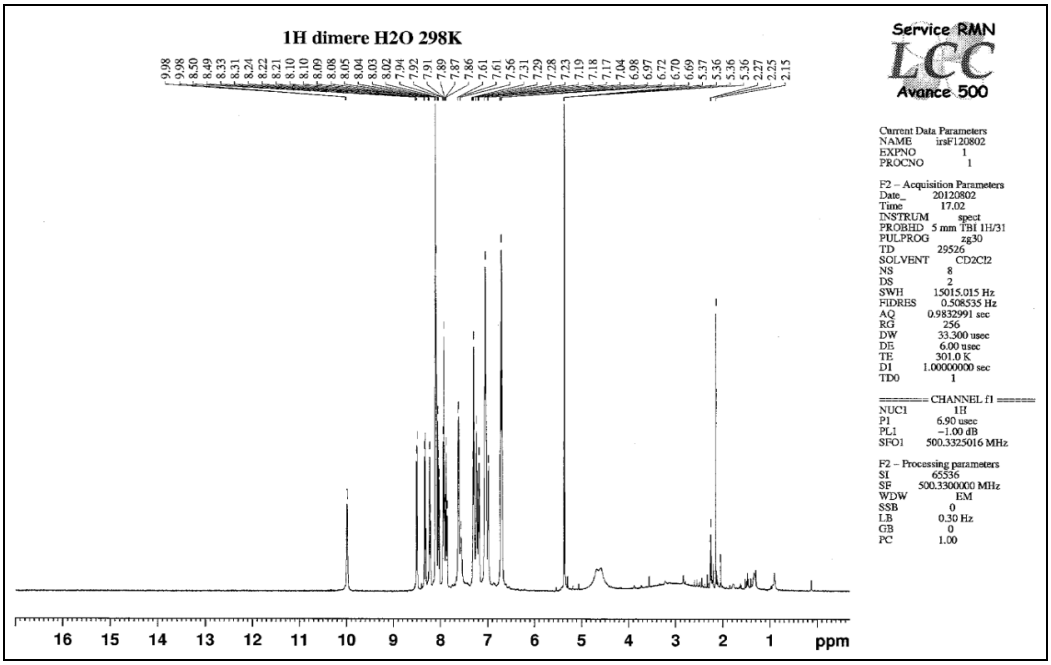


Figure S8 : ^{1}H NMR spectra of complex **3** in CD_2Cl_2 at 298K.

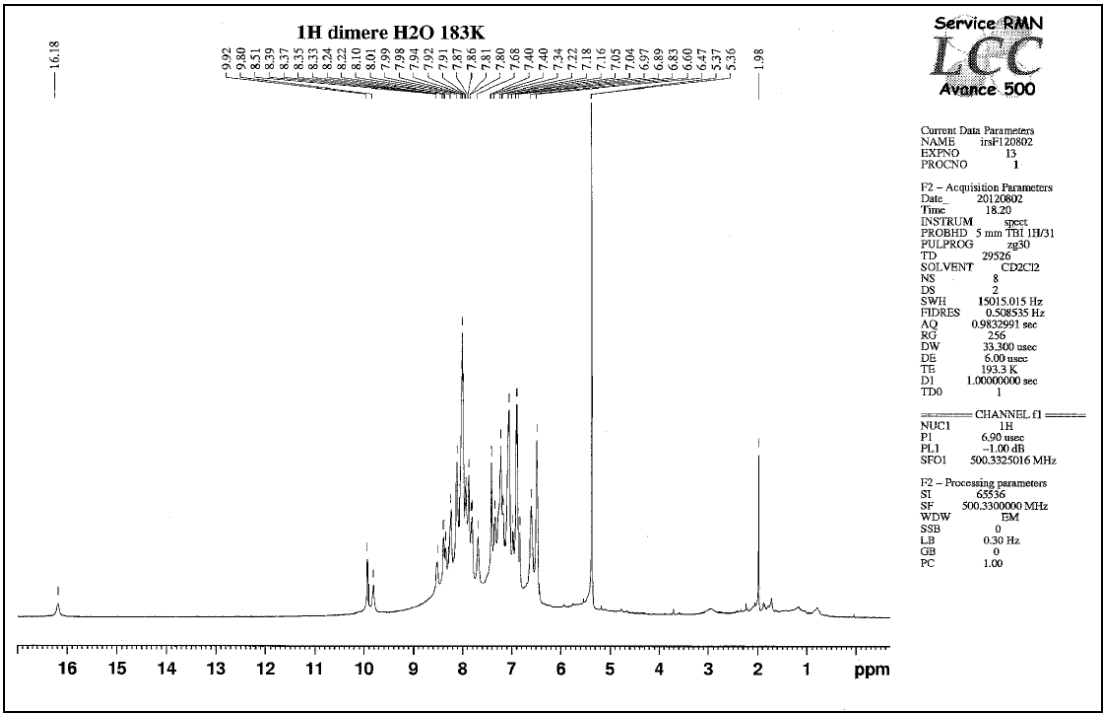


Figure S9 : ^{1}H NMR spectra of complex **3** in CD_2Cl_2 at 183K.

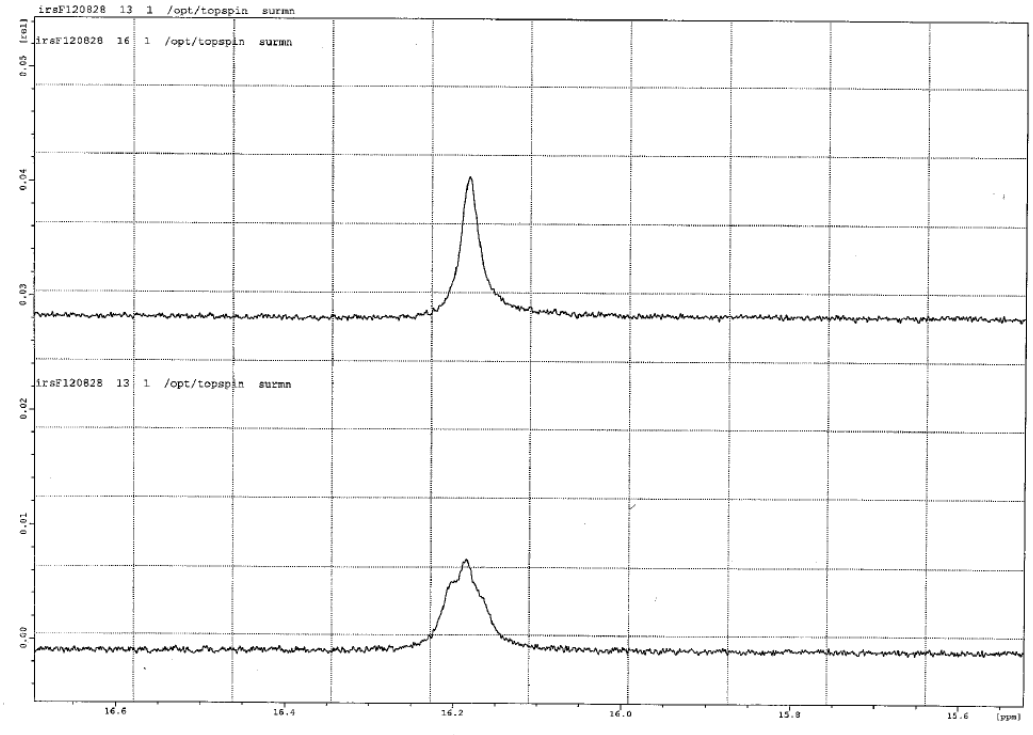


Figure S10 : $^{1}H\{^{31}P\}$ (top) and ^{1}H NMR (under) spectra of complex **3** in CD_2Cl_2 at 183K.

Luminescence quantum yields have been calculated using the optically dilute method,[6] employing $[Ru(bpy)_3]^{2+}$ in air-equilibrated aqueous solution as quantum yield standard (0.028).[7] Experimental uncertainties on the absorption and photophysical data are as follows: absorption maxima, 2 nm; molar absorption, 20%; luminescence maxima, 4 nm; luminescence lifetimes, 10%; luminescence quantum yields, 20%.

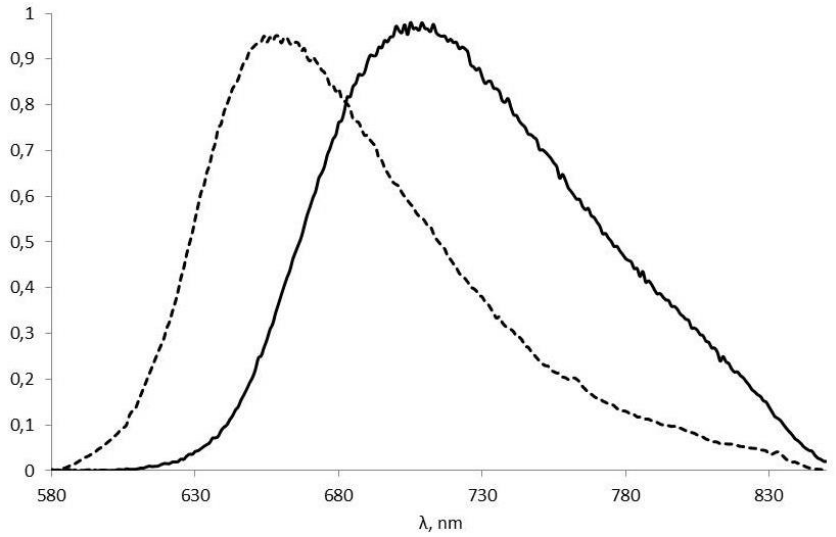


Figure S11. Luminescence spectra of **1** in acetonitrile at room temperature (solid line) and in butyronitrile at 77 K (dashed line). Spectra are normalized and uncorrected for PMT response.

Table 9. Selected photophysical data of phosphoryl complexes **1**, **2** and **3**.

	298 K[a]				77 K[b]	
	Absorption[c] λ, nm (ε, M^{-1} cm^{-1})	Emission[d] λmax, nm	Em τ, ns	Em ϕ(10^-4)	Emission[d] λmax, nm	Em τ (μs)
1	480 (5560)	705 (745)	55	8	658 (685)	3.6
2	436 (11950)	*no detectable emission*				
3	438 (11600)	*no detectable emission*				

(a) Data at 298 K are in acetonitrile; (b) Emission data at 77 K are in butyronitrile; (c) Only the lowest-energy maximum is reported; (d) Corrected values in parenthesis.

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