Electronic Supplementary Material (ESI) for Dalton Transactions

Formation of a Dicationic Ruthenium Benzyl Complex by Halide Abstraction from a Grubbs-Type Second-Generation Benzylidene

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Supporting Information

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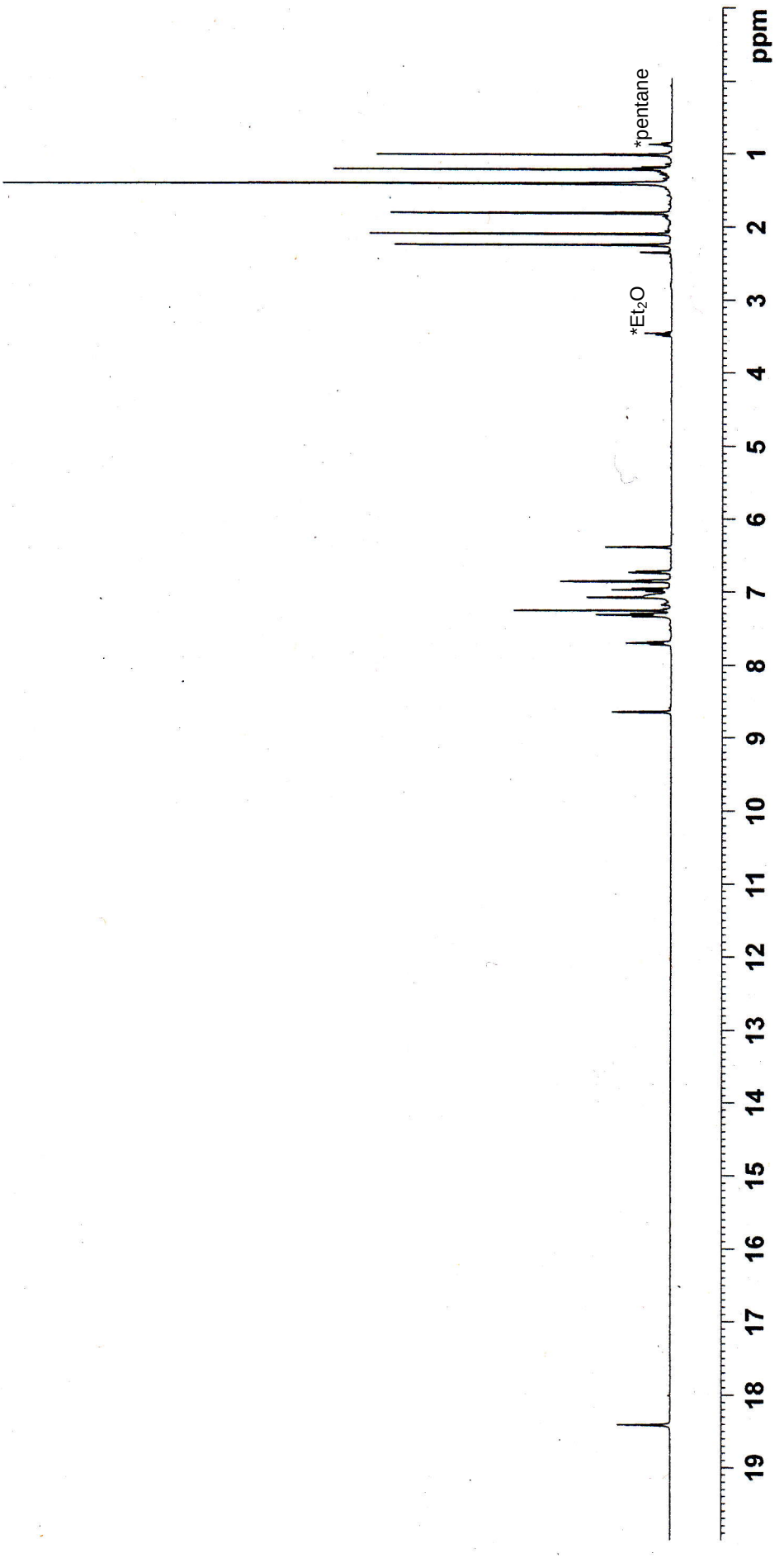
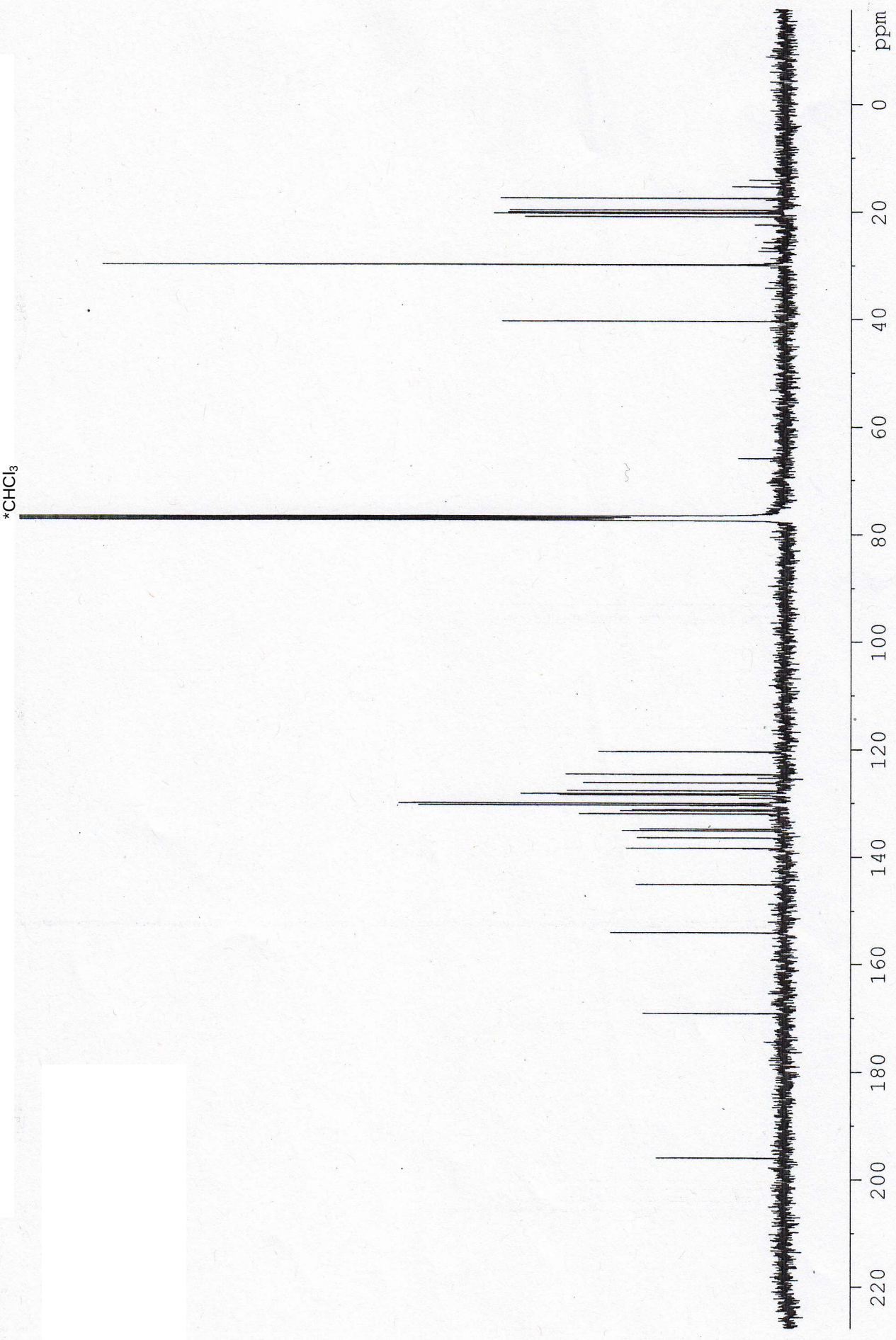
General Considerations. All manipulations involving air-sensitive materials were carried out in oven-dried glassware and performed under nitrogen using standard Schlenk line techniques or in a nitrogen atmosphere glovebox. All glassware and cannulae were dried overnight at 160 °C for at least 12 h prior to use. Solvents used in the preparation of air and/or moisture sensitive compounds were dried using an MBraun Solvent Purification System fitted with alumina columns and stored over molecular sieves under dinitrogen. Silver hexafluorophosphate was purchased from Alfa Aesar and used without further purification. C^Imine[1] and $RuCl_2(PCy_3)_2(CHPh)$[2] can be prepared using published procedures. NMR solvents were purchased from Cambridge Isotope Laboratories and were degassed using three freeze-pump-thaw cycles. $CDCl_3$ was vacuum distilled from CaH_2 and stored under dinitrogen. NMR spectra were recorded on a Bruker AV 400 (^1H at 400 MHz, ^{13}C at 100MHz) or Bruker AV 300 (^1H at 300 MHz, ^{13}C at 75.5 MHz) spectrometer and are at room temperature unless otherwise stated. The spectra were referenced internally relative to the residual protio-solvent (^1H) and solvent (^{13}C) resonances and chemical shifts were reported with respect to δ = 0 ppm for tetramethylsilane. *J*-coupling constants are reported in Hertz (Hz). The multiplicity of signals is reported as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), broad (br) or a combination of any of these. Where ^{13}C spectra are reported, the ^1H and ^{13}C assignments were confirmed by two-dimensional ^1H-^1H, and ^{13}C-^1H correlation NMR experiments. The proton or carbon attributed to the resonance is sometimes italicized for clarity. Elemental composition was determined by Guelph Chemical Laboratories Incorporated.

Synthesis of $RuCl_2$(C^Imine)(CHPh) (1): A solution of C^Imine (65.2 mg, 0.175 mmol) in toluene (10 mL) was added to a solution of $RuCl_2(PCy_3)_2$(CHPh) (119 mg, 0.144 mmol) in toluene (6 mL). The reaction mixture was stirred for 24 h. Volatiles were removed under reduced pressure. The solid was subsequently washed with pentane (2 × 6 mL) and diethyl ether (3 × 6 mL) to give compound **1** as a green solid (67 mg, 0.11 mmol, 76%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 18.41 (s, 1H, C*H*Ph), 8.65 (s, 1H, NC*H*CN$_{(mesityl)}$), 7.70 (t, ^3J = 7.6 Hz, 1H, *p*-C*H*$_{(phenyl)}$), 7.32 (t, ^3J = 7.6 Hz, 2H, *m*-C*H*$_{(phenyl)}$), 7.08 (d, ^3J = 2.0 Hz, 1H, NCC*H*N$_{(mesityl)}$), 7.06 (br, 2H, *o*-C*H*$_{(phenyl)}$), 6.97 (t, ^3J = 7.5 Hz, 1H, *p*-C*H*$_{(2,6\text{-}xylyl)}$), 6.86 (s, 1H, *m*-C*H*$_{(mesityl)}$), 6.84 (s, 1H, *m*-C*H*$_{(2,6\text{-}xylyl)}$), 6.73 (d, ^3J = 7.5 Hz, 1H, *m*-C*H*$_{(2,6\text{-}xylyl)}$), 6.40 (s, 1H, *m*-C*H*$_{(mesityl)}$), 2.25 (s, 3H, *o*-C*H*$_{3(mesityl)}$), 2.10 (s, 3H, *p*-C*H*$_{3(mesityl)}$), 1.81 (s, 3H, *o*-C*H*$_{3(2,6\text{-}xylyl)}$), 1.41 (s, 9H, C(C*H*$_3$)$_{3(imine)}$), 1.22 (s, 3H, *o*-C*H*$_{3(2,6\text{-}xylyl)}$), 1.02 ppm (s, 3H, *o*-C*H*$_{3(mesityl)}$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 318.4 (*C*HPh), 196.1 (N*C*N$_{(mesityl)}$), 169.2 (*C*=N), 154.2 (*C*$_{ipso(phenyl)}$), 145.2 (*C*$_{ipso(2,6\text{-}xylyl)}$), 138.5 (*p*-*C*$_{(mesityl)}$), 136.5 (*C*$_{ipso(mesityl)}$), 135.2 (*o*-*C*$_{(mesityl)}$), 134.9 (*o*-*C*$_{(mesityl)}$), 132.1 (*p*-C*H*$_{(phenyl)}$), 131.5 (*o*-*C*$_{(2,6\text{-}xylyl)}$), 131.3 (*o*-*C*$_{(2,6\text{-}xylyl)}$), 130.5 (*o*-C*H*$_{(phenyl)}$), 130.2 (*m*-C*H*$_{(phenyl)}$), 128.6 (*m*-*C*H$_{(mesityl)}$), 128.5 (*m*-*C*H$_{(mesityl)}$), 128.4 (*m*-*C*H$_{(2,6\text{-}xylyl)}$), 127.8 (*m*-*C*H$_{(2,6\text{-}xylyl)}$), 126.3 (*p*-*C*H$_{(2,6\text{-}xylyl)}$), 124.8 (NC*C*N$_{(mesityl)}$), 120.5 (N*C*CN$_{(mesityl)}$), 40.5 (*C*(CH$_3$)$_{3(imine)}$), 30.0 (C(*C*H$_3$)$_{3(imine)}$), 21.0 (*p*-*C*H$_{3(mesityl)}$), 20.4 (*o*-*C*H$_{3(2,6\text{-}xylyl)}$), 20.2 (*o*-*C*H$_{3(2,6\text{-}xylyl)}$), 19.8 (*o*-*C*H$_{3(mesityl)}$), 17.6 ppm (*o*-*C*H$_{3(mesityl)}$); elemental analysis calcd (%) for $C_{32}H_{37}N_3Cl_2Ru$: C 60.47, H 5.87, N 6.61; found C 60.22, H 5.74, N 6.37.

^{1}H NMR (400 MHz; $CDCl_3$) of compound **1**

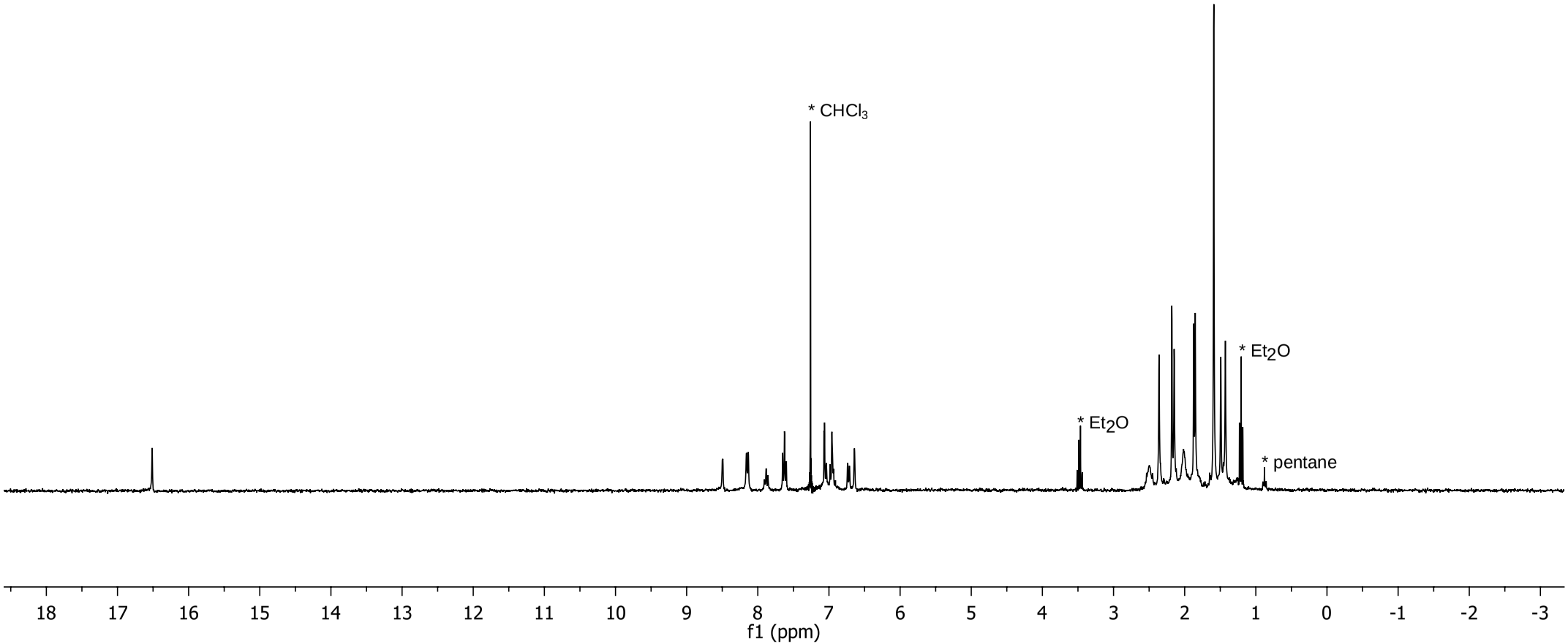




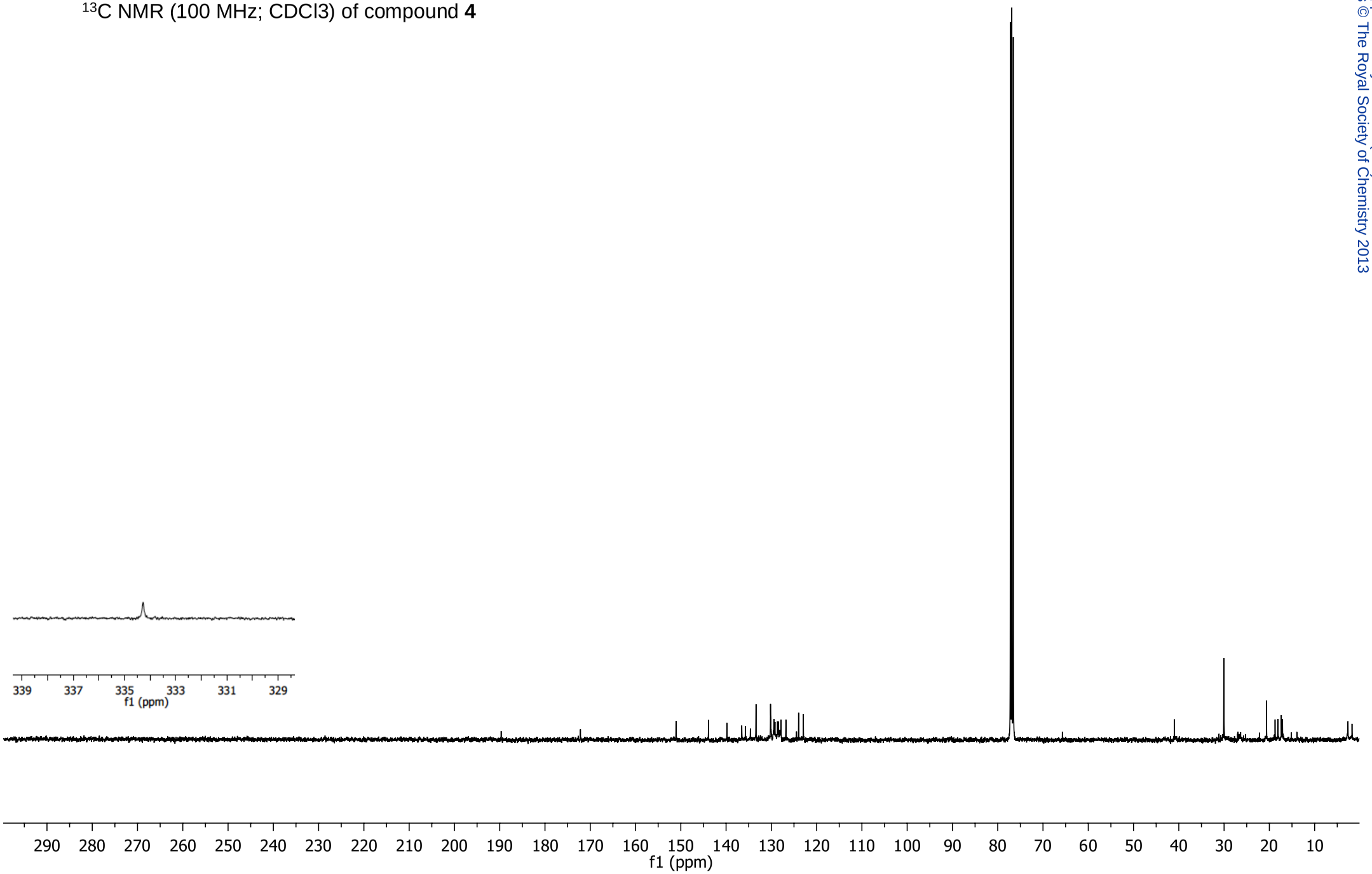
^{13}C NMR (100 MHz; $CDCl_3$) of compound **1**

Synthesis of [Ru(C^Imine)(MeCN)$_4$(CHPh)][PF$_6$]$_2$ (4). $RuCl_2$(C^Imine)(CHPh) (**1**) (41.7 mg, 65.6 μmol) was dissolved in a minimal amount of MeCN (5 mL). $AgPF_6$ (33.2 mg, 131 μmol) was added as a solid to the solution mixture. The solution was stirred stir for 4 h at room temperature, filtered and concentrated in vacuo. Diethyl ether was added until the product precipitated out of solution. X-ray quality crystals formed upon a solution of **4** in $CDCl_3$ standing at room temperature and were used for X-ray diffraction analysis. Yield: 47 mg, 47 μmol, 72%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 16.51 (s, 1H, C*H*Ph), 8.49 (s, 1H, NC*H*CHN$_{(mesityl)}$), 8.13 (d, J = 7.0 Hz, 2H, *m*-C*H*$_{(2,6\text{-xylyl})}$), 7.87 (t, J = 7.3 Hz, 1H, *p*-C*H*$_{(2,6\text{-xylyl})}$), 7.63 (t, J = 7.8 Hz, 2H, *o*-C*H*$_{(phenyl)}$), 7.05 (s, 2H, *m*-C*H*$_{(mesityl)}$), 6.96 (m, 2H, *m*-C*H*$_{(phenyl)}$), 6.71 (d, J = 7.8 Hz, 1H, , *p*-C*H*$_{(phenyl)}$), 6.63 (s, 1H, NCHC*H*N$_{(mesityl)}$), 2.49 (br s, 3H, C*H*$_{3(MeCN)}$), 2.36 (s, 3H, *o*-C*H*$_{3(mesityl)}$), 2.18 (s, 3H, *p*-C*H*$_{3(mesityl)}$), 2.15 (s, 3H, *o*-C*H*$_{3(2,6\text{-xylyl})}$), 2.02 (br s, 3H, C*H*$_{3(MeCN)}$), 1.87 (s, 3H, C*H*$_{3(MeCN)}$), 1.85 (s, 3H, C*H*$_{3(MeCN)}$), 1.59 (s, 9H, C(C*H*$_3$)$_{3(imine)}$), 1.49 (s, 3H, *o*-C*H*$_{3(2,6\text{-xylyl})}$), 1.43 ppm (s, 3H, *o*-C*H*$_{3(mesityl)}$). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 334.3 (*C*HPh), 189.8 (NCN(mesityl)), 172.3 (*C*=N), 151.2, 144.0, 139.9, 136.6 (*p*-*C*H$_{(2,6\text{-xylyl})}$), 135.8, 134.8, 133.5 (*m*-*C*H$_{(2,6\text{-xylyl})}$), 132.5, 130.3 (*o*-*C*H$_{(phenyl)}$), 129.5, 129.3 (*m*-*C*H$_{(phenyl)}$), 128.7 (NCH*C*HN$_{(mesityl)}$), 128.6 (*C*(CH$_3$)$_{(2,6\text{-xylyl})}$), 128.3 (*C*(CH$_3$)$_{(2,6\text{-xylyl})}$), 128.0 (*p*-*C*H$_{(phenyl)}$), 126.9, 124.6, 124.1 (*m*-*C*H$_{(mesityl)}$), 123.1 (NCHCHN$_{(mesityl)}$), 63.8, 41.1 (*C*(CH$_3$)$_{3(imine)}$), 30.1 (C(*C*H$_3$)$_{3(imine)}$), 20.7 (*p*-C*H*$_{3(mesityl)}$), 18.9 (*o*-C*H*$_{3(mesityl)}$), 18.3 (*o*-C*H*$_{3(mesityl)}$), 17.5 (*o*-C*H*$_{3(2,6\text{-xylyl})}$), 17.2 (*o*-C*H*$_{3(2,6\text{-xylyl})}$), 3.7 (C*H*$_{3(MeCN)}$), 2.8 (C*H*$_{3(MeCN)}$), 2.2 (C*H*$_{3(MeCN)}$), 1.9 ppm (C*H*$_{3(MeCN)}$); elemental analysis calcd (%) for $C_{40}H_{49}F_{12}N_7P_2Ru$ (%): C 47.15, H 4.85, N 9.62; found C 47.41, H 5.09, N 9.39.

^{1}H NMR (400 MHz; CDCl3) of compound **4**



^{13}C NMR (100 MHz; CDCl3) of compound **4**



X-ray Crystallography. Details of the X-ray crystal data and structure refinement for **4** are provided as supplementary materials. Crystallographic data were collected at the University of Toronto on a Bruker Kappa APEX-DUO diffractometer using a monochromated Mo-Kα radiation (Bruker Triumph; λ = 0.71073 Å) at 150K. Data were measured using a combination of ϕ scans and ω scans, and were processed using APEX2 and SAINT.[3] Absorption corrections were carried out using SADABS.[3] Compound **4** was solved using Superflip[4] and refined using WinGX[5] with SHELXS-97 for full-matrix least-squares refinement that was based on F^2.[6] All H atoms were included in calculated positions and allowed to refine in riding-motion approximation with U_{iso} tied to the carrier atom..

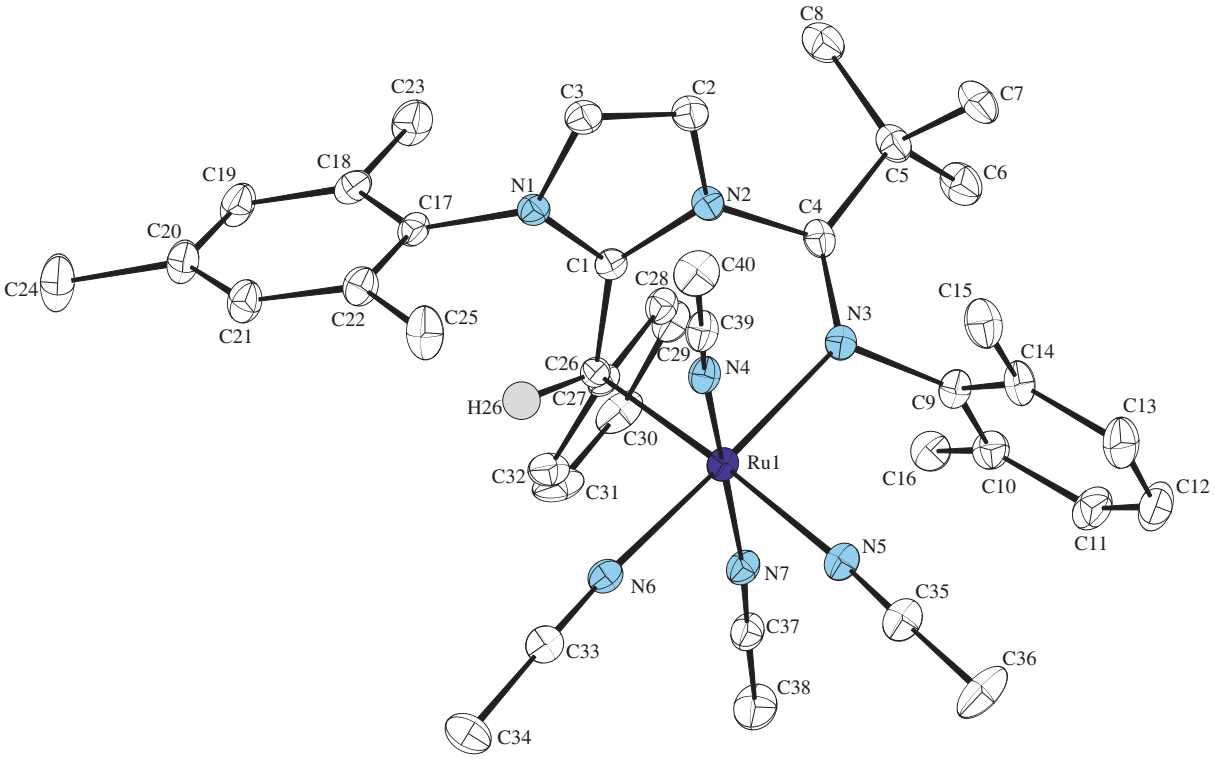


Figure 1. ORTEP diagram of complex **4** (30% probability level). Two hexafluorophosphate anions, two chloroform free solvent molecules and all hydrogen atoms, except for the benzylic proton H26, are omitted for clarity reasons.

Table 1. Crystal data and structure refinement for compound **4**.

CCDC deposition number	942610	
Identification code	d1397	
Empirical formula	C42 H51 Cl6 F12 N7 P2 Ru	
Formula weight	1257.61	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 16.913(3) Å	α= 90°.
	b = 15.631(2) Å	β= 95.168(3)°.
	c = 20.393(3) Å	γ = 90°.
Volume	5369.4(14) Å^3	
Z	4	
Density (calculated)	1.554 Mg/m^3	
Absorption coefficient	0.730 mm^{-1}	
F(000)	2540	
Crystal size	0.230 x 0.110 x 0.040 mm^3	
Theta range for data collection	1.50 to 27.57°.	
Index ranges	-21<=h<=21, -20<=k<=20, -23<=l<=26	
Reflections collected	47744	
Independent reflections	12360 [R(int) = 0.0488]	
Completeness to theta = 27.57°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6597	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	12360 / 0 / 643	
Goodness-of-fit on F^2	1.029	
Final R indices [I>2sigma(I)]	R1 = 0.0596, wR2 = 0.1534	
R indices (all data)	R1 = 0.0858, wR2 = 0.1691	
Largest diff. peak and hole	1.856 and -1.539 e.Å^{-3}	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for compound **4**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	798(2)	3251(2)	1318(2)	24(1)
C(1S)	6492(3)	-52(3)	785(2)	40(1)
C(2)	-128(3)	2931(3)	496(2)	32(1)
C(2S)	8652(3)	6715(4)	1965(3)	51(1)
C(3)	513(3)	3201(3)	227(2)	32(1)
C(4)	-474(2)	2592(3)	1639(2)	28(1)
C(5)	-1363(2)	2829(3)	1522(2)	34(1)
C(6)	-1729(3)	2977(4)	2177(2)	44(1)
C(7)	-1834(3)	2107(3)	1153(2)	43(1)
C(8)	-1497(3)	3678(3)	1134(2)	43(1)
C(9)	-536(3)	1502(3)	2471(2)	32(1)
C(10)	-630(3)	1672(3)	3132(2)	35(1)
C(11)	-904(3)	1007(3)	3510(2)	45(1)
C(12)	-1081(3)	211(4)	3247(3)	53(1)
C(13)	-1011(3)	66(3)	2591(3)	49(1)
C(14)	-731(3)	700(3)	2185(2)	37(1)
C(15)	-608(3)	464(3)	1486(2)	43(1)
C(16)	-501(3)	2535(3)	3449(2)	36(1)
C(17)	1805(2)	3881(3)	641(2)	28(1)
C(18)	1785(3)	4773(3)	699(2)	33(1)
C(19)	2471(3)	5225(3)	604(2)	40(1)
C(20)	3160(3)	4818(3)	450(2)	40(1)
C(21)	3157(3)	3943(3)	390(2)	38(1)
C(22)	2487(3)	3453(3)	483(2)	34(1)
C(23)	1029(3)	5228(3)	856(3)	46(1)
C(24)	3909(3)	5322(4)	364(3)	60(2)
C(25)	2518(3)	2492(3)	422(3)	47(1)
C(26)	1255(2)	3266(2)	1947(2)	23(1)
C(27)	1024(2)	3892(2)	2455(2)	26(1)
C(28)	275(2)	4243(3)	2473(2)	29(1)
C(29)	86(3)	4790(3)	2977(2)	37(1)

C(30)	664(3)	5008(3)	3472(2)	42(1)
C(31)	1417(3)	4691(3)	3451(2)	45(1)
C(32)	1606(3)	4147(3)	2948(2)	35(1)
C(33)	2997(3)	1704(3)	2411(2)	31(1)
C(34)	3844(3)	1584(3)	2559(3)	44(1)
C(35)	1078(3)	-46(3)	2674(2)	39(1)
C(36)	1066(4)	-926(3)	2900(3)	59(2)
C(37)	1368(3)	2402(3)	3697(2)	33(1)
C(38)	1481(3)	2659(4)	4383(2)	49(1)
C(39)	1080(3)	1167(3)	755(2)	31(1)
C(40)	1054(3)	773(3)	102(2)	44(1)
Cl(1S)	7119(1)	451(1)	266(1)	51(1)
Cl(2S)	5871(1)	-794(1)	351(1)	54(1)
Cl(3S)	7069(1)	-560(1)	1429(1)	67(1)
Cl(4S)	9306(1)	6109(1)	1524(1)	57(1)
Cl(5S)	7949(1)	6032(2)	2261(2)	125(1)
Cl(6S)	8255(2)	7560(2)	1513(1)	136(1)
F(1)	5129(2)	3443(3)	830(3)	112(2)
F(2)	5199(3)	2124(6)	408(3)	185(4)
F(3)	6250(2)	2729(3)	916(2)	86(1)
F(4)	5625(3)	1639(3)	1410(3)	127(2)
F(5)	5566(3)	2930(3)	1792(2)	93(1)
F(6)	4470(2)	2365(3)	1216(2)	88(1)
F(7)	1965(2)	8907(3)	767(2)	83(1)
F(8)	1560(3)	7566(3)	567(2)	93(1)
F(9)	1682(2)	8061(2)	1583(2)	64(1)
F(10)	490(3)	7778(4)	1031(2)	118(2)
F(11)	908(3)	9185(3)	1248(2)	106(2)
F(12)	769(2)	8671(2)	235(2)	68(1)
N(1)	1086(2)	3412(2)	737(2)	26(1)
N(2)	34(2)	2982(2)	1181(2)	27(1)
N(3)	-114(2)	2095(2)	2066(2)	26(1)
N(4)	1106(2)	1481(2)	1256(2)	28(1)
N(5)	1074(2)	636(2)	2490(2)	31(1)
N(6)	2336(2)	1787(2)	2302(2)	28(1)
N(7)	1241(2)	2230(2)	3154(2)	29(1)

P(1)	1204(1)	8372(1)	927(1)	39(1)
P(2)	5377(1)	2537(1)	1082(1)	48(1)
Ru(1)	1138(1)	1916(1)	2196(1)	25(1)

Table 3. Bond lengths [Å] and angles [°] for compound **4**.

C(1)-N(1)	1.345(5)
C(1)-N(2)	1.364(5)
C(1)-C(26)	1.438(5)
C(1S)-Cl(1S)	1.750(5)
C(1S)-Cl(2S)	1.752(5)
C(1S)-Cl(3S)	1.754(5)
C(1S)-H(1S)	0.9800
C(2)-C(3)	1.328(6)
C(2)-N(2)	1.401(5)
C(2)-H(2)	0.9300
C(2S)-Cl(6S)	1.712(6)
C(2S)-Cl(5S)	1.745(6)
C(2S)-Cl(4S)	1.764(6)
C(2S)-H(2S)	0.9800
C(3)-N(1)	1.394(5)
C(3)-H(3)	0.9300
C(4)-N(3)	1.279(5)
C(4)-N(2)	1.457(5)
C(4)-C(5)	1.547(6)
C(5)-C(7)	1.538(6)
C(5)-C(6)	1.539(6)
C(5)-C(8)	1.551(7)
C(6)-H(6A)	0.9600
C(6)-H(6B)	0.9600
C(6)-H(6C)	0.9600
C(7)-H(7A)	0.9600
C(7)-H(7B)	0.9600
C(7)-H(7C)	0.9600
C(8)-H(8A)	0.9600
C(8)-H(8B)	0.9600
C(8)-H(8C)	0.9600
C(9)-C(10)	1.398(6)
C(9)-C(14)	1.408(6)
C(9)-N(3)	1.468(5)

C(10)-C(11)	1.396(6)
C(10)-C(16)	1.503(6)
C(11)-C(12)	1.377(8)
C(11)-H(11)	0.9300
C(12)-C(13)	1.374(8)
C(12)-H(12)	0.9300
C(13)-C(14)	1.400(7)
C(13)-H(13)	0.9300
C(14)-C(15)	1.505(6)
C(15)-H(15A)	0.9600
C(15)-H(15B)	0.9600
C(15)-H(15C)	0.9600
C(16)-H(16A)	0.9600
C(16)-H(16B)	0.9600
C(16)-H(16C)	0.9600
C(17)-C(22)	1.397(6)
C(17)-C(18)	1.399(6)
C(17)-N(1)	1.449(5)
C(18)-C(19)	1.386(6)
C(18)-C(23)	1.522(6)
C(19)-C(20)	1.388(7)
C(19)-H(19)	0.9300
C(20)-C(21)	1.374(7)
C(20)-C(24)	1.515(7)
C(21)-C(22)	1.394(6)
C(21)-H(21)	0.9300
C(22)-C(25)	1.508(6)
C(23)-H(23A)	0.9600
C(23)-H(23B)	0.9600
C(23)-H(23C)	0.9600
C(24)-H(24A)	0.9600
C(24)-H(24B)	0.9600
C(24)-H(24C)	0.9600
C(25)-H(25A)	0.9600
C(25)-H(25B)	0.9600
C(25)-H(25C)	0.9600

C(26)-C(27)	1.502(5)
C(26)-Ru(1)	2.184(4)
C(26)-H(26)	1.02(5)
C(27)-C(28)	1.384(6)
C(27)-C(32)	1.401(6)
C(28)-C(29)	1.395(6)
C(28)-H(28)	0.9300
C(29)-C(30)	1.383(7)
C(29)-H(29)	0.9300
C(30)-C(31)	1.371(7)
C(30)-H(30)	0.9300
C(31)-C(32)	1.391(6)
C(31)-H(31)	0.9300
C(32)-H(32)	0.9300
C(33)-N(6)	1.127(5)
C(33)-C(34)	1.449(6)
C(34)-H(34A)	0.9600
C(34)-H(34B)	0.9600
C(34)-H(34C)	0.9600
C(35)-N(5)	1.130(6)
C(35)-C(36)	1.452(7)
C(36)-H(36A)	0.9600
C(36)-H(36B)	0.9600
C(36)-H(36C)	0.9600
C(37)-N(7)	1.141(5)
C(37)-C(38)	1.452(6)
C(38)-H(38A)	0.9600
C(38)-H(38B)	0.9600
C(38)-H(38C)	0.9600
C(39)-N(4)	1.131(5)
C(39)-C(40)	1.464(6)
C(40)-H(40A)	0.9600
C(40)-H(40B)	0.9600
C(40)-H(40C)	0.9600
F(1)-P(2)	1.551(5)
F(2)-P(2)	1.523(5)

F(3)-P(2)	1.572(4)
F(4)-P(2)	1.596(5)
F(5)-P(2)	1.579(4)
F(6)-P(2)	1.605(4)
F(7)-P(1)	1.592(4)
F(8)-P(1)	1.604(4)
F(9)-P(1)	1.576(3)
F(10)-P(1)	1.553(4)
F(11)-P(1)	1.534(4)
F(12)-P(1)	1.602(3)
N(3)-Ru(1)	2.130(3)
N(4)-Ru(1)	2.030(3)
N(5)-Ru(1)	2.094(4)
N(6)-Ru(1)	2.028(4)
N(7)-Ru(1)	2.006(3)

N(1)-C(1)-N(2)	106.9(3)
N(1)-C(1)-C(26)	125.1(4)
N(2)-C(1)-C(26)	127.7(3)
Cl(1S)-C(1S)-Cl(2S)	111.1(3)
Cl(1S)-C(1S)-Cl(3S)	109.3(3)
Cl(2S)-C(1S)-Cl(3S)	110.3(3)
Cl(1S)-C(1S)-H(1S)	108.7
Cl(2S)-C(1S)-H(1S)	108.7
Cl(3S)-C(1S)-H(1S)	108.7
C(3)-C(2)-N(2)	107.5(4)
C(3)-C(2)-H(2)	126.2
N(2)-C(2)-H(2)	126.2
Cl(6S)-C(2S)-Cl(5S)	114.3(4)
Cl(6S)-C(2S)-Cl(4S)	111.9(3)
Cl(5S)-C(2S)-Cl(4S)	109.0(3)
Cl(6S)-C(2S)-H(2S)	107.1
Cl(5S)-C(2S)-H(2S)	107.1
Cl(4S)-C(2S)-H(2S)	107.1
C(2)-C(3)-N(1)	107.8(4)
C(2)-C(3)-H(3)	126.1

N(1)-C(3)-H(3)	126.1
N(3)-C(4)-N(2)	114.8(3)
N(3)-C(4)-C(5)	130.2(4)
N(2)-C(4)-C(5)	115.0(3)
C(7)-C(5)-C(6)	107.8(4)
C(7)-C(5)-C(4)	110.7(4)
C(6)-C(5)-C(4)	111.3(4)
C(7)-C(5)-C(8)	109.4(4)
C(6)-C(5)-C(8)	105.2(4)
C(4)-C(5)-C(8)	112.2(4)
C(5)-C(6)-H(6A)	109.5
C(5)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6B)	109.5
C(5)-C(6)-H(6C)	109.5
H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5
C(5)-C(7)-H(7A)	109.5
C(5)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	109.5
C(5)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5
C(5)-C(8)-H(8A)	109.5
C(5)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
C(5)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
C(10)-C(9)-C(14)	121.7(4)
C(10)-C(9)-N(3)	121.7(4)
C(14)-C(9)-N(3)	115.9(4)
C(11)-C(10)-C(9)	117.6(4)
C(11)-C(10)-C(16)	118.2(4)
C(9)-C(10)-C(16)	124.1(4)
C(12)-C(11)-C(10)	122.0(5)
C(12)-C(11)-H(11)	119.0

C(10)-C(11)-H(11)	119.0
C(13)-C(12)-C(11)	119.5(5)
C(13)-C(12)-H(12)	120.2
C(11)-C(12)-H(12)	120.2
C(12)-C(13)-C(14)	121.5(5)
C(12)-C(13)-H(13)	119.3
C(14)-C(13)-H(13)	119.3
C(13)-C(14)-C(9)	117.7(4)
C(13)-C(14)-C(15)	117.9(4)
C(9)-C(14)-C(15)	124.2(4)
C(14)-C(15)-H(15A)	109.5
C(14)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
C(14)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
C(10)-C(16)-H(16A)	109.5
C(10)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
C(10)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
C(22)-C(17)-C(18)	121.6(4)
C(22)-C(17)-N(1)	120.6(4)
C(18)-C(17)-N(1)	117.8(4)
C(19)-C(18)-C(17)	118.0(4)
C(19)-C(18)-C(23)	121.4(4)
C(17)-C(18)-C(23)	120.6(4)
C(18)-C(19)-C(20)	121.8(4)
C(18)-C(19)-H(19)	119.1
C(20)-C(19)-H(19)	119.1
C(21)-C(20)-C(19)	118.7(4)
C(21)-C(20)-C(24)	120.2(4)
C(19)-C(20)-C(24)	121.0(4)
C(20)-C(21)-C(22)	122.1(4)
C(20)-C(21)-H(21)	118.9

C(22)-C(21)-H(21)	118.9
C(21)-C(22)-C(17)	117.7(4)
C(21)-C(22)-C(25)	120.1(4)
C(17)-C(22)-C(25)	122.2(4)
C(18)-C(23)-H(23A)	109.5
C(18)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5
C(18)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
C(20)-C(24)-H(24A)	109.5
C(20)-C(24)-H(24B)	109.5
H(24A)-C(24)-H(24B)	109.5
C(20)-C(24)-H(24C)	109.5
H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5
C(22)-C(25)-H(25A)	109.5
C(22)-C(25)-H(25B)	109.5
H(25A)-C(25)-H(25B)	109.5
C(22)-C(25)-H(25C)	109.5
H(25A)-C(25)-H(25C)	109.5
H(25B)-C(25)-H(25C)	109.5
C(1)-C(26)-C(27)	118.3(3)
C(1)-C(26)-Ru(1)	98.0(2)
C(27)-C(26)-Ru(1)	115.8(3)
C(1)-C(26)-H(26)	105(3)
C(27)-C(26)-H(26)	113(3)
Ru(1)-C(26)-H(26)	105(3)
C(28)-C(27)-C(32)	117.0(4)
C(28)-C(27)-C(26)	125.0(4)
C(32)-C(27)-C(26)	118.1(4)
C(27)-C(28)-C(29)	122.2(4)
C(27)-C(28)-H(28)	118.9
C(29)-C(28)-H(28)	118.9
C(30)-C(29)-C(28)	119.7(4)
C(30)-C(29)-H(29)	120.1

C(28)-C(29)-H(29)	120.1
C(31)-C(30)-C(29)	119.0(4)
C(31)-C(30)-H(30)	120.5
C(29)-C(30)-H(30)	120.5
C(30)-C(31)-C(32)	121.3(4)
C(30)-C(31)-H(31)	119.3
C(32)-C(31)-H(31)	119.3
C(31)-C(32)-C(27)	120.7(4)
C(31)-C(32)-H(32)	119.7
C(27)-C(32)-H(32)	119.7
N(6)-C(33)-C(34)	179.0(5)
C(33)-C(34)-H(34A)	109.5
C(33)-C(34)-H(34B)	109.5
H(34A)-C(34)-H(34B)	109.5
C(33)-C(34)-H(34C)	109.5
H(34A)-C(34)-H(34C)	109.5
H(34B)-C(34)-H(34C)	109.5
N(5)-C(35)-C(36)	178.6(6)
C(35)-C(36)-H(36A)	109.5
C(35)-C(36)-H(36B)	109.5
H(36A)-C(36)-H(36B)	109.5
C(35)-C(36)-H(36C)	109.5
H(36A)-C(36)-H(36C)	109.5
H(36B)-C(36)-H(36C)	109.5
N(7)-C(37)-C(38)	175.9(5)
C(37)-C(38)-H(38A)	109.5
C(37)-C(38)-H(38B)	109.5
H(38A)-C(38)-H(38B)	109.5
C(37)-C(38)-H(38C)	109.5
H(38A)-C(38)-H(38C)	109.5
H(38B)-C(38)-H(38C)	109.5
N(4)-C(39)-C(40)	179.0(5)
C(39)-C(40)-H(40A)	109.5
C(39)-C(40)-H(40B)	109.5
H(40A)-C(40)-H(40B)	109.5
C(39)-C(40)-H(40C)	109.5

H(40A)-C(40)-H(40C)	109.5
H(40B)-C(40)-H(40C)	109.5
C(1)-N(1)-C(3)	109.2(3)
C(1)-N(1)-C(17)	126.0(3)
C(3)-N(1)-C(17)	123.7(3)
C(1)-N(2)-C(2)	108.5(3)
C(1)-N(2)-C(4)	126.8(3)
C(2)-N(2)-C(4)	122.9(3)
C(4)-N(3)-C(9)	122.8(3)
C(4)-N(3)-Ru(1)	124.8(3)
C(9)-N(3)-Ru(1)	112.1(3)
C(39)-N(4)-Ru(1)	173.7(3)
C(35)-N(5)-Ru(1)	175.9(4)
C(33)-N(6)-Ru(1)	174.7(3)
C(37)-N(7)-Ru(1)	174.1(4)
F(11)-P(1)-F(10)	98.6(3)
F(11)-P(1)-F(9)	93.3(2)
F(10)-P(1)-F(9)	92.6(2)
F(11)-P(1)-F(7)	87.4(3)
F(10)-P(1)-F(7)	173.8(3)
F(9)-P(1)-F(7)	88.55(18)
F(11)-P(1)-F(12)	89.6(2)
F(10)-P(1)-F(12)	89.6(2)
F(9)-P(1)-F(12)	176.1(2)
F(7)-P(1)-F(12)	88.9(2)
F(11)-P(1)-F(8)	175.8(3)
F(10)-P(1)-F(8)	85.4(3)
F(9)-P(1)-F(8)	87.8(2)
F(7)-P(1)-F(8)	88.6(3)
F(12)-P(1)-F(8)	89.2(2)
F(2)-P(2)-F(1)	93.5(4)
F(2)-P(2)-F(3)	90.0(3)
F(1)-P(2)-F(3)	89.2(3)
F(2)-P(2)-F(5)	177.8(4)
F(1)-P(2)-F(5)	88.6(3)
F(3)-P(2)-F(5)	90.4(3)

F(2)-P(2)-F(4)	91.7(4)
F(1)-P(2)-F(4)	174.5(3)
F(3)-P(2)-F(4)	92.4(3)
F(5)-P(2)-F(4)	86.1(3)
F(2)-P(2)-F(6)	88.2(3)
F(1)-P(2)-F(6)	88.5(2)
F(3)-P(2)-F(6)	177.1(3)
F(5)-P(2)-F(6)	91.5(3)
F(4)-P(2)-F(6)	90.0(3)
N(7)-Ru(1)-N(6)	85.56(14)
N(7)-Ru(1)-N(4)	173.68(14)
N(6)-Ru(1)-N(4)	90.50(14)
N(7)-Ru(1)-N(5)	87.57(13)
N(6)-Ru(1)-N(5)	87.25(14)
N(4)-Ru(1)-N(5)	87.31(13)
N(7)-Ru(1)-N(3)	94.98(13)
N(6)-Ru(1)-N(3)	177.84(13)
N(4)-Ru(1)-N(3)	89.15(13)
N(5)-Ru(1)-N(3)	94.86(13)
N(7)-Ru(1)-C(26)	89.30(14)
N(6)-Ru(1)-C(26)	90.57(14)
N(4)-Ru(1)-C(26)	95.68(14)
N(5)-Ru(1)-C(26)	176.31(14)
N(3)-Ru(1)-C(26)	87.35(13)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for compound **4**. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	26(2)	23(2)	24(2)	0(1)	3(2)	2(2)
C(1S)	45(3)	39(2)	35(2)	5(2)	9(2)	8(2)
C(2)	34(2)	38(2)	22(2)	-4(2)	1(2)	-4(2)
C(2S)	54(3)	52(3)	48(3)	3(2)	8(2)	7(2)
C(3)	35(2)	41(2)	21(2)	-1(2)	1(2)	-1(2)
C(4)	29(2)	31(2)	24(2)	-10(2)	4(2)	-8(2)
C(5)	25(2)	45(3)	33(2)	-4(2)	3(2)	-2(2)
C(6)	32(2)	59(3)	41(3)	-5(2)	9(2)	4(2)
C(7)	30(2)	57(3)	43(3)	-11(2)	-3(2)	-8(2)
C(8)	32(2)	51(3)	46(3)	-2(2)	2(2)	4(2)
C(9)	33(2)	29(2)	35(2)	1(2)	9(2)	-2(2)
C(10)	35(2)	38(2)	32(2)	0(2)	7(2)	1(2)
C(11)	53(3)	53(3)	33(2)	8(2)	13(2)	-4(2)
C(12)	54(3)	46(3)	60(3)	15(3)	17(3)	-10(2)
C(13)	49(3)	34(3)	64(3)	-4(2)	10(2)	-13(2)
C(14)	32(2)	32(2)	47(3)	-5(2)	8(2)	-10(2)
C(15)	44(3)	39(3)	47(3)	-16(2)	8(2)	-12(2)
C(16)	39(2)	42(3)	29(2)	-6(2)	7(2)	1(2)
C(17)	32(2)	29(2)	22(2)	2(2)	5(2)	-3(2)
C(18)	38(2)	32(2)	29(2)	8(2)	6(2)	5(2)
C(19)	44(3)	28(2)	50(3)	8(2)	14(2)	-1(2)
C(20)	38(2)	38(2)	44(3)	6(2)	12(2)	-7(2)
C(21)	36(2)	37(2)	43(2)	3(2)	16(2)	2(2)
C(22)	36(2)	36(2)	32(2)	1(2)	9(2)	-1(2)
C(23)	46(3)	32(2)	61(3)	6(2)	15(2)	7(2)
C(24)	49(3)	46(3)	88(4)	8(3)	28(3)	-9(2)
C(25)	44(3)	34(2)	65(3)	-9(2)	24(2)	-2(2)
C(26)	25(2)	23(2)	22(2)	1(1)	2(1)	-1(1)
C(27)	35(2)	19(2)	23(2)	3(2)	2(2)	-3(2)
C(28)	35(2)	25(2)	27(2)	-2(2)	4(2)	-5(2)
C(29)	46(3)	32(2)	33(2)	-2(2)	10(2)	-1(2)

C(30)	73(3)	27(2)	27(2)	-2(2)	9(2)	2(2)
C(31)	75(4)	29(2)	28(2)	-2(2)	-17(2)	-1(2)
C(32)	42(2)	28(2)	34(2)	0(2)	-7(2)	2(2)
C(33)	38(2)	27(2)	30(2)	-5(2)	5(2)	2(2)
C(34)	34(2)	48(3)	49(3)	-8(2)	0(2)	10(2)
C(35)	51(3)	33(2)	32(2)	-4(2)	9(2)	-3(2)
C(36)	107(5)	31(3)	42(3)	8(2)	18(3)	-5(3)
C(37)	37(2)	30(2)	32(2)	2(2)	4(2)	-6(2)
C(38)	61(3)	58(3)	28(2)	-5(2)	4(2)	-13(3)
C(39)	37(2)	25(2)	32(2)	-6(2)	9(2)	-6(2)
C(40)	58(3)	41(3)	34(2)	-12(2)	7(2)	-1(2)
Cl(1S)	63(1)	45(1)	45(1)	12(1)	10(1)	-6(1)
Cl(2S)	57(1)	53(1)	50(1)	7(1)	1(1)	-6(1)
Cl(3S)	65(1)	82(1)	51(1)	31(1)	-11(1)	-9(1)
Cl(4S)	52(1)	61(1)	59(1)	14(1)	15(1)	13(1)
Cl(5S)	83(1)	106(2)	200(3)	3(2)	80(2)	-4(1)
Cl(6S)	208(3)	115(2)	89(2)	40(1)	39(2)	104(2)
F(1)	67(3)	108(4)	157(4)	83(3)	-12(3)	-13(2)
F(2)	115(4)	348(10)	98(4)	-137(5)	52(3)	-105(5)
F(3)	50(2)	133(4)	76(3)	-8(3)	12(2)	-3(2)
F(4)	143(5)	46(2)	191(6)	6(3)	17(4)	24(3)
F(5)	140(4)	84(3)	57(2)	-15(2)	12(2)	22(3)
F(6)	73(3)	84(3)	115(3)	21(2)	46(2)	-11(2)
F(7)	72(2)	105(3)	70(2)	37(2)	-9(2)	-34(2)
F(8)	101(3)	85(3)	86(3)	-32(2)	-33(2)	34(2)
F(9)	71(2)	71(2)	43(2)	21(2)	-19(2)	-24(2)
F(10)	82(3)	162(5)	103(3)	76(3)	-32(2)	-74(3)
F(11)	157(4)	95(3)	65(2)	-32(2)	5(3)	51(3)
F(12)	91(3)	43(2)	63(2)	7(2)	-36(2)	-4(2)
N(1)	26(2)	30(2)	22(2)	0(1)	2(1)	0(1)
N(2)	26(2)	32(2)	23(2)	-4(1)	4(1)	-2(1)
N(3)	29(2)	26(2)	22(2)	-4(1)	4(1)	-5(1)
N(4)	32(2)	22(2)	32(2)	-2(1)	7(1)	-2(1)
N(5)	38(2)	28(2)	27(2)	-2(1)	7(1)	-1(2)
N(6)	34(2)	23(2)	28(2)	0(1)	4(1)	2(1)
N(7)	35(2)	24(2)	28(2)	1(1)	3(1)	-2(1)

P(1)	46(1)	34(1)	35(1)	0(1)	-7(1)	-5(1)
P(2)	58(1)	42(1)	49(1)	-5(1)	22(1)	-2(1)
Ru(1)	29(1)	22(1)	24(1)	-2(1)	4(1)	-1(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for compound **4**.

	x	y	z	U(eq)
H(1S)	6162	384	973	48
H(2)	-598	2743	271	38
H(2S)	8965	6955	2349	61
H(3)	570	3243	-221	39
H(6A)	-2268	3165	2090	66
H(6B)	-1429	3406	2428	66
H(6C)	-1717	2452	2423	66
H(7A)	-1835	1610	1429	65
H(7B)	-1591	1969	759	65
H(7C)	-2370	2292	1039	65
H(8A)	-1406	3586	682	65
H(8B)	-1136	4104	1321	65
H(8C)	-2033	3869	1159	65
H(11)	-969	1106	3952	55
H(12)	-1247	-225	3513	63
H(13)	-1153	-465	2411	58
H(15A)	-151	101	1482	65
H(15B)	-528	974	1238	65
H(15C)	-1068	167	1292	65
H(16A)	-1004	2806	3484	55
H(16B)	-185	2882	3185	55
H(16C)	-230	2467	3880	55
H(19)	2469	5818	645	48
H(21)	3616	3668	283	45
H(23A)	1123	5833	881	68
H(23B)	874	5026	1270	68
H(23C)	614	5111	515	68
H(24A)	4327	4936	273	89
H(24B)	4063	5635	760	89
H(24C)	3811	5715	3	89

H(25A)	3016	2327	267	70
H(25B)	2091	2301	115	70
H(25C)	2468	2237	844	70
H(28)	-116	4109	2139	35
H(29)	-425	5007	2979	44
H(30)	543	5364	3815	50
H(31)	1810	4842	3780	54
H(32)	2124	3951	2939	42
H(34A)	4014	1865	2966	66
H(34B)	4121	1823	2211	66
H(34C)	3959	984	2598	66
H(36A)	601	-1019	3128	88
H(36B)	1532	-1037	3192	88
H(36C)	1056	-1305	2529	88
H(38A)	1142	3136	4454	73
H(38B)	2025	2820	4490	73
H(38C)	1351	2190	4657	73
H(40A)	826	1169	-222	66
H(40B)	735	265	95	66
H(40C)	1582	628	5	66
H(26)	1830(30)	3330(30)	1840(20)	40(13)

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