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Ruthenium-Stabilized Low Coordinate Phosphorus:

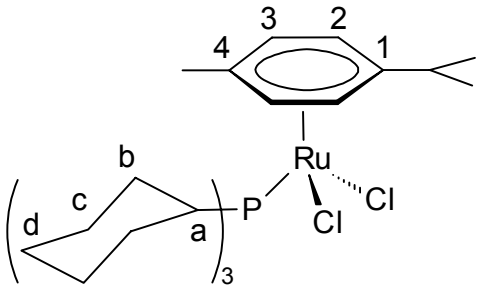
First Structural Evidence for Monomeric Metaphosphonate

Richard Menye-Biyogo, Fabien Delpech*, Annie Castel, Heinz Gornitzka and Pierre Rivière*.

General Considerations. All reactions were carried out under argon atmosphere using standard Schlenk techniques. Solvents were dried and distilled according to standard procedures and degassed prior to use. All reagents were purchased from Aldrich and were used without further purification. NMR spectra were recorded in $CDCl_3$, C_6D_6 or C_7D_8 on Bruker AC 200 or ARX 400 instruments. Infrared spectra were recorded with a Perkin Elmer 1600 FT spectrometer. Elemental analyses were done by the Centre de Microanalyses de l'Ecole Nationale Supérieure de Chimie de Toulouse. ^1H and $^{13}C\{^1H\}$ NMR assignments were confirmed by ^1H COSY, HSQC(^1H - ^{13}C) and HMQC(^1H - ^{13}C) experiments.

Example of atom labeling used in the NMR assignments of **1**-**4** is given in Chart 1.

Chart 1



(η^6-*p*-cymene)$RuCl_2(PH_2Mes^*)$ (**1**) : To a red slurry of [(η^6-*p*-cymene)$RuCl_2$]$_2$ (0.255 g, 0.41 mmol) in CH_2Cl_2 (10 mL) was added Mes^*PH_2 (0.248 g, 0.89 mmol) and the resulting suspension was stirred for 1 h at room temperature. The solvent was evaporated and the red solid washed with pentane giving a red powder in 90% yield. m.p. 168 °C.

^{31}P NMR (81 MHz, C_6D_6): δ = -26.9 ppm (t, ^1J(P,H) = 388.7 Hz). ^{1}H NMR (200 MHz, C_6D_6): δ = 1.08 (s, 3 H, CH_3 *p*-cymene), 1.18 (d, ^3J(H,H) = 6.8 Hz, 6 H, CH(CH_3)$_2$ *p*-cymene), 1.25 (s, 9 H, *p*-C(CH_3)$_3$), 1.50 (s, 18 H, *o*-C(CH_3)$_3$), 2.93 (septet, ^3J(H,H) = 6.8 Hz, 1 H, CH(CH$_3$)$_2$ *p*-cymene), 4.49 (AB, ^3J(H,H) = 5.4 Hz, 2 H, C$_3H$ *p*-cymene), 5.10 (AB, ^3J(H,H) = 5.4 Hz, 2 H, C$_2H$ *p*-cymene), 6.49 (d, ^1J(H,P) = 388.7 Hz, 2H, PH_2), 7.51 ppm (s, 2H, *m*-Mes*). ^{13}C{^{1}H} (50 MHz, C_6D_6): δ = 17.6 (s, *C*H$_3$ *p*-cymene), 22.4 (s, CH(*C*H$_3$)$_2$ *p*-cymene), 30.8 (s, *C*H(CH$_3$)$_2$ *p*-cymene), 31.3 (s, *p*-C(*C*H$_3$)$_3$), 33.4 (s, *o*-C(*C*H$_3$)$_3$), 35.2 (s, *p*-*C*(CH$_3$)$_3$), 38.6 (s, *o*-*C*(CH$_3$)$_3$), 84.2 (s, *C*$_3$ *p*-cymene), 87.0 (d, ^2J(C,P) = 4.6 Hz, *C*$_2$ *p*-cymene), 98,4 (s, *C*$_4$ *p*-cymene), 111.6 (d, ^3J(C,P) = 7.4 Hz, *C*$_1$ *p*-cymene), 122.8 (d, ^3J(C,P) = 9.2 Hz, *m*-Mes*), 151.9 (br s, *p*-Mes*), 155.6 ppm (d, ^2J(C,P) = 4.6 Hz, *o*-Mes*); elemental analysis (%) calcd for $C_{28}H_{45}Cl_2PRu$: C 57.53, H 7.76; found: C 58.11, H 8.24.

(η^6-*p*-cymene)$RuCl_2(PR_3)$ (**2a** : R = Cy, **2b** : R = Ph) were prepared by analogous method in 91 % and 95 % yield respectively.

2a: m.p.: 172.5 °C. ^{31}P NMR (81 MHz, $CDCl_3$): δ = 24.9 ppm (s). ^{1}H NMR (200 MHz, $CDCl_3$) δ = 1.23 (d, ^3J(H,H) = 6.8 Hz, 6 H, CH(CH_3)$_2$ *p*-cymene), 1.38 (m, 12 H, C$_c$$H_2$), 1.70 (m, 12 H, C$_b$$H_2$), 1.90 (s, 3 H, C$H_3$ *p*-cymene), 2.25 (m, 6 H, C$_d$$H_2$), 2.53 (m, 3 H, C$_a$$H$), 2.94 (septet, ^3J(H,H) = 6.8 Hz, 1 H, CH(CH$_3$)$_2$ *p*-cymene), 5.32 (AB, ^3J(H,H)= 5.9 Hz, 2 H, C$_3H$ *p*-cymene), 5.46 ppm (AB, ^3J(H,H) = 5.9 Hz, 2 H, C$_2H$ *p*-cymene). ^{13}C{^{1}H} (50 MHz, $CDCl_3$): δ = 18.0 (s,

*C*H$_3$ *p*-cymene), 22.6 (s, CH(*C*H$_3$)$_2$ *p*-cymene), 26.6 (s, C_d), 27.7 (d, ^3J(C,P) = 9.2 Hz, C_c), 29.8 (s, C_b), 30.7 (s, *C*H(CH$_3$)$_2$ *p*-cymene), 35.9 (d, ^1J(C,P) = 18.5 Hz, C_a), 84.0 (d, ^2J(C,P) = 4.6 Hz, C_3 *p*-cymene), 88.4 (d, ^2J(C,P) = 3.7 Hz, C_2 *p*-cymene), 94.5 (s, C_4 *p*-cymene), 107.0 ppm (s, C_1 *p*-cymene); elemental analysis (%) calcd for $C_{28}H_{47}Cl_2PRu$: C 57.33, H 8.08; found: C 57.77, H 8.17.

2b: m.p.: 170 °C. ^{31}P NMR (81 MHz, $CDCl_3$): δ = 24.4 ppm (s). ^{1}H NMR (200 MHz, $CDCl_3$): 1.09 (d, ^3J(H,H)= 6.8 Hz, 6 H, CH(C*H*$_3$)$_2$ *p*-cymene), 1.86 (s, 3 H, C*H*$_3$ *p*-cymene), 2.85 (septet, ^3J(H,H) = 6.8 Hz, 1 H, C*H*(CH$_3$)$_2$ *p*-cymene), 4.98 (AB, ^3J(H,H) = 5.8 Hz, 2 H, C$_3$*H* *p*-cymene), 5.19 (AB, ^3J(H,H)= 5.8 Hz, 2 H, C$_2$*H* *p*-cymene), 7.38 (s, 9 H, *o*-PPh$_3$ and *p*-PPh$_3$), 7.83 ppm (m, 6 H, *m*-PPh$_3$). ^{13}C{^{1}H} (50 MHz, $CDCl_3$): δ = 17.8 (s, *C*H$_3$ *p*-cymene), 21.9 (s, CH(*C*H$_3$)$_2$ *p*-cymene), 30.3 (s, *C*H(CH$_3$)$_2$ *p*-cymene), 87.2 (d, ^2J(C,P) = 4.6 Hz, C_2 *p*-cymene), 89.1 (s, C_3 *p*-cymene), 95.9 (s, C_4 *p*-cymene), 111.3 (s, C_1 *p*-cymene), 128.0 (d, ^2J(C,P) = 9.2 Hz, *o*-PPh$_3$), 130.3 (s, *p*-PPh$_3$), 133.4 (s, *ipso*-PPh$_3$), 134.4 ppm (d, ^3J(C,P) = 9.2 Hz, *m*-PPh$_3$); elemental analysis (%) calcd for $C_{28}H_{29}Cl_2PRu$: C 59.16, H 5.14; found: C 58.88, H 5.11.

(η^6-*p*-cymene)(PR$_3$)Ru(PMes*) (**3a** : R = Cy, **3b** : R = Ph)

3a: m.p.: 167.5 °C (dec.). ^{31}P NMR (81 MHz, C_6D_6): δ = 35.2 (d, ^2J(P,P) = 15.3 Hz, *P*Cy$_3$), 811.4 ppm (d, ^2J(P,P) = 15.3 Hz, *P*Mes*). ^{1}H NMR (200 MHz, C_6D_6): δ = 1.05 (d, ^3J(H,H) = 6.6 Hz, 6 H, CH(C*H*$_3$)$_2$ *p*-cymene), 1.31 (m, 12 H, C$_c$*H*$_2$), 1.57 (s, 9 H, *p*-C(C*H*$_3$)$_3$), 1.73 (s, 18 H, *o*-C(C*H*$_3$)$_3$), 1.74 (s, 3 H, C*H*$_3$ *p*-cymene), 1.93 (m, 6 H, C$_d$*H*$_2$), 2.11 (m, 12 H, C$_b$*H*$_2$), 2.56 (m, 4 H, C*H*(CH$_3$)$_2$ *p*-cymene and C$_a$*H*), 4.71 (AB, ^3J(H,H) = 5.9 Hz, 2 H, C$_3$*H* *p*-cymene), 4.79 (AB, ^3J(H,H) = 5.9 Hz, 2 H, C$_2$*H* *p*-cymene), 7.56 ppm (d, ^4J(H,P) = 3.9 Hz, 2 H, *m*-Mes*). ^{13}C{^{1}H}

NMR (50 MHz, C_6D_6): δ = 18.7 (s, CH$_3$ *p*-cymene), 24.4 (s, CH(CH$_3$)$_2$ *p*-cymene), 27.4 (s, C_d), 28.4 (d, ^3J(C,P) = 9.2 Hz, C_c), 30.3 (s, C_b), 31.3 (s, CH(CH$_3$)$_2$ *p*-cymene), 32.0 (s, *p*-C(CH$_3$)$_3$), 32.8 (s, *o*-C(CH$_3$)$_3$), 34.9 (s, *p*-C(CH$_3$)$_3$), 36.8 (s, C_a), 38.8 (s, *o*-C(CH$_3$)$_3$), 81.5 (s, C_3 *p*-cymene), 86.1 (s, C_2 *p*-cymene), 90.0 (s, C_4 *p*-cymene), 103.5 (s, C_1 *p*-cymene), 119.1 (s, *m*-Mes*), 145.4 (s, *p*-Mes*), 146.0 (s, *o*-Mes*C_o), 176.5 ppm (br s, *ipso*-Mes*); elemental analysis (%) calcd for $C_{46}H_{76}P_2Ru$: C 69.75, H 9.67; found: C 70.25, H 9.73.

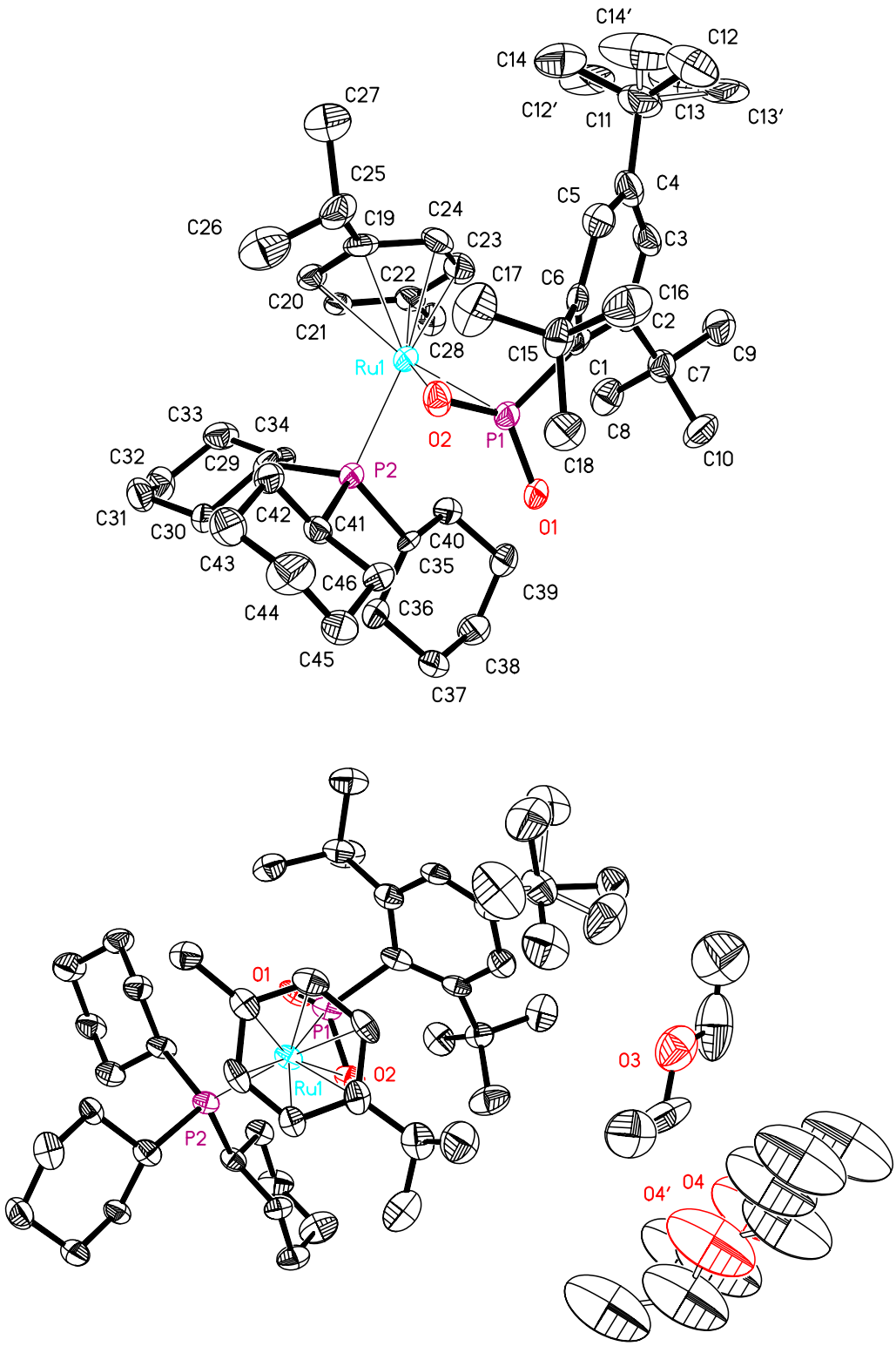
3b: m.p.: 140°C. ^{31}P NMR (81 MHz, C_6D_6): δ = 38.8 (d, ^2J(P,P) = 45.8 Hz, PCy$_3$), 835.4 ppm (d, ^2J(P,P) = 45.8 Hz, PMes*). ^{1}H NMR (200 MHz, C_6D_6): δ = 0.93 (d, ^3J(H,H)= 6.6 Hz, 6 H, CH(CH_3)$_2$ *p*-cymene), 1.54 (s, 9 H, *p*-C(CH_3)$_3$), 1.63 (s, 18 H, *o*-C(CH_3)$_3$), 1.77 (s, 3 H, CH_3 *p*-cymene), 2.42 (septet, ^3J(H,H) = 6.6 Hz, 1 H, CH(CH$_3$)$_2$ *p*-cymene), 4.58 (AB, ^3J(H,H) = 6.1 Hz, 2 H, C_3H *p*-cymene), 4.61 (AB, ^3J(H,H) = 6.1 Hz, 2 H, C_2H *p*-cymene), 7.12 (m, 9 H, *o*-PPh$_3$ and *p*-PPh$_3$), 7.54 (s, 2 H, *m*-Mes*), 7.94 ppm (m, 6 H, *m*-PPh$_3$). ^{13}C{^{1}H} NMR (50 MHz, C_6D_6): δ = 18.9 (s, CH$_3$ *p*-cymene), 24.4 (s, CH(CH$_3$)$_2$ *p*-cymene), 30.8 (s, CH(CH$_3$)$_2$ *p*-cymene), 32.0 (s, *p*-C(CH$_3$)$_3$), 32.8 (d, ^4J(C,P) = 6.4 Hz, *o*-C(CH$_3$)$_3$), 34.9 (s, *p*-C(CH$_3$)$_3$), 38.7 (s, *o*-C(CH$_3$)$_3$), 84.7 (d, ^2J(C,P) = 2.8 Hz, C_2 *p*-cymene), 87.2 (d, ^2J(C,P) = 2.8 Hz, C_3 *p*-cymene), 91.5 (s, C_4 *p*-cymene), 105.0 (s, C_1 *p*-cymene), 119.4 (s, *m*-Mes*), 127.7 (s, *o*-PPh$_3$), 129.1 (s, *p*-PPh$_3$), 135.3 (d, ^3J(C,P) = 11.1 Hz, *m*-PPh$_3$), 139.6 (d, ^1J(C,P) = 38.8 Hz, *ipso*-PPh$_3$), 145.7 (s, *p*-Mes*), 145.9 (s, *o*-Mes*), 183.6 ppm (br s, *ipso*-Mes*); elemental analysis (%) calcd for $C_{46}H_{58}P_2Ru$: C 71.38, H 7.55; found: C 71.15, H 7.72.

[(η^6-*p*-cymene)(PPh$_3$)Ru(η^2-OPOMes*)] (**4b**)

m.p.: 115°C. ^{31}P NMR (81 MHz, C_6D_6): δ = 25.7 (d, ^2J(P,P) = 54.9 Hz, *P*Ph$_3$), 38.5 ppm (d, ^2J(P,P) = 54.9 Hz, *P*O$_2$Mes*). ^{1}H NMR (200 MHz, C_6D_6): δ = 1.01 (d, ^3J(H,H) = 6.8 Hz, 3 H, CH(C*H*$_3$)$_2$ *p*-cymene), 1.16 (d, ^3J(H,H) = 6.8 Hz, 3 H, CH(C*H*$_3$)$_2$ *p*-cymene), 1.37 (s, 9 H, *p*-C(C*H*$_3$)$_3$), 1.44 (s, 3 H, CH$_3$ *p*-cymene), 1.83 (s, 9 H, *o*-C(C*H*$_3$)$_3$), 1.95 (s, 9 H, *o*-C(C*H*$_3$)$_3$), 2.45 (septet, ^3J(H,H) = 6.8 Hz, 1 H, C*H*(CH$_3$)$_2$ *p*-cymene), 3.21 (s, 1 H, C$_2$*H* *p*-cymene), 3.54 (s, 1 H, C$_3$*H* *p*-cymene), 5.31 (s, 1 H, C$_3$*H* *p*-cymene), 5.37 (s, 1 H, C$_2$*H* *p*-cymene), 7.05 (m, 9 H, *o*-PPh$_3$ and *p*-PPh$_3$), 7.41 (s, 1 H, *m*-Mes*), 7.51 (d, ^3J(H,P) = 2.5 Hz, 1 H, *m*-Mes*), 7.73 (m, 3 H, *m*-PPh$_3$), 7.95 ppm (m, 3 H, *m*-PPh$_3$). ^{13}C{^{1}H} NMR (50 MHz, C_6D_6): δ = 18.3 (s, *C*H$_3$ *p*-cymene), 24.3 (s, CH(*C*H$_3$)$_2$ *p*-cymene), 25.0 (s, CH(*C*H$_3$)$_2$ *p*-cymene), 31.5 (s, *p*-C(*C*H$_3$)$_3$), 31.8 (s, *C*H(CH$_3$)$_2$ *p*-cymene), 33.6 (s, *o*-C(*C*H$_3$)$_3$), 33.8 (s, *o*-C(*C*H$_3$)$_3$), 34.9 (s, *p*-*C*(CH$_3$)$_3$)), 39.6 (d, ^3J(C,P) = 2.8 Hz, *o*-*C*(CH$_3$)$_3$), 40.6 (d, ^3J(C,P) = 2.8 Hz, *o*-*C*(CH$_3$)$_3$), 78.7 (d, ^2J(C,P) = 10.2 Hz, *C$_2$* *p*-cymene), 88.6 (s, *C$_3$* *p*-cymene), 89.0 (d, ^{2}J(C,P) = 8.3 Hz, *C$_2$* *p*-cymene), 90.4 (s, *C$_4$* *p*-cymene), 94.2 (s, *C$_3$* *p*-cymene), 111.2 (s, *C$_1$* *p*-cymene), 119.3 (d, ^3J(C,P) = 13.9 Hz, *m*-Mes*), 121.7 (d, ^3J(C,P) = 11.1 Hz, *m*-Mes*), 127.7 (s, *o*-PPh$_3$), 127.9 (s, *o*-PPh$_3$), 129.4 (s, *p*-PPh$_3$), 132.4 (d, ^3J(C,P) = 10.2 Hz, *m*-PPh$_3$), 134.8 (d, ^3J(C,P) = 11.1 Hz, *m*-PPh$_3$), 136.8 (d, ^1J(C,P) = 44.4 Hz, *ipso*-PPh$_3$), 148.0 (d, ^4J(C,P) = 3.7 Hz, *p*-Mes*), 153.7 (br s, *ipso*-Mes*), 153.9 (s, *o*-Mes*), 154.3 ppm (s, *o*-Mes*); IR (nujol): $\overline{\nu}$ = 1153, 925 cm^{-1} (asym and sym OPO); elemental analysis (%) calcd for $C_{46}H_{58}O_2P_2Ru$: C 68.55, H 7.25; found: C 68.92, H 7.45.

X-ray crystallographic analysis.

Data for the structure was collected at low temperatures using an oil-coated shock-cooled crystal on a Bruker-AXS CCD 1000 diffractometer with MoKα radiation (λ = 0.71073 Å). The structures were solved by direct methods (SHELXS-97, G. M. Sheldrick, *Acta Crystallogr.* **1990**, *A46*, 467-473) and all non hydrogen atoms were refined anisotropically using the least-squares method on F^2 (SHELXL-97, Program for Crystal Structure Refinement, G. M. Sheldrick, University of Göttingen **1997**). CCDC 213805 and 213806 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk)


C14′
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C28
C15
C9
Ru1
C1
C7
O2
P1
C8
C33
C34
C18
C10
C32
C29
P2
C31
C42
C41
O1
C30
C40
C43
C35
C46
C39
C44
C36
C45
C38
C37
O1
P1
O3
Ru1
O2
P2
O4′
O4

4a

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

Identification code	4a	
Empirical formula	C53.20 H95 O3.80 P2 Ru	
Formula weight	958.50	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 10.2558(13) Å	α= 90°.
	b = 34.669(4) Å	β= 94.842(3)°.
	c = 15.654(2) Å	γ = 90°.
Volume	5545.9(12) $Å^3$	
Z	4	
Density (calculated)	1.148 Mg/m^3	
Absorption coefficient	0.379 mm^{-1}	
F(000)	2074	
Crystal size	0.1 x 0.1 x 0.5 mm^3	
Theta range for data collection	5.11 to 22.72°.	
Index ranges	-11<=h<=11, -36<=k<=37, -14<=l<=17	
Reflections collected	23262	
Independent reflections	7362 [R(int) = 0.1222]	
Completeness to theta = 22.72°	98.7 %	
Absorption correction	Semi-empirical	
Max. and min. transmission	1.000000 and 0.833008	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7362 / 203 / 635	
Goodness-of-fit on F^2	0.989	
Final R indices [I>2sigma(I)]	R1 = 0.0632, wR2 = 0.1193	
R indices (all data)	R1 = 0.1234, wR2 = 0.1358	
Largest diff. peak and hole	0.692 and -0.563 $e.Å^{-3}$	

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

	x	y	z	U(eq)
Ru(1)	6856(1)	1450(1)	1086(1)	26(1)
P(1)	4616(2)	1481(1)	861(1)	28(1)
O(1)	3754(4)	1664(1)	162(3)	37(1)
O(2)	5264(4)	1732(1)	1616(3)	33(1)
C(1)	3872(6)	1066(2)	1409(4)	26(2)
C(2)	3795(6)	697(2)	1014(4)	32(2)
C(3)	3959(6)	378(2)	1557(5)	33(2)
C(5)	3844(6)	763(2)	2788(5)	36(2)
C(6)	3659(6)	1091(2)	2282(4)	28(2)
C(7)	3373(7)	640(2)	48(4)	35(2)
C(8)	4395(7)	775(2)	-557(4)	44(2)
C(9)	3070(7)	217(2)	-178(5)	50(2)
C(10)	2103(7)	870(2)	-160(5)	48(2)
C(4)	4099(7)	403(2)	2438(5)	37(2)
C(11)	4510(8)	58(2)	3020(5)	52(2)
C(12)	4560(20)	-322(4)	2589(13)	81(7)
C(13)	3423(18)	18(6)	3724(11)	65(5)
C(14)	5787(15)	163(4)	3580(12)	74(6)
C(12')	5914(17)	-57(7)	2802(19)	86(10)
C(13')	3670(30)	-315(6)	2606(18)	67(8)
C(14')	4260(40)	98(9)	3922(13)	106(12)
C(15)	3101(6)	1457(2)	2716(4)	33(2)
C(16)	1985(7)	1315(2)	3240(5)	53(2)
C(17)	4113(8)	1654(2)	3345(5)	57(2)
C(18)	2471(7)	1752(2)	2078(5)	44(2)
C(19)	7880(7)	1251(2)	2359(4)	34(2)
C(20)	8841(6)	1402(2)	1863(4)	29(2)
C(21)	8933(6)	1269(2)	1018(4)	30(2)
C(22)	8133(6)	967(2)	632(4)	31(2)
C(23)	7169(7)	821(2)	1142(5)	39(2)
C(24)	7056(7)	953(2)	1982(5)	35(2)

C(25)	7710(7)	1373(2)	3260(5)	44(2)
C(26)	8144(9)	1783(2)	3462(5)	62(2)
C(27)	8426(9)	1085(2)	3892(5)	65(3)
C(28)	8334(7)	804(2)	-234(4)	37(2)
P(2)	7034(2)	2007(1)	212(1)	25(1)
C(29)	8815(6)	2124(2)	104(4)	29(2)
C(30)	9196(6)	2553(2)	25(4)	30(2)
C(31)	10672(7)	2593(2)	42(4)	39(2)
C(32)	11260(7)	2357(2)	-647(5)	43(2)
C(33)	10846(7)	1933(2)	-596(5)	41(2)
C(34)	9356(6)	1899(2)	-634(4)	28(2)
C(35)	6150(6)	1991(2)	-864(4)	29(2)
C(36)	6275(7)	2340(2)	-1456(4)	35(2)
C(37)	5259(7)	2312(2)	-2233(4)	41(2)
C(38)	5395(8)	1931(2)	-2723(4)	48(2)
C(39)	5316(7)	1588(2)	-2126(4)	40(2)
C(40)	6333(7)	1618(2)	-1364(4)	34(2)
C(41)	6415(6)	2462(2)	662(4)	28(2)
C(42)	6944(7)	2512(2)	1611(4)	30(2)
C(43)	6590(7)	2907(2)	1956(5)	43(2)
C(44)	5122(8)	2964(2)	1855(5)	57(2)
C(45)	4584(7)	2931(2)	920(5)	44(2)
C(46)	4932(6)	2531(2)	548(4)	33(2)
C(47)	5460(14)	1125(4)	5451(9)	97(5)
C(48)	4093(17)	1185(3)	5605(8)	116(6)
O(3)	3280(9)	864(2)	5310(5)	84(2)
C(49)	1924(15)	859(5)	5511(10)	121(6)
C(50)	1290(16)	512(5)	5143(11)	137(6)
C(51)	9670(20)	-267(5)	8161(18)	179(3)
C(52)	10180(20)	20(6)	7625(19)	179(3)
O(4)	9444(15)	374(4)	7558(13)	179(3)
C(53)	9470(20)	788(5)	7453(18)	179(3)
C(54)	8600(20)	1011(5)	6948(16)	179(3)
C(51')	10770(40)	1089(9)	6620(30)	179(3)
C(52')	10030(50)	959(8)	7320(30)	179(3)
O(4')	10180(30)	530(7)	7320(20)	179(3)

C(53')	10000(50)	254(9)	7980(30)	179(3)
C(54')	10080(50)	-153(9)	7800(40)	179(3)

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

Ru(1)-O(2)	2.130(4)
Ru(1)-C(23)	2.204(6)
Ru(1)-C(24)	2.220(6)
Ru(1)-C(21)	2.231(6)
Ru(1)-C(22)	2.276(6)
Ru(1)-C(19)	2.279(7)
Ru(1)-C(20)	2.288(6)
Ru(1)-P(1)	2.2963(17)
Ru(1)-P(2)	2.3830(17)
P(1)-O(1)	1.491(5)
P(1)-O(2)	1.569(4)
P(1)-C(1)	1.868(6)
C(1)-C(6)	1.405(8)
C(1)-C(2)	1.419(8)
C(2)-C(3)	1.398(8)
C(2)-C(7)	1.551(9)
C(3)-C(4)	1.377(9)
C(5)-C(6)	1.389(8)
C(5)-C(4)	1.396(8)
C(6)-C(15)	1.569(8)
C(7)-C(9)	1.532(8)
C(7)-C(10)	1.540(9)
C(7)-C(8)	1.543(9)
C(4)-C(11)	1.540(9)
C(11)-C(14')	1.464(19)
C(11)-C(12)	1.484(15)
C(11)-C(14)	1.556(15)
C(11)-C(12')	1.559(17)
C(11)-C(13)	1.638(15)
C(11)-C(13')	1.658(18)
C(15)-C(17)	1.530(9)
C(15)-C(18)	1.533(9)
C(15)-C(16)	1.544(9)
C(19)-C(20)	1.405(8)

C(19)-C(24)	1.432(9)
C(19)-C(25)	1.497(9)
C(20)-C(21)	1.411(8)
C(21)-C(22)	1.433(9)
C(22)-C(23)	1.416(9)
C(22)-C(28)	1.498(8)
C(23)-C(24)	1.405(9)
C(25)-C(26)	1.513(9)
C(25)-C(27)	1.548(9)
P(2)-C(35)	1.845(6)
P(2)-C(41)	1.862(6)
P(2)-C(29)	1.894(6)
C(29)-C(34)	1.536(8)
C(29)-C(30)	1.545(8)
C(30)-C(31)	1.517(8)
C(31)-C(32)	1.519(8)
C(32)-C(33)	1.532(8)
C(33)-C(34)	1.529(8)
C(35)-C(40)	1.532(8)
C(35)-C(36)	1.535(8)
C(36)-C(37)	1.535(9)
C(37)-C(38)	1.541(9)
C(38)-C(39)	1.517(8)
C(39)-C(40)	1.521(9)
C(41)-C(46)	1.535(8)
C(41)-C(42)	1.548(8)
C(42)-C(43)	1.525(8)
C(43)-C(44)	1.513(10)
C(44)-C(45)	1.524(10)
C(45)-C(46)	1.558(8)
C(47)-C(48)	1.457(13)
C(48)-O(3)	1.442(11)
O(3)-C(49)	1.451(12)
C(49)-C(50)	1.461(13)
C(51)-C(52)	1.430(16)
C(52)-O(4)	1.443(15)

O(4)-C(53)	1.444(14)
C(53)-C(54)	1.380(16)
C(51')-C(52')	1.457(18)
C(52')-O(4')	1.494(17)
O(4')-C(53')	1.437(17)
C(53')-C(54')	1.445(18)

O(2)-Ru(1)-C(23)	123.6(2)
O(2)-Ru(1)-C(24)	98.3(2)
C(23)-Ru(1)-C(24)	37.0(2)
O(2)-Ru(1)-C(21)	156.0(2)
C(23)-Ru(1)-C(21)	65.7(2)
C(24)-Ru(1)-C(21)	77.0(2)
O(2)-Ru(1)-C(22)	159.97(19)
C(23)-Ru(1)-C(22)	36.8(2)
C(24)-Ru(1)-C(22)	66.5(2)
C(21)-Ru(1)-C(22)	37.1(2)
O(2)-Ru(1)-C(19)	96.4(2)
C(23)-Ru(1)-C(19)	67.1(3)
C(24)-Ru(1)-C(19)	37.1(2)
C(21)-Ru(1)-C(19)	65.5(2)
C(22)-Ru(1)-C(19)	79.4(2)
O(2)-Ru(1)-C(20)	120.2(2)
C(23)-Ru(1)-C(20)	77.7(2)
C(24)-Ru(1)-C(20)	65.0(2)
C(21)-Ru(1)-C(20)	36.3(2)
C(22)-Ru(1)-C(20)	66.6(2)
C(19)-Ru(1)-C(20)	35.8(2)
O(2)-Ru(1)-P(1)	41.32(12)
C(23)-Ru(1)-P(1)	101.10(19)
C(24)-Ru(1)-P(1)	99.83(18)
C(21)-Ru(1)-P(1)	162.20(18)
C(22)-Ru(1)-P(1)	125.50(18)
C(19)-Ru(1)-P(1)	121.96(17)
C(20)-Ru(1)-P(1)	156.72(16)
O(2)-Ru(1)-P(2)	87.09(11)

C(23)-Ru(1)-P(2)	143.8(2)
C(24)-Ru(1)-P(2)	169.84(19)
C(21)-Ru(1)-P(2)	94.59(16)
C(22)-Ru(1)-P(2)	110.04(16)
C(19)-Ru(1)-P(2)	134.02(18)
C(20)-Ru(1)-P(2)	104.86(16)
P(1)-Ru(1)-P(2)	89.91(6)
O(1)-P(1)-O(2)	120.1(2)
O(1)-P(1)-C(1)	115.2(3)
O(2)-P(1)-C(1)	104.2(3)
O(1)-P(1)-Ru(1)	130.98(19)
O(2)-P(1)-Ru(1)	63.66(16)
C(1)-P(1)-Ru(1)	109.6(2)
P(1)-O(2)-Ru(1)	75.02(16)
C(6)-C(1)-C(2)	118.1(5)
C(6)-C(1)-P(1)	120.2(4)
C(2)-C(1)-P(1)	120.2(5)
C(3)-C(2)-C(1)	116.8(6)
C(3)-C(2)-C(7)	120.0(6)
C(1)-C(2)-C(7)	122.8(6)
C(4)-C(3)-C(2)	123.7(6)
C(6)-C(5)-C(4)	121.9(6)
C(5)-C(6)-C(1)	118.7(6)
C(5)-C(6)-C(15)	116.8(6)
C(1)-C(6)-C(15)	124.2(6)
C(9)-C(7)-C(10)	107.2(6)
C(9)-C(7)-C(8)	106.5(5)
C(10)-C(7)-C(8)	108.6(6)
C(9)-C(7)-C(2)	112.5(6)
C(10)-C(7)-C(2)	107.5(5)
C(8)-C(7)-C(2)	114.3(6)
C(3)-C(4)-C(5)	116.3(6)
C(3)-C(4)-C(11)	122.8(6)
C(5)-C(4)-C(11)	120.9(7)
C(14')-C(11)-C(12)	122.6(16)
C(14')-C(11)-C(4)	115.8(13)

C(12)-C(11)-C(4)	116.1(10)
C(14')-C(11)-C(14)	69.0(14)
C(12)-C(11)-C(14)	113.7(11)
C(4)-C(11)-C(14)	109.1(7)
C(14')-C(11)-C(12')	118.4(17)
C(12)-C(11)-C(12')	66.7(10)
C(4)-C(11)-C(12')	106.3(9)
C(14)-C(11)-C(12')	55.5(11)
C(14')-C(11)-C(13)	34.3(15)
C(12)-C(11)-C(13)	106.4(11)
C(4)-C(11)-C(13)	107.2(9)
C(14)-C(11)-C(13)	103.2(10)
C(12')-C(11)-C(13)	144.9(12)
C(14')-C(11)-C(13')	108.9(15)
C(12)-C(11)-C(13')	33.5(10)
C(4)-C(11)-C(13')	105.5(10)
C(14)-C(11)-C(13')	142.0(11)
C(12')-C(11)-C(13')	100.1(12)
C(13)-C(11)-C(13')	80.5(12)
C(17)-C(15)-C(18)	110.3(6)
C(17)-C(15)-C(16)	107.0(6)
C(18)-C(15)-C(16)	105.5(5)
C(17)-C(15)-C(6)	112.8(5)
C(18)-C(15)-C(6)	114.0(5)
C(16)-C(15)-C(6)	106.7(5)
C(20)-C(19)-C(24)	117.2(6)
C(20)-C(19)-C(25)	124.0(6)
C(24)-C(19)-C(25)	118.7(6)
C(20)-C(19)-Ru(1)	72.4(4)
C(24)-C(19)-Ru(1)	69.2(4)
C(25)-C(19)-Ru(1)	131.0(4)
C(19)-C(20)-C(21)	120.2(6)
C(19)-C(20)-Ru(1)	71.7(4)
C(21)-C(20)-Ru(1)	69.6(4)
C(20)-C(21)-C(22)	123.5(6)
C(20)-C(21)-Ru(1)	74.0(3)

C(22)-C(21)-Ru(1)	73.2(4)
C(23)-C(22)-C(21)	115.2(6)
C(23)-C(22)-C(28)	122.1(6)
C(21)-C(22)-C(28)	122.6(6)
C(23)-C(22)-Ru(1)	68.8(3)
C(21)-C(22)-Ru(1)	69.8(3)
C(28)-C(22)-Ru(1)	133.3(4)
C(24)-C(23)-C(22)	121.9(6)
C(24)-C(23)-Ru(1)	72.1(4)
C(22)-C(23)-Ru(1)	74.4(3)
C(23)-C(24)-C(19)	121.8(6)
C(23)-C(24)-Ru(1)	70.8(4)
C(19)-C(24)-Ru(1)	73.7(3)
C(19)-C(25)-C(26)	114.0(6)
C(19)-C(25)-C(27)	109.4(6)
C(26)-C(25)-C(27)	111.0(6)
C(35)-P(2)-C(41)	102.3(3)
C(35)-P(2)-C(29)	109.1(3)
C(41)-P(2)-C(29)	102.3(3)
C(35)-P(2)-Ru(1)	116.43(19)
C(41)-P(2)-Ru(1)	115.1(2)
C(29)-P(2)-Ru(1)	110.3(2)
C(34)-C(29)-C(30)	108.7(5)
C(34)-C(29)-P(2)	111.7(4)
C(30)-C(29)-P(2)	117.8(4)
C(31)-C(30)-C(29)	110.1(5)
C(30)-C(31)-C(32)	113.3(6)
C(31)-C(32)-C(33)	110.5(5)
C(34)-C(33)-C(32)	110.7(5)
C(33)-C(34)-C(29)	110.7(5)
C(40)-C(35)-C(36)	109.7(5)
C(40)-C(35)-P(2)	114.7(4)
C(36)-C(35)-P(2)	117.9(4)
C(37)-C(36)-C(35)	110.0(5)
C(36)-C(37)-C(38)	111.3(6)
C(39)-C(38)-C(37)	110.7(5)

C(38)-C(39)-C(40)	111.2(6)
C(39)-C(40)-C(35)	110.6(5)
C(46)-C(41)-C(42)	110.9(5)
C(46)-C(41)-P(2)	117.0(4)
C(42)-C(41)-P(2)	110.8(4)
C(43)-C(42)-C(41)	111.5(6)
C(44)-C(43)-C(42)	110.2(6)
C(43)-C(44)-C(45)	111.6(6)
C(44)-C(45)-C(46)	110.5(6)
C(41)-C(46)-C(45)	110.6(5)
O(3)-C(48)-C(47)	112.1(11)
C(48)-O(3)-C(49)	118.7(12)
O(3)-C(49)-C(50)	109.2(12)
C(51)-C(52)-O(4)	114.7(17)
C(52)-O(4)-C(53)	147.0(16)
C(54)-C(53)-O(4)	127.2(19)
C(51')-C(52')-O(4')	104(2)
C(53')-O(4')-C(52')	130(3)
O(4')-C(53')-C(54')	119(3)

Symmetry transformations used to generate equivalent atoms:

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

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ru(1)	19(1)	24(1)	35(1)	3(1)	-4(1)	1(1)
P(1)	20(1)	22(1)	41(1)	0(1)	-4(1)	2(1)
O(1)	18(3)	31(2)	60(3)	7(2)	-8(2)	-3(2)
O(2)	24(3)	27(2)	48(3)	-5(2)	4(2)	0(2)
C(1)	8(4)	22(4)	46(5)	3(3)	-10(3)	4(3)
C(2)	20(4)	32(4)	44(5)	-2(4)	1(3)	-1(3)
C(3)	38(5)	20(4)	43(5)	-3(4)	3(4)	-7(3)
C(5)	29(4)	38(4)	40(5)	2(4)	2(3)	0(3)
C(6)	16(4)	25(4)	43(5)	-2(3)	-3(3)	-4(3)
C(7)	30(4)	28(4)	46(5)	-5(4)	-1(4)	-2(3)
C(8)	41(5)	47(4)	43(5)	-12(4)	-2(4)	0(4)
C(9)	49(5)	38(4)	59(5)	-6(4)	-12(4)	-5(4)
C(10)	36(5)	41(4)	61(5)	-4(4)	-20(4)	8(4)
C(4)	33(5)	25(4)	53(5)	-1(4)	5(4)	-5(3)
C(11)	62(5)	30(4)	64(5)	14(4)	4(4)	8(4)
C(12)	130(20)	37(8)	73(12)	-1(7)	17(13)	36(12)
C(13)	101(13)	45(9)	52(11)	8(9)	15(9)	-7(11)
C(14)	76(10)	57(10)	85(14)	25(9)	-15(9)	17(8)
C(12')	62(11)	61(16)	130(20)	51(17)	-12(12)	41(10)
C(13')	88(17)	32(10)	75(16)	27(10)	-21(17)	15(12)
C(14')	210(40)	59(19)	52(11)	14(11)	4(18)	30(30)
C(15)	21(4)	37(4)	42(4)	-9(4)	5(3)	2(4)
C(16)	46(5)	61(5)	52(5)	4(4)	7(4)	16(4)
C(17)	47(6)	58(5)	65(6)	-28(5)	2(4)	9(4)
C(18)	29(5)	41(4)	64(5)	3(4)	11(4)	13(4)
C(19)	32(4)	39(4)	31(4)	15(4)	-1(3)	7(4)
C(20)	22(4)	34(4)	32(4)	8(4)	0(3)	2(3)
C(21)	13(4)	32(4)	43(5)	18(4)	3(3)	4(3)
C(22)	22(4)	26(4)	46(5)	8(4)	5(4)	9(3)
C(23)	36(5)	23(4)	58(5)	0(4)	-2(4)	4(3)
C(24)	27(4)	26(4)	52(5)	17(4)	8(4)	2(3)

C(25)	21(4)	60(5)	49(5)	9(4)	-1(3)	6(4)
C(26)	70(7)	71(6)	46(5)	-6(5)	2(5)	17(5)
C(27)	71(7)	70(6)	54(5)	14(5)	-7(5)	-2(5)
C(28)	30(4)	33(4)	47(5)	-7(4)	3(4)	3(3)
P(2)	22(1)	23(1)	30(1)	1(1)	-3(1)	0(1)
C(29)	17(4)	36(4)	34(4)	6(3)	-7(3)	0(3)
C(30)	26(4)	31(4)	34(4)	3(3)	-2(3)	-6(3)
C(31)	41(5)	35(4)	39(5)	1(4)	3(4)	-12(4)
C(32)	33(5)	54(5)	44(5)	3(4)	7(4)	-12(4)
C(33)	34(5)	44(4)	46(5)	12(4)	6(4)	9(4)
C(34)	23(4)	32(4)	27(4)	9(3)	-2(3)	-3(3)
C(35)	24(4)	26(4)	33(4)	8(3)	-16(3)	-3(3)
C(36)	26(4)	35(4)	43(5)	0(4)	-5(3)	-1(3)
C(37)	47(5)	32(4)	42(5)	11(4)	-8(4)	-6(4)
C(38)	55(6)	48(5)	38(5)	6(4)	-14(4)	-6(4)
C(39)	41(5)	44(4)	34(4)	-4(4)	-9(4)	-7(4)
C(40)	37(5)	28(4)	35(4)	3(3)	-4(3)	-1(3)
C(41)	26(4)	20(3)	38(4)	2(3)	3(3)	1(3)
C(42)	33(4)	25(4)	30(4)	-4(3)	-4(3)	1(3)
C(43)	52(5)	31(4)	44(5)	-10(4)	-2(4)	2(4)
C(44)	61(6)	44(5)	63(6)	-15(4)	-1(5)	20(4)
C(45)	40(5)	26(4)	64(6)	-6(4)	-5(4)	8(4)
C(46)	27(4)	30(4)	39(5)	5(3)	-5(3)	3(3)
C(47)	102(12)	89(10)	96(11)	18(8)	-27(9)	12(9)
C(48)	220(20)	61(9)	60(9)	-16(7)	-58(11)	12(12)
O(3)	100(7)	83(6)	67(5)	6(5)	-4(5)	19(5)
C(49)	114(15)	158(15)	98(12)	39(12)	57(11)	59(12)
C(50)	109(14)	155(16)	144(16)	-6(13)	-2(11)	5(13)
C(51)	104(6)	113(5)	318(8)	13(6)	19(6)	-14(5)
C(52)	105(6)	113(5)	318(7)	13(6)	19(6)	-15(5)
O(4)	105(6)	113(5)	318(7)	13(6)	19(6)	-15(5)
C(53)	106(6)	113(5)	318(7)	13(6)	19(6)	-15(5)
C(54)	105(6)	113(5)	318(8)	13(6)	20(6)	-15(5)
C(51')	106(6)	113(5)	318(8)	13(6)	19(6)	-15(5)
C(52')	106(6)	113(5)	318(7)	13(6)	19(6)	-15(5)
O(4')	106(6)	113(5)	318(7)	13(6)	19(6)	-15(5)

C(53')	105(6)	113(5)	318(7)	13(6)	19(6)	-15(5)
C(54')	105(6)	113(5)	318(7)	13(6)	19(6)	-15(5)

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

	x	y	z	U(eq)
H(1A)	2954	1138	1207	31
H(3)	3975	129	1304	40
H(5)	3795	784	3390	43
H(8A)	4038	745	-1154	66
H(8B)	5190	619	-457	66
H(8C)	4607	1047	-444	66
H(9A)	2394	121	175	75
H(9B)	3866	62	-68	75
H(9C)	2756	198	-785	75
H(10A)	1735	808	-742	71
H(10B)	2294	1147	-121	71
H(10C)	1470	803	251	71
H(12A)	4574	-528	3019	121
H(12B)	5356	-337	2284	121
H(12C)	3791	-352	2180	121
H(13A)	3616	-212	4077	98
H(13B)	2549	-6	3424	98
H(13C)	3455	247	4090	98
H(14A)	5645	398	3908	111
H(14B)	6496	206	3209	111
H(14C)	6024	-49	3976	111
H(12D)	6528	151	2980	129
H(12E)	5917	-98	2183	129
H(12F)	6181	-295	3107	129
H(13D)	3944	-550	2920	100
H(13E)	3829	-345	2001	100
H(13F)	2732	-272	2652	100
H(14D)	3877	-141	4121	159
H(14E)	3651	312	3985	159
H(14F)	5085	151	4266	159

H(16A)	2339	1137	3688	79
H(16B)	1323	1182	2860	79
H(16C)	1584	1536	3507	79
H(17A)	4812	1763	3030	85
H(17B)	4485	1464	3761	85
H(17C)	3690	1861	3647	85
H(18A)	1971	1940	2385	66
H(18B)	1883	1618	1648	66
H(18C)	3155	1885	1793	66
H(20)	9431	1593	2098	35
H(21)	9558	1387	687	35
H(23)	6581	629	910	47
H(24)	6414	841	2309	42
H(25)	6755	1357	3342	52
H(26A)	9090	1804	3426	94
H(26B)	7932	1850	4042	94
H(26C)	7690	1959	3048	94
H(27A)	8107	823	3762	98
H(27B)	8256	1152	4480	98
H(27C)	9369	1096	3833	98
H(28A)	8905	578	-168	55
H(28B)	8740	1000	-577	55
H(28C)	7487	729	-522	55
H(29)	9306	2028	641	35
H(30A)	8782	2660	-517	36
H(30B)	8875	2701	506	36
H(31A)	11070	2511	610	46
H(31B)	10894	2868	-35	46
H(32A)	12227	2375	-571	52
H(32B)	10966	2462	-1219	52
H(33A)	11174	1788	-1078	49
H(33B)	11237	1819	-54	49
H(34A)	9108	1624	-595	33
H(34B)	8967	2001	-1189	33
H(35)	5205	1989	-750	34
H(36A)	6137	2581	-1137	42

H(36B)	7166	2348	-1655	42
H(37A)	5376	2532	-2623	49
H(37B)	4369	2330	-2035	49
H(38A)	4689	1913	-3193	58
H(38B)	6245	1927	-2980	58
H(39A)	5458	1347	-2445	48
H(39B)	4431	1577	-1919	48
H(40A)	7221	1613	-1567	41
H(40B)	6250	1394	-980	41
H(41)	6815	2676	343	33
H(42A)	6573	2308	1961	36
H(42B)	7907	2483	1662	36
H(43A)	6907	2926	2570	51
H(43B)	7022	3111	1641	51
H(44A)	4908	3222	2076	68
H(44B)	4699	2768	2199	68
H(45A)	4958	3139	581	53
H(45B)	3622	2964	877	53
H(46A)	4478	2325	846	39
H(46B)	4629	2520	-69	39
H(47A)	5813	908	5799	146
H(47B)	5963	1358	5609	146
H(47C)	5524	1068	4843	146
H(48A)	4026	1222	6227	139
H(48B)	3771	1423	5307	139
H(49A)	1466	1091	5273	145
H(49B)	1882	859	6141	145
H(50A)	1194	535	4517	206
H(50B)	425	484	5358	206
H(50C)	1826	286	5308	206
H(51A)	9801	-186	8762	268
H(51B)	10123	-512	8089	268
H(51C)	8732	-301	8001	268
H(52A)	10219	-90	7044	215
H(52B)	11090	80	7852	215
H(53A)	9471	895	8039	215

H(53B)	10347	846	7261	215
H(54A)	7748	883	6885	268
H(54B)	8928	1045	6382	268
H(54C)	8515	1264	7218	268
H(51D)	11615	956	6645	268
H(51E)	10912	1368	6662	268
H(51F)	10276	1030	6067	268
H(52C)	9098	1033	7216	215
H(52D)	10392	1071	7869	215
H(53C)	9122	302	8185	215
H(53D)	10649	311	8468	215
H(54D)	9203	-253	7625	268
H(54E)	10447	-290	8310	268
H(54F)	10646	-192	7330	268