Supplementary Material (ESI) for Chemical Communications

Supporting Information

Full citation for reference number 9.

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Experimental

Ru_3CO_{12}, $Ph_3PNSiMe_3$, Et_3N, ^tBuOK were purchased pure (Aldrich) and used without prior purification. The solvents were dried and distilled by standard techniques before use. The products were isolated by means of preparative TLC (20x20 silica plates, 1mm). The NMR spectra (chemical shifts in ppm) were recorded on Bruker instruments (Avance 300 for ^1H, AMX400 for ^{31}P and ^{13}C at 300, 100.61 and 161.98 Mhz, respectively). The FTIR spectra were recorded on a Nicolet NEXUS spectrometer equipped with a Continuum FTIR microspectrometer. Elemental (C, H, N) analyses were performed on a Carlo Erba EA 1108 instrument.

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Synthesis of compounds 1a/1b

A suspension of $Ph_3PNSiMe_3$ (200 mg, 0.57 mmol) and $Ru_3(CO)_{12}$ (300 mg, 0.47 mmol) in CH_2Cl_2 (1 mL) was placed under vacuum in a sealed tube and then heated to 130°C. The mixture turned to a brownish-red colour after 1 hour. The reaction was stopped after 3 h and compound **1a/1b** (yield 45%) was isolated by preparative TLC (CH_2Cl_2/Hexane 1:2 mixture, RF: 0.6).

1a: FTIR (KBr disc, νCO, cm^{-1}) 2064m, 2013vs, 1967vs, 1942sh, 1879w, 1814s. elemental analysis, calcd. (%) for $Ru_3PO_9NC_{27}H_{16}$: N 1.68, C 38.95, H 1.94; found: N 1.58, C 38.45, H 2.02.

1b: ^1H NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ = -15.2 (d, 1H, $^3J(^1H,^{31}P)$ = 1.1 Hz ; μ-H), 7.7-7.3 (m, 15H; Ph); $^1H\{^{31}P\}$ NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ = -15.2 (s, 1H; μ-H), 7.7-7.3 (m, 15H; Ph); ^1H NMR (400 MHz, d_8-toluene, TMS): δ = -14.75 (s, 1H, $^3J(^1H,^{31}P)$ = 1.1 Hz, unmodified in the range 293-213 K; μ-H), 7.8-7.3 (m, 15H; Ph); $^{31}P\{^1H\}$ NMR (161.98 MHz, $CDCl_3$, 25°C, ext. ref 85% H_3PO_4): δ = 52.0 (s); $^{31}P\{^1H\}$ NMR (161.98 MHz, d_8-toluene, 25°C, ext. ref 85% H_3PO_4): δ = 50.7 (s, unmodified in the range 293-213 K); $^{13}C\{^1H\}$ NMR (100.61 MHz, $CDCl_3$, 25°C, TMS): δ = 195.0 (s, CO, strong), 203 (s,CO, weak), 133 – 127 (m, Ph); FTIR (KBr disc, νCO, cm^{-1}) 2071m, 2039s, 2011vs, 1992vs, 1967s, 1948s, 1948s, 1935s; FTIR (CH_2Cl_2, νCO, cm^{-1}) 2073w, 2047vs, 2017vs, 1990s, 1943w(sh); FTIR (Hexane, νCO, cm^{-1}) 2075m, 2048vs, 2020vs, 2012m(sh), 1997s, 1989m(sh), 1982m, 1960w, 1953w, 1947w; elemental analysis, calcd. (%) for $Ru_3PO_9NC_{37}H_{16}$: N 1.68, C 38.95, H 1.94; found: N 1.74, C 38.99, H 1.87.

Reaction of $Ph_3PNSiMe_3$ with $Ru_3(CO)_{12}$ in CD_2Cl_2

The aforementioned reaction was repeated by using CD_2Cl_2 instead of CH_2Cl_2 in order to exclude the proton migrations from the solvent.

A suspension of $Ph_3PNSiMe_3$ (100 mg, 0.28 mmol) and $Ru_3(CO)_{12}$ (150 mg, 0.23 mmol) in CD_2Cl_2 (0.5 mL) was placed under vacuum in a sealed tube and then heated to 140°C. The colour turned to brownish-red after 1 hour. The reaction was stopped after 3 h and compound **1a/1b** (yield 36%) was isolated by preparative TLC (CH_2Cl_2/Hexane 1:2 mixture, RF: 0.6).

Reversible 1a-1b conversion

Complex **1b** was dissolved in a CH_2Cl_2/Hexane mixture. After stirring for five minutes, evaporation of the solvent mixture gave compound **1a** in a quantitative yield. In a reversible manner, dissolution of 1a in CH_2Cl_2 followed by evaporation of the solvent gave compound **1b** in a quantitative yield.

Synthesis of cation 2

Starting with 83 mg of compound **1a/b** (0.1 mmol) dissolved in 30 mL of CH_2Cl_2, 11 mg of ^tBuOK (0.1 mmol) was then added to the yellow solution. The colour turned to pale yellow in 5 min. Filtration followed by evaporation of the solvents afforded **2·K** as a yellow powder. Alternatively, 83 mg of compound **1a/b** (0.1 mmol) was dissolved in 30 mL of CH_2Cl_2. 20 mg of Et_3N (0.2 mmol) was then added to the yellow solution. The colour turned to pale yellow in 15 min. Removal of all volatiles afforded **2·HNEt$_3$** as a yellow powder.

2·K: ^1H NMR (300 MHz, $CDCl_3$, 25°C, TMS): 7.8-7.2 (m; Ph); $^{31}P\{^1H\}$ NMR (161.98 MHz, $CDCl_3$, 25°C, ext. ref 85% H_3PO_4): δ = 64.8 (s); FTIR (KBr disc, νCO, cm^{-1}) 2011m, 1967vs, 1920vs, 1768s. FTIR (CH_2Cl_2 solution, νCO, cm^{-1}) 2015m, 1970vs, 1924vs, 1762m; elemental analysis calcd (%) for $KRu_3PO_9NC_{27}H_{15}$: N 1.61, C 37.24, H 1.74; found: N 1.60, C 38.04, H 1.65.

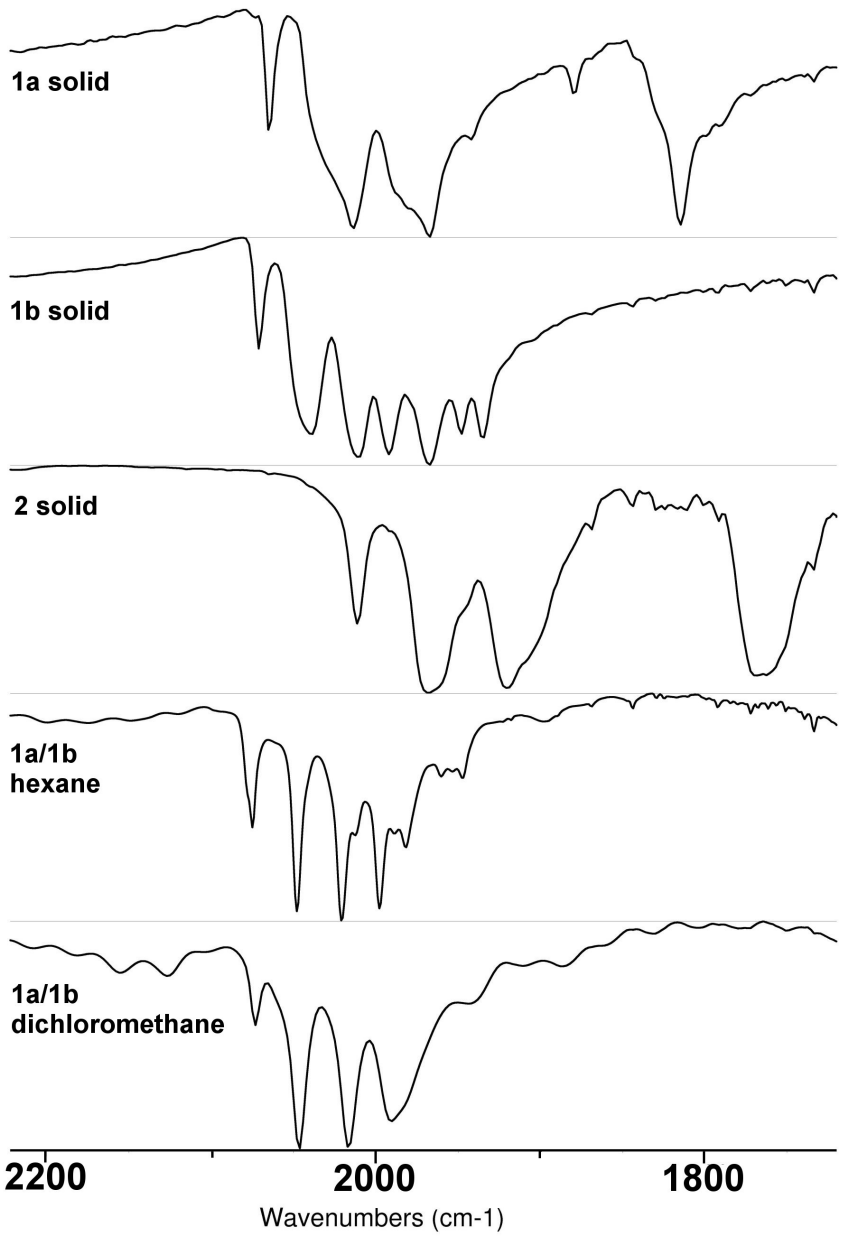

Figure1: Comparison between the FTIR spectra of compounds **1a/1b** (solid, CH_2Cl_2 solution, saturated hexane solution) and **2.**

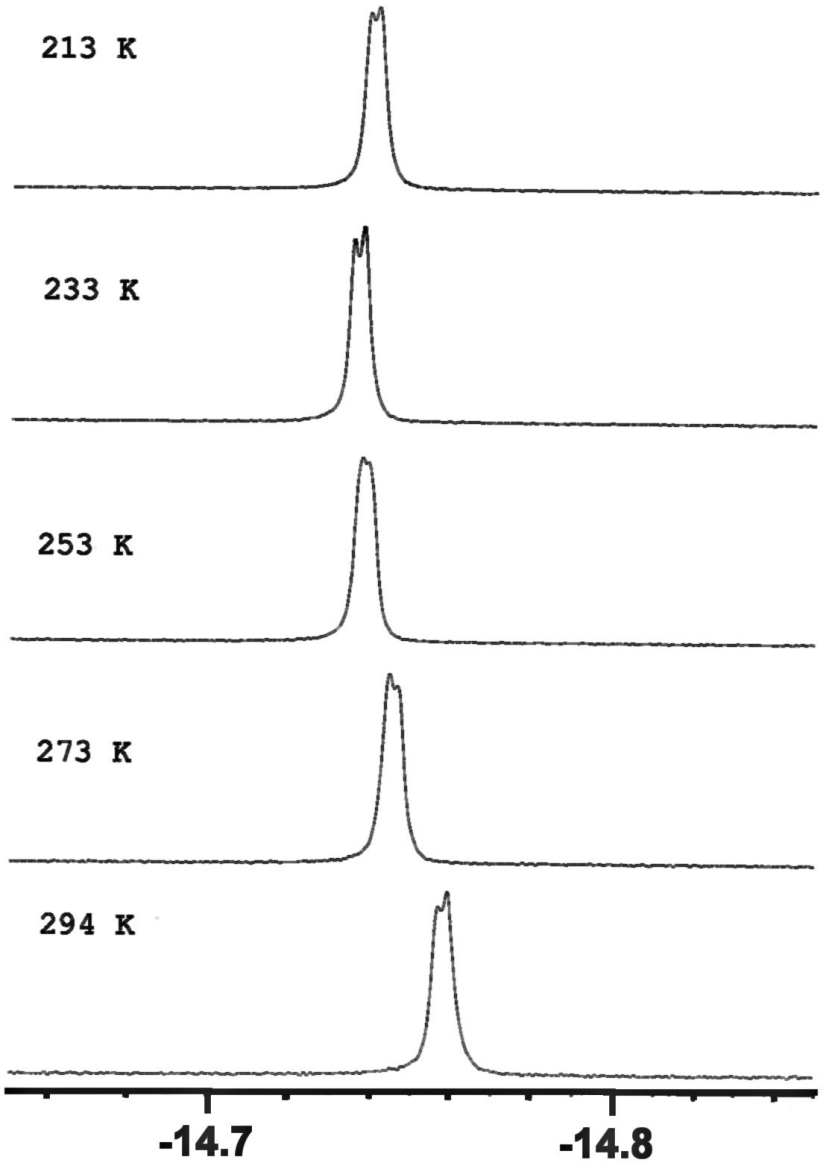

Figure 2: ^{1}H NMR spectra of compound 1a/1b in D_8-toluene (ppm). No other signals detected in the typical hydride range (sw: 50 ppm centred at -10 ppm).

X-ray data collection, structure solution and refinement for compounds 1a and 1b.

Suitable crystals for the X-ray analysis of complexes **1b** and **1b** were obtained by evaporation of a dichloromethane/Hexane and a dichloromethane solution, respectively. The intensity data was collected at room temperature on a Bruker area detector AXS Smart 1000[1] (graphite monochromated MoK_α radiation, λ = 0.71073 Å). Crystallographic and experimental details for the structures are summarized in Table 1. Bruker SADABS software [2] [maximum and minimum transmission coefficient values: 1.000 and 0.709 (**1a**), 1.000 and 0.886 (**1b**)] was used for the absorption correction. The structures were solved by direct methods and refined by full-matrix least-squares procedures (based on F_o^2, SHELX-97)[3] first with isotropic thermal parameters and then with anisotropic thermal parameters in the last cycles of refinement for all the non-hydrogen. For isomer **1a** the hydrogen atoms were found in the F_o^2 map and refined isotropically. For isomer **1b** the hydrogen atoms were introduced into the geometrically calculated positions and refined *riding* on the corresponding parent atoms, except that bound to ruthenium, found in the F_o^2 map and refined isotropically. CCDC-289256 (**1a**), CCDC-289257 (**1b**), contain the supplementary crystallographic data for this paper that can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[1] *SAINT Software Users Guide; SMART Software Users Guide;* Bruker Analytical X-ray Systems: Madison, WI, **1999**;

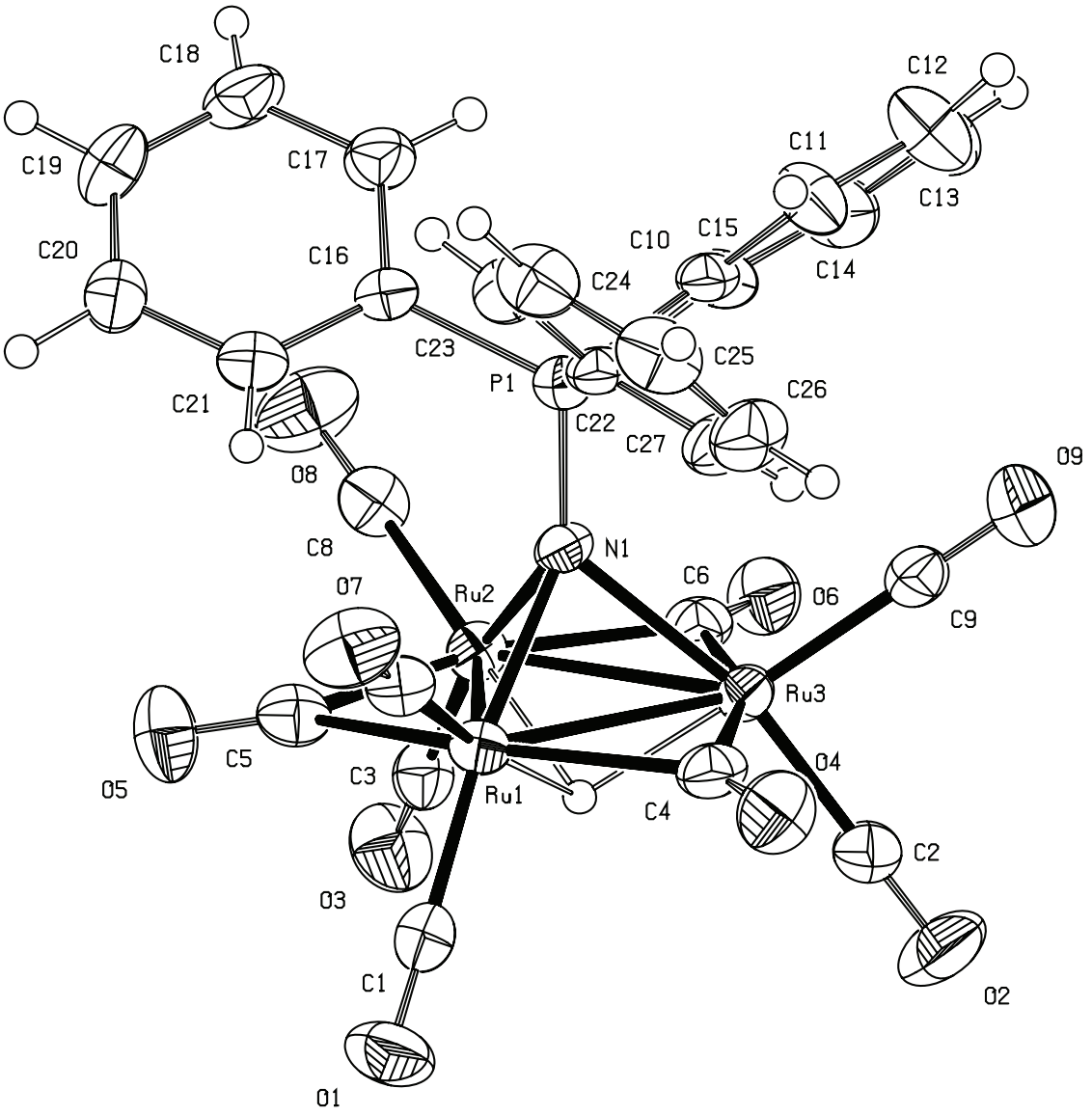
[2] Sheldrick, G. M. *SADABS*; Bruker Analytical X-ray Systems, Madison, WI, **1999**.

[3] Sheldrick, M.; *SHELXL-97*, Program for crystal structure refinement; University of Göttingen: Germany, **1997**.

Table 1: X-ray data collection, structure solution and refinement paramters for compounds 1a and 1b.

Complexes	**1a**	**1b**
Formula	$C_{27}H_{16}N_1O_9P_1Ru_3$	$C_{27}H_{16}N_1O_9P_1Ru_3$
FW	622.17	1276.9
Crystal System	Monoclinic	Monoclinic
Space Group	*P21/n*	*P21/c*
***a*, Å**	9.153(5)	9.359(5)
***b*, Å**	18.797(5)	17.664(5)
***c*, Å**	17.026(5)	18.101(5)
α, °	90	90
β, °	90.88(3)	100.10(3)
γ, °	90	90
***V*, Å^3**	2929 (2)	2946(5)
Z	4	4
D_{calcd}, g cm^{-3}	1.888	1.877
***F*(000)**	1616	1616
Crystal size (mm)	0.21 × 0.18 × 0.12	0.20 × 0.09 × 0.15
μ, cm^{-1}	16.34	16.24
Rflns. collected	15690	13668
Rflns. unique	5731	5036
Rflns. observed [$I > 2\sigma(I)$]	3562	2072
Parameters	420	285
***R* Indices**	*R1* = 0.0306,	*R1* = 0.0411,
[$I>2\sigma(I)$]	*wR2* = 0.0390	*wR2* = 0.1222
***R* Indices**	*R2* = 0.0703,	*R2* = 0.0442,
(all data)	*wR2* = 0.0432	*wR2* = 0.0535

Labelling Scheme For **1a**



Labelling Scheme For **1b**

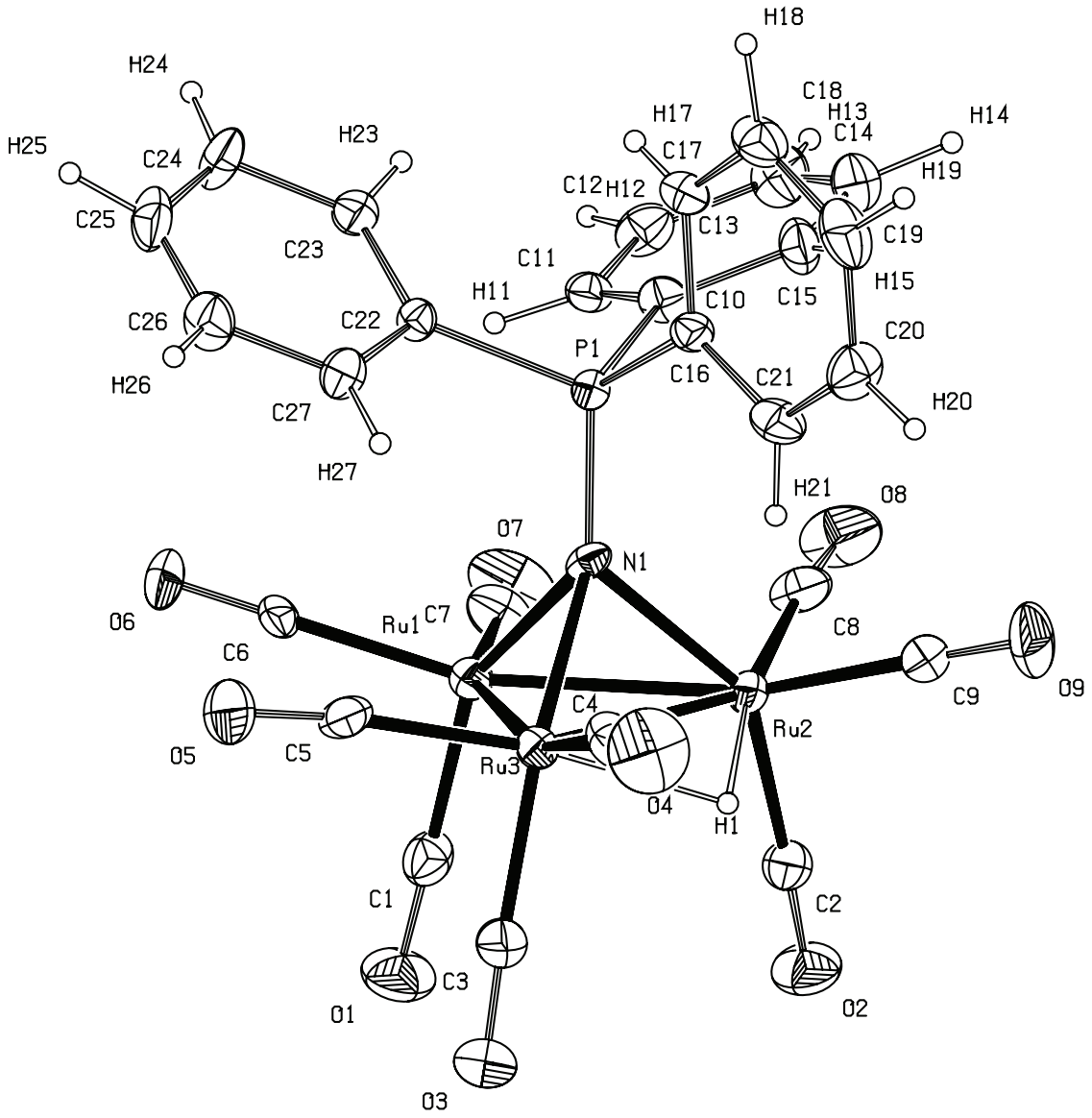


Table 2: Selected bond distances and angles for compounds **1a** and **1b.**

Distances (Å)	**1a** Crystallographic	**1a** Computed (C_{3V})	**1b** Crystallographic	**1b** Computed (C_S)
Ru1-Ru2	2.8421(9)	2.799	2.6667(9)	2.716
Ru1-Ru3	2.8291(9)	2.799	2.6588(9)	2.716
Ru2-Ru3	2.7920(14)	2.799	2.8179(8)	2.868
N1-Ru1	2.196(3)	2.160	2.097(5)	2.113
N1-Ru2	2.184(3)	2.160	2.113(5)	2.119
N1-Ru3	2.163(3)	2.160	2.119(5)	2.119
H1-Ru1	1.82(3)	1.931	-	
H1-Ru2	1.84(3)	1.931	1.85(6)	1.798
H1-Ru3	1.99(3)	1.931	1.92(6)	1.798
P1-N1	1.606(3)	1.586	1.631(5)	1.600
Ru1-C3	2.212(4)	2.156	-	
Ru1-C4	2.157(4)	2.156	-	
Ru2-C4	2.255(5)	2.156	-	
Ru2-C7	2.153(4)	2.156	-	
Ru3-C3	2.201(5)	2.156	-	
Ru3-C7	2.261(5)	2.156	-	

Angles (°)	**1a** Crystallographic	**1a** Computed (C_{3V})	**1b** Crystallographic	**1b** Computed (C_S)
Ru2-Ru1-Ru3	58.98(3)	60.00	63.89(2)	63.75
Ru1-Ru2-Ru3	60.276(13)	60.00	58.19(2)	58.12
Ru1-Ru3-Ru2	60.74(2)	60.00	58.19(2)	58.12
Ru1-N1-Ru2	80.92(10)	80.80	78.59(17)	79.84
Ru1-N1-Ru3	80.94(10)	80.80	78.19(18)	79.84
Ru2-N1-Ru3	79.93(10)	80.80	83.5(2)	85.17
Ru1-H1-Ru2	101.7(7)	92.93	-	
Ru1-H1-Ru3	95.9(6)	92.93	96.8(7)	105.78
Ru2-H1-Ru3	93.4(7)	92.93	-	
P1-N1-Ru1	130.55(18)	131.55	128.5(3)	129.95
P1-N1-Ru2	132.33(17)	131.55	128.5(3)	129.95
P1-N1-Ru3	132.17(16)	131.55	138.2(3)	133.16
Ru1-C4-Ru2	80.17(15)	80.95	-	
Ru1-C3-Ru3	79.75(15)	80.95	-	
Ru2-C7-Ru3	78.43(16)	80.95	-	
N1-Ru1-H1	72.5(9)	74.71	-	
N1-Ru2-H1	72.4(8)	74.71	86.0(19)	83.33
N1-Ru3-H1	70.3(8)	74.71	84.1(19)	83.33

Table 3: Cartesian coordinates for the species $\mathbf{1a_m}$, $\mathbf{1b_m}$, $\mathbf{1c_m}$, $\mathbf{2a_m}$ and $\mathbf{2b_m}$

Model $\mathbf{1a_m}$

O	-4.08922400	1.63012900	0.00000000	P	0.01372700	2.88674300	0.00000000
O	-1.80807800	-0.18878300	3.12974100	N	-0.00001800	1.30041100	0.00000000
O	-3.35588700	-2.61988500	0.00000000	O	2.03729900	1.61943000	3.55054800
C	-3.15939300	0.94804800	0.00000000	Ru	0.80791400	-0.13224500	-1.39962000
C	-2.70586200	-1.67075900	0.00000000	C	2.44749600	-0.14747900	0.00000000
C	-1.22587300	-0.15324300	2.11926700	C	1.35317000	-1.67608800	-2.33708700
Ru	-1.61772600	-0.12951000	0.00000000	C	1.57511300	0.94066500	-2.74086000
O	1.67994300	-2.62661700	2.89669000	O	1.67994300	-2.62661700	-2.89669000
C	1.35317000	-1.67608800	2.33708700	O	3.61401700	-0.17479500	0.00000000
O	-1.80807800	-0.18878300	-3.12974100	O	2.03729900	1.61943000	-3.55054800
H	-0.00079000	-1.18681500	0.00000000	H	-0.61952500	3.49147400	-1.10678600
C	-1.22587300	-0.15324300	-2.11926700	H	-0.61952500	3.49147400	1.10678600
Ru	0.80791400	-0.13224500	1.39962000	H	1.29736500	3.47291600	0.00000000
C	1.57511300	0.94066500	2.74086000				

Model $\mathbf{1b_m}$

O	3.42005100	-0.86571400	2.23237800	C	-0.69973500	1.91256700	2.12791100
O	3.42005100	-0.86571400	-2.23237800	O	-0.63957400	2.99179700	2.52055700
C	2.66164700	-0.56732000	1.41578000	Ru	-0.81065200	0.14389900	-1.43408100
C	2.66164700	-0.56732000	-1.41578000	O	-0.63957400	2.99179700	-2.52055700
O	2.34735500	2.89247900	0.00000000	C	-0.69973500	1.91256700	-2.12791100
C	2.03021900	1.78427200	0.00000000	H	-1.51297700	0.97098200	0.00000000
Ru	1.48867000	-0.03222100	0.00000000	C	-2.64530000	-0.25644100	1.93400100
O	0.49687700	-1.01335000	3.94372100	C	-2.64530000	-0.25644100	-1.93400100
C	0.02670500	-0.57649400	2.98753000	O	-3.72462900	-0.45447300	2.27965800
O	0.49687700	-1.01335000	-3.94372100	O	-3.72462900	-0.45447300	-2.27965800
P	-0.38585400	-2.88405500	0.00000000	H	-1.72305100	-3.33670700	0.00000000
C	0.02670500	-0.57649400	-2.98753000	H	0.18714500	-3.54210500	1.10788100
N	-0.20543900	-1.29428000	0.00000000	H	0.18714500	-3.54210500	-1.10788100
Ru	-0.81065200	0.14389900	1.43408100				

Model $\mathbf{1c_m}$

O	2.33228100	3.34052600	0.85600100	O	2.46554300	-1.42348200	-2.90505100
O	-2.33228100	3.34052600	0.85600100	Ru	-1.38528200	-0.79979300	-0.12512000
C	1.48441200	2.65714400	0.47819600	O	-2.46554300	-1.42348200	-2.90505100
C	-1.48441200	2.65714400	0.47819600	C	-2.07929700	-1.20048300	-1.84466700
O	0.00000000	2.84696400	-2.90505100	C	1.55894800	-2.61411000	0.47819600
C	0.00000000	2.40096500	-1.84466700	C	-1.55894800	-2.61411000	0.47819600
Ru	0.00000000	1.59958600	-0.12512000	O	1.72684000	-3.69007800	0.85600100
O	4.05912100	0.34955200	0.85600100	O	-1.72684000	-3.69007800	0.85600100
C	3.04336000	-0.04303300	0.47819600	H	0.00000000	-1.28041400	3.45745500
O	-4.05912100	0.34955200	0.85600100	H	1.10887100	0.64020700	3.45745500
P	0.00000000	0.00000000	2.86815500	H	-1.10887100	0.64020700	3.45745500
C	-3.04336000	-0.04303300	0.47819600	N	0.00000000	0.00000000	1.27169200
Ru	1.38528200	-0.79979300	-0.12512000	H	0.00000000	0.00000000	-1.15857900
C	2.07929700	-1.20048300	-1.84466700				

Model **2a$_m$**

O	0.00000000	4.15659400	1.58890000	P	0.00000000	0.00000000	2.91781500
O	-3.09112900	1.7846640	0-0.39810600	N	0.00000000	0.00000000	1.34445500
O	0.00000000	3.1568420	0-2.68632000	O	-3.59971600	-2.07829700	1.58890000
C	0.00000000	3.18905800	0.94222200	Ru	1.39786900	-0.80706000	-0.07895000
C	0.00000000	2.56854100	-1.68755700	C	0.00000000	-2.40552700	-0.22552400
C	-2.08324800	1.20276400	-0.22552400	C	2.22442200	-1.28427000	-1.68755700
Ru	0.00000000	1.61412000	-0.07895000	C	2.76180500	-1.59452900	0.94222200
O	-2.73390500	-1.57842100	-2.68632000	O	2.73390500	-1.57842100	-2.68632000
C	-2.22442200	-1.28427000	-1.68755700	O	0.00000000	-3.56932900	-0.39810600
O	3.09112900	1.78466400	-0.39810600	O	3.59971600	-2.07829700	1.58890000
C	2.08324800	1.20276400	-0.22552400	H	1.10250400	0.63653100	3.53703600
Ru	-1.39786900	-0.80706000	-0.07895000	H	-1.10250400	0.63653100	3.53703600
C	-2.76180500	-1.59452900	0.94222200	H	0.00000000	-1.27306200	3.53703600

Model **2b$_m$**

O	3.45716900	-0.63444800	2.32625900	Ru	-0.78929700	0.02591300	1.36448900
O	3.45716900	-0.63444800	-2.32625900	C	-0.98333700	1.87723000	1.67313500
C	2.70785400	-0.39856100	1.47030100	O	-1.11647100	3.00906200	1.88790900
C	2.70785400	-0.39856100	-1.47030100	Ru	-0.78929700	0.02591300	-1.36448900
O	2.18094100	3.02680000	0.00000000	O	-1.11647100	3.00906200	-1.88790900
C	1.93291800	1.89396500	0.00000000	C	-0.98333700	1.87723000	-1.67313500
Ru	1.57527600	0.04029000	0.00000000	C	-2.62613200	-0.42476900	1.61019600
O	0.28010900	-0.62387400	4.16487700	C	-2.62613200	-0.42476900	-1.61019600
C	-0.08386700	-0.40095600	3.08435600	O	-3.74148500	-0.66266900	1.83146500
O	0.28010900	-0.62387400	-4.16487700	O	-3.74148500	-0.66266900	-1.83146500
P	0.04171300	-2.96479600	0.00000000	H	-1.22062000	-3.60535000	0.00000000
C	-0.08386700	-0.40095600	-3.08435600	H	0.69184200	-3.56513200	1.10460800
N	0.00983200	-1.38117700	0.00000000	H	0.69184200	-3.56513200	-1.10460800