Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

New molecular architectures containing low-valent cluster centres with di- and tri-metalated 2-vinylpyrazine ligands: Synthesis and solid-state structures of $Ru_5(CO)_{15}(\mu_5\text{-}C_4H_2N_2CH{=}CH)(\mu\text{-}H)_2$ and $Ru_8(CO)_{24}(\mu_7\text{-}C_4H_2N_2CH{=}C)(\mu\text{-}H)_3$

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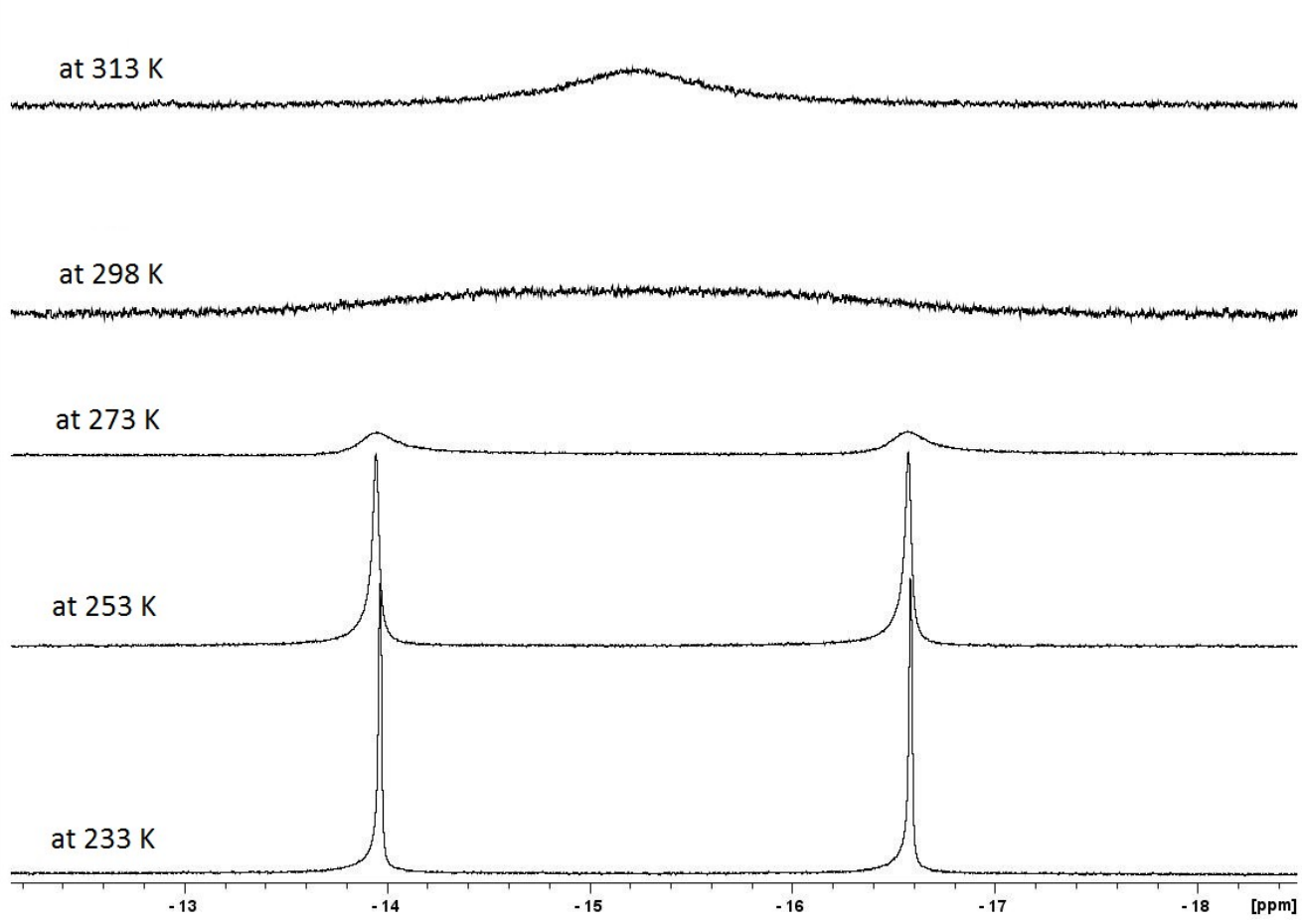

Figure S1. Hydride region of the VT ^{1}H NMR spectra of **2** recorded over the temperature range 233-313 K.

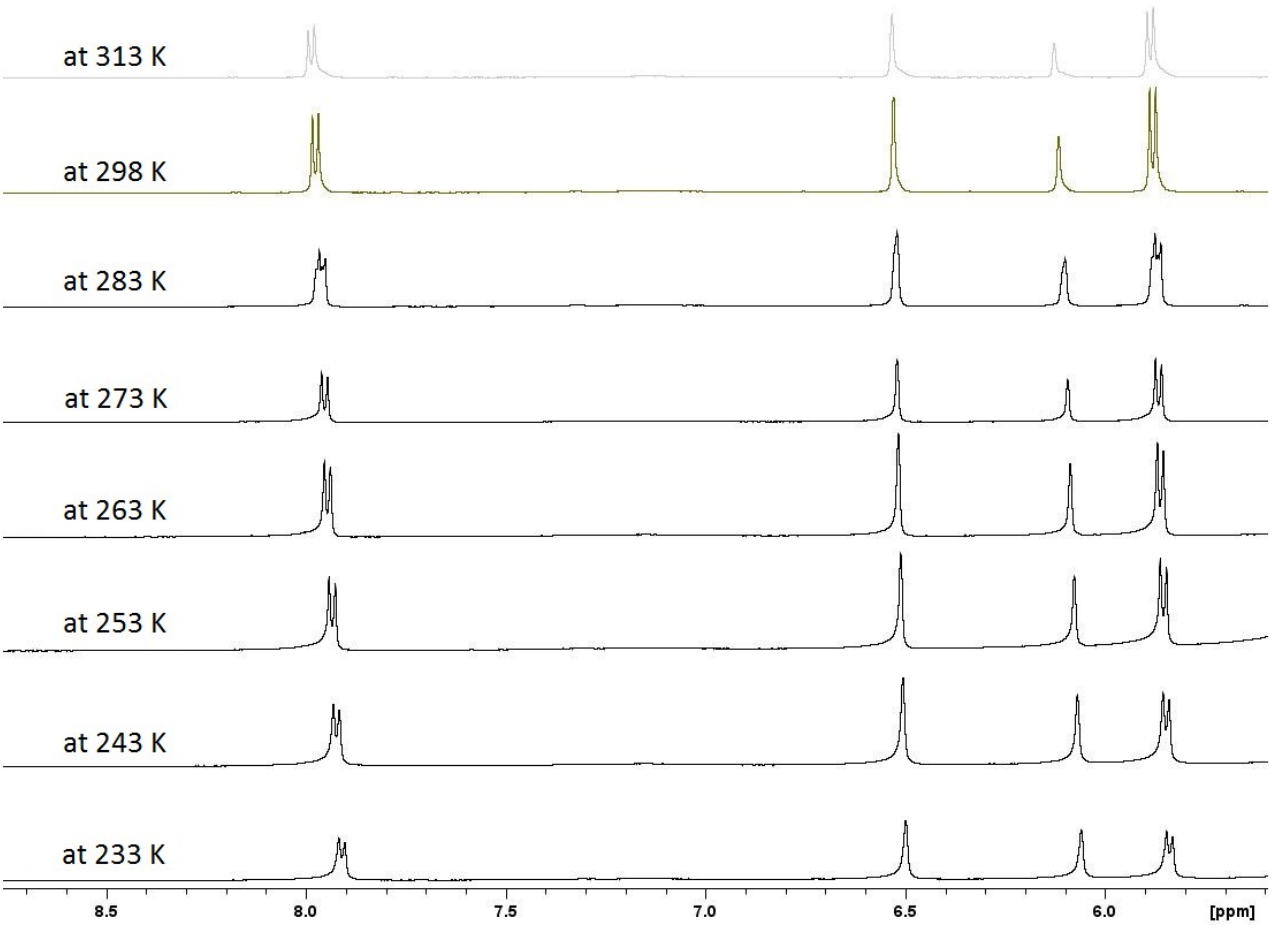

Figure S2. Aromatic region of the VT ^{1}H NMR spectra of **2** recorded over the temperature range 233-313 K.

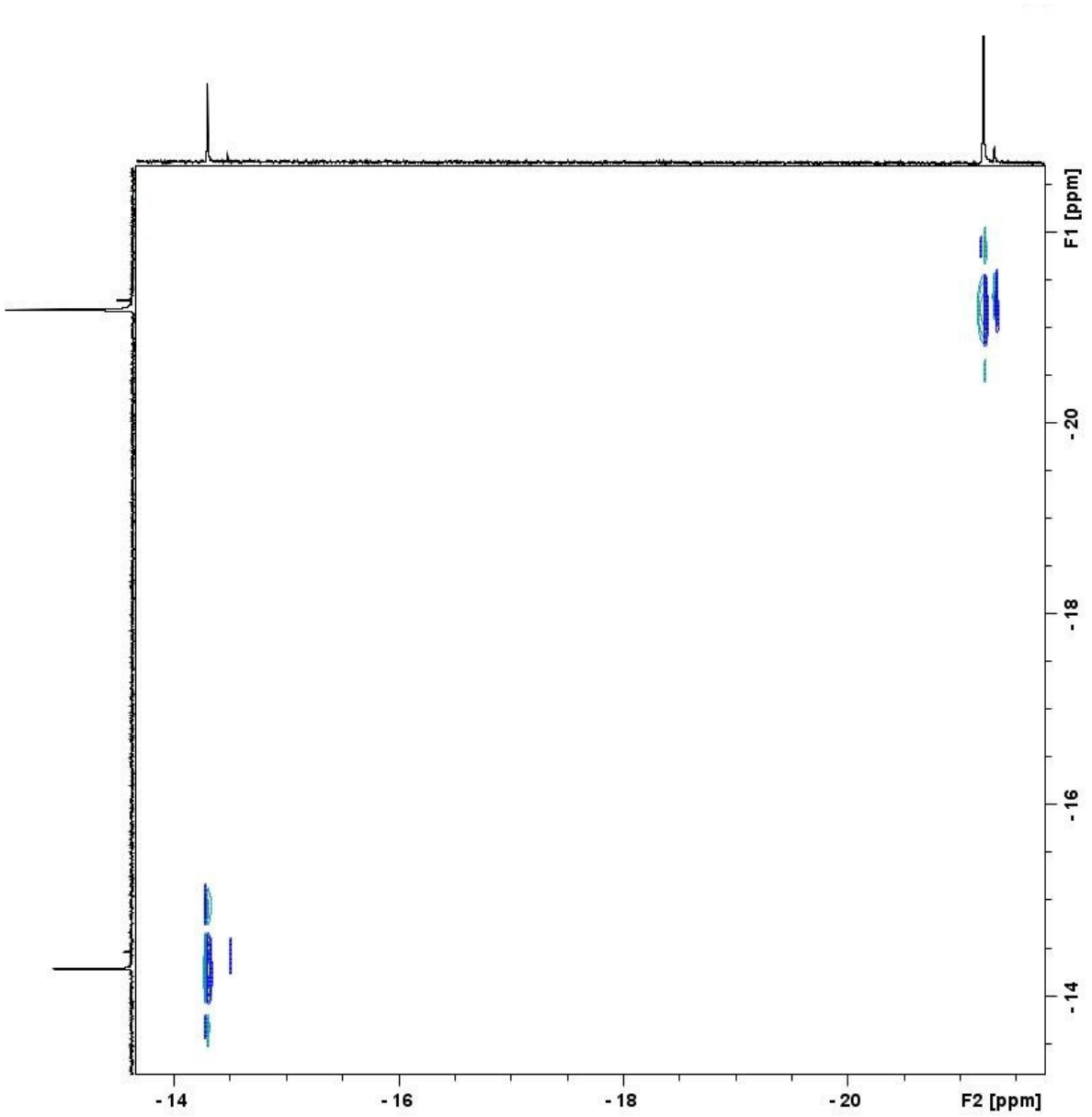

Figure S3. Room temperature EXSY ^{1}H NMR spectrum of **3**.

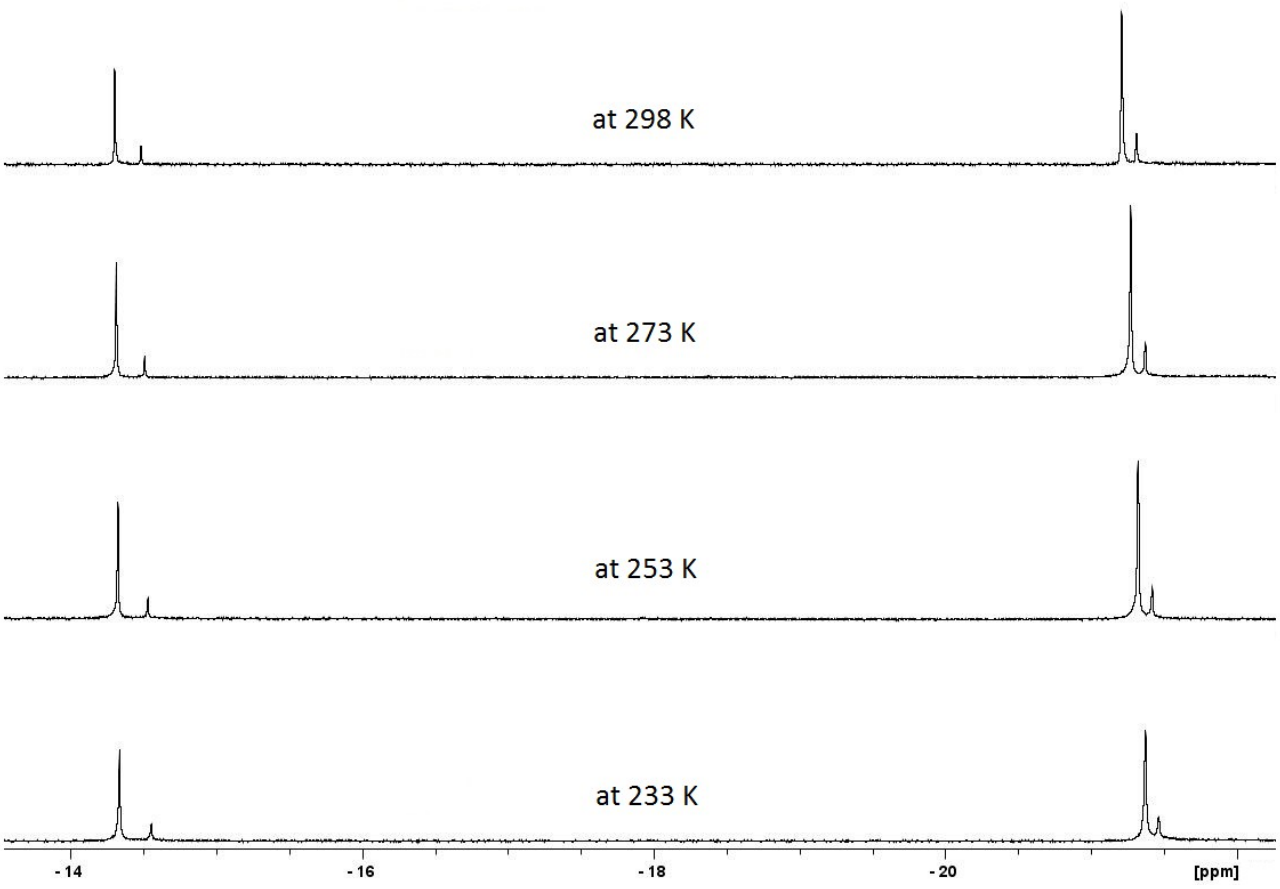

Figure S4. Hydride region of the VT ^{1}H NMR spectra of **3** recorded over the temperature range 233-298 K.

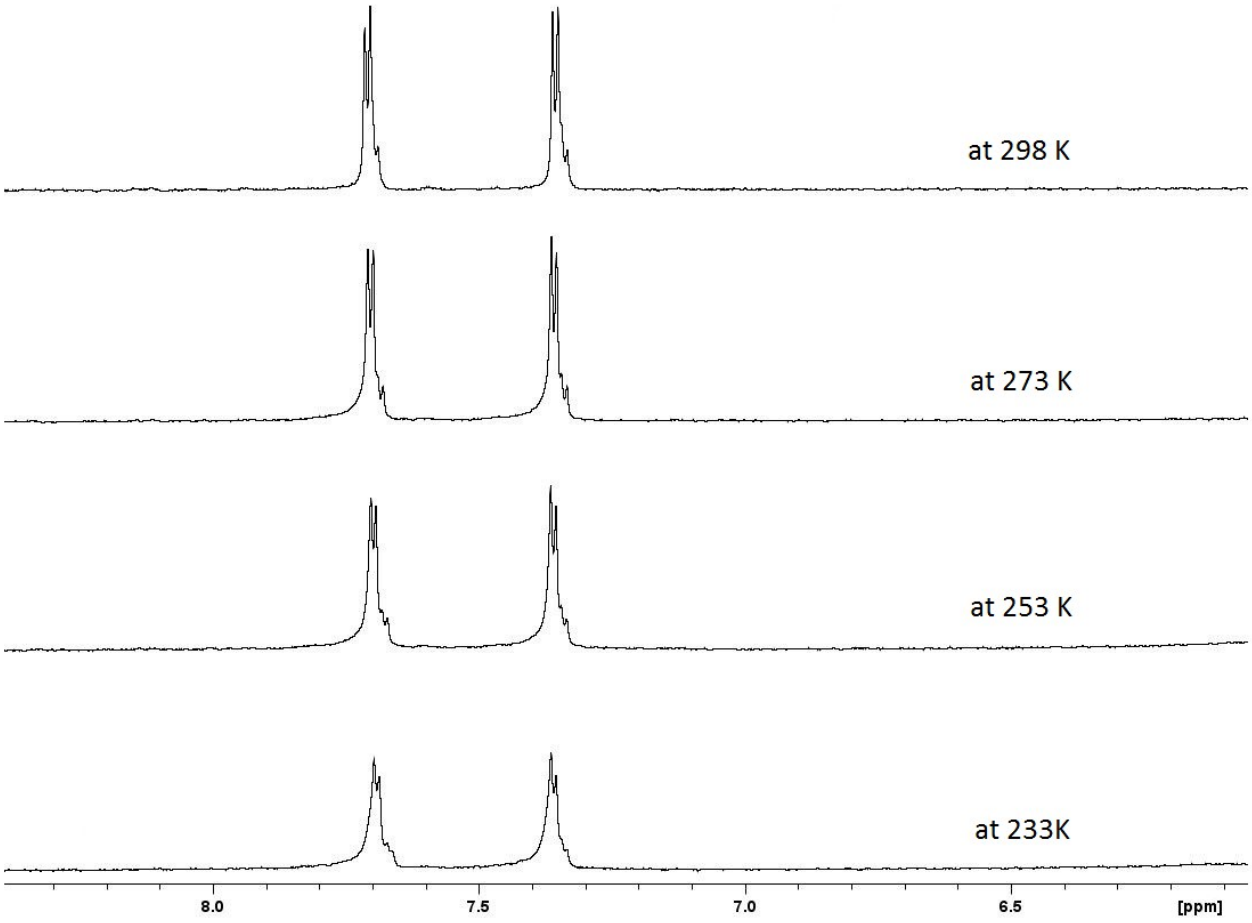

Figure S5. Aromatic region of the VT ^{1}H NMR spectra of **3** recorded over the temperature range 233-298 K.

Table S1. Crystal data and structure refinement details for **1-3**

Compound	**1**	**2**	**3**
CCDC	1881604	1877756	1877757
Empirical formula	$C_{37}H_{28}N_2O_6P_2Ru_8{\cdot}CH_2Cl_2$	$C_{21}H_6N_2O_{15}Ru_5$	$C_{30}H_6N_2O_{24}Ru_8$
Formula weight	1046.69	1031.63	1586.39
Temperature (K)	150.0(2)	150.0(1)	150.0(1)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	monoclinic	triclinic	monoclinic
Space group	*P2₁/c*	*P-1*	*P2₁/c*
Unit cell dimensions			
a (Å)	10.8780(7)	9.2594(5)	10.3141(12)
b (Å)	18.0767(11)	14.0086(8)	31.916(4)
c (Å)	19.8398(12)	23.9807(14)	13.0093(14)
α (°)	90	75.588(2)	90
β (°)	96.527(2)	79.665(2)	100.089(3)
γ (°)	90	77.224(2)	90
Volume (Å^3)	3876.0(4)	2912.5(3)	4216.2(8)
Z	4	4	4
Density (calculated) (Mg/m^3)	1.794	2.353	2.500
Absorption coefficient (mm^{-1})	1.423	2.606	2.873
F(000)	2064	1944	2976
Crystal size (mm^3)	0.25 × 0.10 × 0.03	040 × 0.08 × 0.08	0.19 × 0.11 × 0.06
Θ range for data collection (°)	2.196 to 28.333	2.275 to 28.361	2.489 to 27.102
Index ranges	$-14 \le h \le 14$, $-24 \le k \le 24$, $-26 \le l \le 26$	$-12 \le h \le 12$, $-18 \le k \le 18$, $-31 \le l \le 31$	$-13 \le h \le 12$, $-40 \le k \le 40$, $-16 \le l \le 16$
Reflections collected	62857	151823	61898
Independent reflections [R_{int}]	9637 [R_{int} = 0.1196]	14508 [R_{int} = 0.0259]	9295 [R_{int} = 0.0397]
Data / restraints / parameters	9295 / 1 / 490	14508 / 0 / 792	9295 / 4 / 590
Goodness of fit on F^2	1.027	1.112	1.178
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0570, wR_2 = 0.0894	R_1 = 0.0140, wR_2 = 0.0298	R_1 = 0.0410, wR_2 = 0.0756
R indices (all data)	R_1 = 0.1155, wR_2 = 0.1050	R_1 = 0.0163, wR_2 = 0.0304	R_1 = 0.0528, wR_2 = 0.0786
Largest diff. peak and hole (e. Å^{-3})	1.117 and – 1.141	0.63 and –0.37	1.813 and –1.010

DFT Coordinates and Energies

Species A

HF energy= -2515.53408551
No Imaginary frequency
Zero-point correction= 0.234336 (Hartree/Particle)
Thermal correction to Energy= 0.283231
Thermal correction to Enthalpy= 0.284175
Thermal correction to Gibbs Free Energy= 0.145614
Sum of electronic and zero-point Energies= -2515.299749
Sum of electronic and thermal Energies= -2515.250855
Sum of electronic and thermal Enthalpies= -2515.249911
Sum of electronic and thermal Free Energies= -2515.388471

Coordinates: A

Ru	2.79250000	1.59630000	-0.40080000
Ru	-3.49960000	-1.34450000	-0.56250000
Ru	2.73530000	-1.35900000	-1.02340000
Ru	2.00710000	-0.29830000	1.52460000
Ru	-3.28400000	1.33960000	0.19860000
O	3.21850000	3.37810000	-2.90860000
O	-6.49570000	-1.49430000	-0.06590000
O	1.93720000	3.87120000	1.45770000
N	0.81960000	0.92430000	-0.79470000
N	-1.46960000	-0.66970000	-0.81230000
O	0.82470000	-2.80380000	2.86250000
O	-2.65130000	-3.04180000	1.91520000
O	5.65500000	1.62820000	0.66290000
O	0.07580000	1.72580000	2.75570000
O	-3.48090000	-3.45820000	-2.79050000
O	1.76830000	-4.19360000	-0.39110000
O	-2.49800000	0.14520000	2.93250000
O	1.61730000	-1.28060000	-3.87670000
O	-2.39680000	4.26240000	0.58750000
O	5.69310000	-2.16800000	-1.59770000
O	-6.24980000	1.79340000	0.85390000
O	4.32490000	0.27780000	3.50590000
C	-2.99790000	-2.44370000	1.00210000
C	3.05510000	2.69550000	-2.00440000
C	2.24640000	2.99710000	0.78330000
C	-3.82120000	0.33490000	-1.73470000
H	-4.72650000	0.60250000	-2.28750000
C	0.90820000	-0.42910000	-0.32220000
C	4.58120000	1.65380000	0.26270000
C	4.60670000	-1.89320000	-1.38030000

C	-3.47730000	-2.69490000	-1.93440000
C	-5.36220000	-1.47450000	-0.24200000
C	2.06280000	-1.34080000	-2.82470000
C	-0.33930000	-1.16700000	-0.42710000
H	-0.34580000	-2.22100000	-0.12700000
C	0.79360000	0.94700000	2.31210000
C	-1.55240000	0.73260000	-1.10190000
C	2.12870000	-3.13690000	-0.64380000
C	3.45790000	0.05110000	2.79240000
C	-0.30270000	1.46180000	-1.12580000
H	-0.30820000	2.51850000	-1.41770000
C	-2.75190000	3.17920000	0.44090000
C	-5.13360000	1.64690000	0.63170000
C	-2.79330000	0.59570000	1.91690000
C	-2.68400000	1.13900000	-1.90920000
H	-2.62870000	2.02250000	-2.54960000
C	1.27320000	-1.86790000	2.37420000
H	3.32780000	-1.24790000	0.68160000
H	3.36770000	0.26230000	-1.47780000

Species TSAB

HF energy= -2515.51325229
One Imaginary frequency: 158*i*
Zero-point correction= 0.233499 (Hartree/Particle)
Thermal correction to Energy= 0.281764
Thermal correction to Enthalpy= 0.282708
Thermal correction to Gibbs Free Energy= 0.147314
Sum of electronic and zero-point Energies= -2515.279753
Sum of electronic and thermal Energies= -2515.231489
Sum of electronic and thermal Enthalpies= -2515.230544
Sum of electronic and thermal Free Energies= -2515.365938

Coordinates: TSAB

Ru	2.77750000	1.66420000	-0.61970000
Ru	-3.53020000	-1.31790000	-0.61500000
Ru	2.78180000	-1.33220000	-0.90950000
Ru	1.91420000	-0.35540000	1.52090000
Ru	-3.23360000	1.34160000	0.22900000
O	2.52860000	3.13190000	-3.31540000
O	-6.52180000	-1.45230000	-0.09800000
O	1.85080000	4.01210000	1.17810000
N	0.81820000	0.88890000	-0.84240000
N	-1.48910000	-0.67830000	-0.89140000
O	0.33560000	-2.68520000	2.68140000
O	-2.78570000	-3.14860000	1.80600000
O	5.77720000	2.22090000	-0.31550000
O	0.27010000	1.81980000	2.95080000

O	-3.59300000	-3.36070000	-2.90440000
O	2.08740000	-4.05220000	0.25560000
O	-2.34140000	-0.00870000	2.85440000
O	2.06420000	-2.08360000	-3.80190000
O	-2.25160000	4.22110000	0.68350000
O	5.84340000	-1.85870000	-0.88970000
O	-6.15530000	1.86910000	1.02570000
O	4.24960000	-0.73200000	3.53530000
C	-3.06310000	-2.49340000	0.90960000
C	2.62930000	2.60020000	-2.31040000
C	2.19240000	3.14150000	0.52670000
C	-3.84570000	0.40430000	-1.72200000
H	-4.75840000	0.70530000	-2.24460000
C	0.89000000	-0.47200000	-0.39160000
C	4.65580000	2.04160000	-0.42330000
C	4.70710000	-1.70610000	-0.89620000
C	-3.55830000	-2.62390000	-2.02650000
C	-5.38900000	-1.43040000	-0.27930000
C	2.36940000	-1.76100000	-2.74300000
C	-0.36160000	-1.19300000	-0.51900000
H	-0.36980000	-2.25860000	-0.26380000
C	0.87250000	0.99360000	2.42800000
C	-1.55720000	0.73510000	-1.13230000
C	2.35430000	-3.00600000	-0.14310000
C	3.38190000	-0.58420000	2.80230000
C	-0.29920000	1.44600000	-1.16230000
H	-0.29910000	2.50460000	-1.44800000
C	-2.64800000	3.15410000	0.51540000
C	-5.05720000	1.68810000	0.74550000
C	-2.68640000	0.49800000	1.88060000
C	-2.69660000	1.18930000	-1.90200000
H	-2.63910000	2.09050000	-2.51720000
C	0.93410000	-1.81050000	2.24110000
H	3.23540000	0.59500000	0.72970000
H	3.24470000	0.31250000	-1.66640000

Species B

HF energy= -2515.51463586
No Imaginary frequency
Zero-point correction= 0.234363 (Hartree/Particle)
Thermal correction to Energy= 0.283223
Thermal correction to Enthalpy= 0.284167
Thermal correction to Gibbs Free Energy= 0.147197
Sum of electronic and zero-point Energies= -2515.280272
Sum of electronic and thermal Energies= -2515.231413
Sum of electronic and thermal Enthalpies= -2515.230468
Sum of electronic and thermal Free Energies= -2515.367438

Coordinates: B

Ru	2.73050000	1.70960000	-0.58630000
Ru	-3.54930000	-1.29900000	-0.60050000
Ru	2.77910000	-1.32090000	-0.85800000
Ru	1.87070000	-0.36190000	1.52760000
Ru	-3.21370000	1.35220000	0.24670000
O	2.72020000	2.84370000	-3.45400000
O	-6.52660000	-1.36230000	0.00420000
O	1.58350000	4.21400000	0.81840000
N	0.79770000	0.89660000	-0.85700000
N	-1.50590000	-0.67480000	-0.91400000
O	0.42630000	-2.78460000	2.66330000
O	-2.76770000	-3.14200000	1.79660000
O	5.69150000	2.30170000	-0.02570000
O	0.27960000	1.73230000	3.13480000
O	-3.69500000	-3.32830000	-2.89980000
O	1.96670000	-4.11390000	0.01860000
O	-2.23520000	-0.00110000	2.84010000
O	2.38110000	-1.89630000	-3.86180000
O	-2.18520000	4.21770000	0.68980000
O	5.80140000	-1.82610000	-0.34990000
O	-6.12150000	1.85970000	1.10930000
O	4.43960000	-0.89110000	3.18750000
C	-3.05910000	-2.48350000	0.90700000
C	2.73230000	2.43480000	-2.38960000
C	2.02010000	3.30160000	0.29450000
C	-3.87590000	0.42900000	-1.69700000
H	-4.79760000	0.74120000	-2.19690000
C	0.87220000	-0.46090000	-0.39920000
C	4.58830000	2.11160000	-0.24030000
C	4.68380000	-1.68140000	-0.56340000
C	-3.62780000	-2.59860000	-2.01780000
C	-5.40010000	-1.37680000	-0.21340000
C	2.55720000	-1.65770000	-2.75260000
C	-0.37680000	-1.18510000	-0.53740000
H	-0.38510000	-2.24990000	-0.27930000
C	0.82940000	0.90200000	2.56250000
C	-1.57480000	0.73850000	-1.15230000
C	2.27300000	-3.04860000	-0.28910000
C	3.47400000	-0.67940000	2.60680000
C	-0.31880000	1.45010000	-1.18660000
H	-0.32200000	2.50710000	-1.47870000
C	-2.60610000	3.15930000	0.52550000
C	-5.02710000	1.69160000	0.80760000
C	-2.61730000	0.50490000	1.87990000
C	-2.72430000	1.20380000	-1.89840000

H	-2.67200000	2.10860000	-2.50900000
C	0.97440000	-1.87930000	2.21780000
H	2.85900000	1.09510000	1.06200000
H	3.37850000	0.30750000	-1.44700000

Species TSBC

HF energy= -2515.51034300
One Imaginary frequency: 147*i*
Zero-point correction= 0.232946 (Hartree/Particle)
Thermal correction to Energy= 0.281814
Thermal correction to Enthalpy= 0.282759
Thermal correction to Gibbs Free Energy= 0.143084
Sum of electronic and zero-point Energies= -2515.277397
Sum of electronic and thermal Energies= -2515.228529
Sum of electronic and thermal Enthalpies= -2515.227584
Sum of electronic and thermal Free Energies= -2515.367259

Coordinates: TSBC

Ru	2.74550000	1.69900000	-0.26840000
Ru	-3.54170000	-1.26520000	-0.37360000
Ru	2.68360000	-1.27560000	-0.94920000
Ru	2.13160000	-0.55140000	1.65490000
Ru	-3.37360000	1.50050000	-0.02100000
O	3.05640000	2.31540000	-3.28660000
O	-6.56720000	-1.34550000	-0.06780000
O	1.53820000	4.38970000	0.62970000
N	0.79860000	0.90620000	-0.54000000
N	-1.49490000	-0.66760000	-0.59530000
O	1.45660000	-3.45690000	2.22830000
O	-2.79230000	-2.40510000	2.42850000
O	5.60770000	2.47390000	0.51400000
O	0.30240000	0.52360000	3.88700000
O	-3.39090000	-3.74170000	-2.18590000
O	1.62030000	-4.12780000	-0.93510000
O	-2.74930000	0.85100000	2.92820000
O	1.81870000	-0.68810000	-3.84240000
O	-2.64020000	4.48830000	-0.12700000
O	5.62280000	-2.25050000	-1.25470000
O	-6.39150000	1.93230000	0.36450000
O	4.81280000	-0.63920000	3.21380000
C	-3.12680000	-2.03350000	1.39760000
C	2.95160000	2.09460000	-2.17280000
C	1.99520000	3.40230000	0.28680000
C	-3.73880000	0.20990000	-1.82060000
H	-4.58490000	0.39080000	-2.49000000
C	0.88070000	-0.45660000	-0.09270000
C	4.54510000	2.19900000	0.20310000

C	4.53830000	-1.89850000	-1.14440000
C	-3.43900000	-2.83790000	-1.48170000
C	-5.42390000	-1.34570000	-0.16680000
C	2.19500000	-0.92220000	-2.78230000
C	-0.38160000	-1.16440000	-0.16570000
H	-0.41660000	-2.19870000	0.19400000
C	0.97390000	0.16350000	3.03020000
C	-1.54130000	0.69810000	-1.03360000
C	2.02030000	-3.05050000	-0.92660000
C	3.80540000	-0.62760000	2.66700000
C	-0.29310000	1.42600000	-0.98930000
H	-0.27860000	2.46480000	-1.33920000
C	-2.92810000	3.37500000	-0.08940000
C	-5.25870000	1.80210000	0.23670000
C	-2.98360000	1.09770000	1.83110000
C	-2.58260000	0.98870000	-2.00080000
H	-2.45780000	1.76990000	-2.75450000
C	1.73640000	-2.36970000	1.97870000
H	2.50350000	1.27130000	1.42950000
H	3.61410000	0.15040000	-0.35990000

Species C

HF energy= -2515.53384353
No Imaginary frequency
Zero-point correction= 0.234449 (Hartree/Particle)
Thermal correction to Energy= 0.283259
Thermal correction to Enthalpy= 0.284203
Thermal correction to Gibbs Free Energy= 0.146092
Sum of electronic and zero-point Energies= -2515.299394
Sum of electronic and thermal Energies= -2515.250585
Sum of electronic and thermal Enthalpies= -2515.249641
Sum of electronic and thermal Free Energies= -2515.387751

Coordinates: C

Ru	2.84170000	1.55320000	-0.39190000
Ru	-3.49420000	-1.33090000	-0.47190000
Ru	2.71800000	-1.19730000	-0.94160000
Ru	2.06200000	-0.45490000	1.73360000
Ru	-3.40430000	1.39850000	0.13600000
O	3.17100000	2.07930000	-3.38750000
O	-6.51770000	-1.53350000	-0.20570000
O	2.39750000	4.50730000	0.46330000
N	0.80790000	0.96760000	-0.53310000
N	-1.46350000	-0.64110000	-0.61100000
O	0.91960000	-3.17630000	2.55460000
O	-2.78040000	-2.78320000	2.19260000
O	5.86180000	1.43960000	0.04450000

O	0.00740000	1.32580000	3.14780000
O	-3.25060000	-3.59700000	-2.53230000
O	1.97920000	-4.17610000	-0.79640000
O	-2.90670000	0.45840000	3.03070000
O	1.55010000	-0.78960000	-3.73250000
O	-2.64300000	4.37200000	0.37650000
O	5.71710000	-1.46730000	-1.70760000
O	-6.42900000	1.82610000	0.45530000
O	4.29170000	-0.39970000	3.91250000
C	-3.08830000	-2.28700000	1.20650000
C	3.04300000	1.85320000	-2.26980000
C	2.54310000	3.40850000	0.17830000
C	-3.73670000	0.26680000	-1.77160000
H	-4.59010000	0.48160000	-2.42150000
C	0.91020000	-0.40000000	-0.10580000
C	4.73260000	1.50840000	-0.14010000
C	4.60970000	-1.39350000	-1.42460000
C	-3.33240000	-2.77370000	-1.73850000
C	-5.37460000	-1.49020000	-0.29350000
C	2.03730000	-0.94480000	-2.70390000
C	-0.34080000	-1.13330000	-0.20040000
H	-0.34600000	-2.18950000	0.09250000
C	0.75410000	0.61100000	2.65930000
C	-1.54620000	0.75010000	-0.95030000
C	2.26530000	-3.06620000	-0.86110000
C	3.47090000	-0.43320000	3.12010000
C	-0.30330000	1.49280000	-0.91530000
H	-0.30020000	2.54080000	-1.23750000
C	-2.94590000	3.26700000	0.28430000
C	-5.29400000	1.68800000	0.35900000
C	-3.08640000	0.80780000	1.95040000
C	-2.60380000	1.08910000	-1.88380000
H	-2.50230000	1.93510000	-2.56760000
C	1.34240000	-2.15470000	2.26000000
H	2.73340000	1.17780000	1.37530000
H	3.36580000	-1.26540000	0.76790000