Electronic Supplementary Information for

"Octahedral to trigonal prismatic distortion driven by subjacent orbital π antibonding interactions and modulated by ligand redox noninnocence"

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General Procedures. Except as noted, all procedures were carried out on the benchtop without precautions to exclude air or moisture. When necessary, chlorinated solvents were dried over 4 Å molecular sieves, followed by CaH_2. $Pb(ONO^Q)_2$ was prepared by a modification[S1] of the method of McGarvey and coworkers.[S2] Di-μ-chlorobis[(*p*-cymene)chloroosmium(II)][S3] and $Pb(DOPO^Q)_2$[S4] were prepared using published procedures. All other reagents were commercially available and used without further purification. ^1H and $\{^1H\}^{13}C$ NMR spectra were measured using a Bruker Avance DPX-400 or -500 spectrometer and were referenced to the solvent residual signals. Infrared spectra were recorded on a JASCO FT/IR-6300 spectrometer using the ATR attachment. UV-visible spectra were measured in a 1-cm quartz cell on a Thermo Scientific Evolution Array spectrophotometer. Mass spectra were measured on a Bruker micrOTOF II spectrometer using electrospray ionization; isotope envelopes agreed with the proposed formulations. Elemental analyses were performed by Robertson Microlit Laboratories (Ledgewood, NJ, USA).

Bis(2,4,6,8-tetra-*tert*-butyl-1,9-dioxophenoxazinato)ruthenium, $Ru(DOPO)_2$. In the drybox, di-μ-chlorobis[(*p*-cymene)chlororuthenium(II)] (Strem, 0.0598 g, 0.0975 mmol) and bis(2,4,6,8-tetra-*tert*-butyl-1,9-dioxophenoxazinato)lead(II), $Pb(DOPO^Q)_2$ (0.2042 g, 0.1891 mmol, 1.94 equiv per Ru dimer) were weighed into a 20-mL scintillation vial and dissolved in 5 mL $CHCl_3$ to give a teal solution. The vial was capped and removed from the drybox. It was placed in a 60 ˚C oil bath for 24 h. After removing the vial from the oil bath and allowing it to cool to room temperature, the mixture was gravity filtered in the air. To the filtrate was added 5 mL acetonitrile, causing precipitation of blue crystals. After standing 1 h at room temperature, the mixture was suction filtered on a glass frit and the precipitate washed thoroughly with 15 mL CH_3CN. The wash was combined with the original filtrate to yield a second crop after 48 h standing, and a third crop after 72 h, which were isolated as described above to give a combined

yield of 0.1003 g $Ru(DOPO)_2$ (55%). ^1H NMR ($CDCl_3$): δ 1.13, 1.67 (s, 36H each, ^tBu), 7.42 (s, 4H, Ar*H*). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 29.53, 31.14 ($C(CH_3)_3$), 34.44, 35.29 ($C(CH_3)_3$), 122.86, 132.52, 136.72, 136.83, 142.13, 176.68 (RuO*C*). IR (cm^{-1}): 2921 (s), 1599 (w), 1567 (w), 1528 (m), 1491 (m), 1414 (m), 1355 (w), 1328 (m), 1285 (m), 1241 (s), 1168 (w), 1055 (s), 884 (w), 825 (w), 780 (w), 710 (w), 616 (w), 495 (s). ESI-MS: m/z = 975.4823 (M^+ + H, calcd 975.4835). UV-Vis (CH_2Cl_2): λ_{max} = 292 nm (ε = 22400 L mol^{-1} cm^{-1}), 386 nm (11200 L mol^{-1} cm^{-1}), 492 nm (sh, 6300 L mol^{-1} cm^{-1}), 594 nm (24100 L mol^{-1} cm^{-1}). Anal. Calcd for $C_{56}H_{76}N_2O_6Ru$: C, 69.04; H, 7.86; N, 2.88. Found: C, 68.01; H, 7.80; N, 2.98.

Bis(2,4,6,8-tetra-*tert*-butyl-1,9-dioxophenoxazinato)osmium, $Os(DOPO)_2$. In the drybox, di-μ-chlorobis[(*p*-cymene)chloroosmium(II)] (0.0580 g, 0.0734 mmol) and $Pb(DOPO^Q)_2$ (0.1585 g, 0.1468 mmol, 2.00 equiv per Os dimer) were reacted and worked up as described above for the ruthenium analogue to yield 0.0875 g $Os(DOPO)_2$ (56%). ^1H NMR ($CDCl_3$): δ 1.25, 1.64 (s, 36H each, ^tBu), 6.31 (s, 4H, Ar*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 29.01, 31.05 ($C(CH_3)_3$), 34.05, 34.84 ($C(CH_3)_3$), 123.94, 127.12, 128.58, 132.87, 140.83, 175.03 (OsO*C*). IR (cm^{-1}): 2961 (s), 2850 (m), 1613 (m), 1538 (m), 1497 (m), 1407 (s), 1341 (w), 1291 (m), 1246 (m), 1203 (w), 1099 (w), 1047 (m), 874 (w), 822 (w), 784 (w), 725 (w), 626 (m), 526 (m). ESI-MS: m/z = 1065.5367 (M^+ + H, calcd 1065.5396). UV-Vis (CH_2Cl_2): λ_{max} = 283 nm (ε = 37000 L mol^{-1} cm^{-1}), 377 nm (14500 L mol^{-1} cm^{-1}), 491 nm (33400 L mol^{-1} cm^{-1}), 650 nm (sh, 6200 L mol^{-1} cm^{-1}). Anal. Calcd for $C_{56}H_{76}N_2O_6Os$: C, 63.25; H, 7.20; N, 2.63. Found: C, 63.22; H, 7.02; N, 2.34.

Bis[bis(3,5-di-*tert*-butyl-2-oxyphenyl)amido]ruthenium, $Ru(ONO)_2$. In the drybox, $[Ru(p\text{-cymene})Cl_2]_2$ (Strem, 0.0599 g, 0.0978 mmol) and lead(II) bis(3,5-di-*tert*-butyl-1,2-quinone-(3,5-di-*tert*-butyl-2-hydroxy-1-phenyl)imine), $Pb(ONO^Q)_2$ (0.2046 g, 0.1945 mmol, 2.00 equiv per Ru dimer) were weighed into a 20-mL scintillation vial. The mixture was

dissolved in 5 mL $CHCl_3$, resulting in a purple solution. The vial was capped securely, removed from the drybox, and allowed to stand for 24 h at room temperature. The mixture was worked up as described for $Ru(DOPO)_2$ to yield 0.0917 g $Ru(ONO)_2$ (50%). ^{1}H NMR ($CDCl_3$): δ 1.19, 1.41 (s, 36H each, ^{t}Bu), 7.27 (d, 2 Hz, 2H, Ar*H*), 8.01 (d, 2 Hz, 2H, Ar*H*). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 30.23, 31.73 ($C(CH_3)_3$), 35.21, 35.78 ($C(CH_3)_3$), 114.62, 124.86, 140.84, 142.72, 145.47, 177.65 (RuO*C*). IR (cm^{-1}): 2953 (s), 1550 (w), 1463 (m), 1384 (w), 1360 (s), 1304 (m), 1232 (s) , 1011 (m), 910 (m), 852 (w), 829 (w), 759(w), 647 (w), 621 (w), 542 (m). ESI-MS: 947.5298 (M^+ + H, calcd 947.5250). UV-Vis (CH_2Cl_2) λ_{max} = 271 nm (sh, ε = 28600 L mol^{-1} cm^{-1}), 453 nm (sh, 16300 L mol^{-1} cm^{-1}), 527 nm (21600 L mol^{-1} cm^{-1}). Anal. Calcd for $C_{56}H_{80}N_2O_4Ru$: C, 71.08; H, 8.52; N, 2.96. Found: C, 70.91; H, 8.82; N, 2.67.

Bis[bis(3,5-di-*tert*-butyl-2-oxyphenyl)amido]osmium, $Os(ONO)_2$. The compound was prepared using the same procedure as the ruthenium analogue using 0.0652 g [Os(*p*-cymene)Cl_2]$_2$ (0.0825 mmol) and 0.1690 g $Pb(ONO^Q)_2$ (0.1607 mmol, 1.95 equiv per Os dimer). Yield 0.0759 g (46%). ^{1}H NMR ($CDCl_3$): δ 1.24, 1.45 (s, 36H each, ^{t}Bu), 7.05, 8.03 (sl br s, 4H, Ar*H*). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 30.39, 32.29 ($C(CH_3)_3$), 35.23, 35.92 ($C(CH_3)_3$), 113.39 122.87, 139.20, 142.22, 146.04, 173.86 (OsO*C*). IR (cm^{-1}): 2954 (s), 2867 (m), 1461 (m), 1361 (m), 1307 (w), 1234 (m), 1182 (m), 1109 (w), 1051 (w), 1011 (w), 910 (w), 851 (w), 758 (w), 620 (w), 542 (w), 512 (w). ESI-MS: 1037.5829 (M^+ + H, calcd 1037.5810). UV-Vis (CH_2Cl_2): λ_{max} = 275 nm (sh, ε = 8900 L mol^{-1} cm^{-1}), 368 (sh, 2800 L mol^{-1} cm^{-1}), 450 nm (9900 L mol^{-1} cm^{-1}), 493 nm (9700 L mol^{-1} cm^{-1}), 583 (sh, 4800 L mol^{-1} cm^{-1}). Anal. Calcd for $C_{56}H_{80}N_2O_4Os$: C, 64.96; H, 7.79; N, 2.71. Found: C, 64.66; H, 7.77; N, 2.46.

Electrochemistry. Electrochemical measurements were performed in the drybox using a Metrohm Autolab PGSTAT128N potentiostat. A standard three-electrode setup was used, with glassy carbon working and counter electrodes and a silver/silver chloride pseudo-reference

electrode. The electrodes were connected to the potentiostat through electrical conduits in the drybox wall. Samples were 1 mM in CH_2Cl_2 with 100 mM $[Bu_4N]PF_6$ as supporting electrolyte. Potentials were referenced to ferrocene/ferrocenium at 0 V,[S5] with the reference potential established by spiking the solution with a small amount of decamethylferrocene (E^o = –0.565 V).[S6] Cyclic voltammograms were recorded with a scan rate of 120 mV s^{-1}.

Variable-Temperature NMR. Variable-temperature ^{1}H NMR spectra of $Os(ONO)_2$ and $Ru(ONO)_2$ were measured on CD_2Cl_2 solutions on a Varian VXR-500 spectrometer between –80 ºC and room temperature. Spectra of $Ru(ONO)_2$ showed two aromatic and two *tert*-butyl resonances at all temperatures. Spectra of $Os(ONO)_2$ showed changes consistent with an unsymmetrical structure (four aromatic and four *tert*-butyl peaks) undergoing a dynamic process resulting in exchange of the inequivalent ends of the ONO ligand (Figure S5). The spectral lineshape of the aromatic regions in the temperature range of –40 ºC to 10º C was simulated using the program *iNMR* (http://www.inmr.net) to determine the rate of exchange. The values of $\ln(k/T)$ were plotted against $1/T$ to determine activation parameters for the exchange process (Figure S6).

Calculations. Geometry optimizations and orbital calculations used the hybrid B3LYP method, using the Gaussian09 suite of programs.[S7] Second- and third-row metal complexes used an SDD basis set for the metal atoms and a 6-31G* basis set for all other atoms, while first-row metal complexes used a 6-31G* basis set for all atoms. Starting geometries were generated from known crystal structures, with all *tert*-butyl groups replaced by hydrogen atoms, and all calculations were performed on singlet states. (Thus, the calculated structure of $(ONO)_2Fe$ differs substantially from the experimentally determined structure, which corresponds to a quintet.[S8]) Optimized geometries were confirmed to be minima by frequency analysis. For $Os(ONO)_2$ and $[Re(ONO)_2]^-$, calculations were also performed on complexes constrained to

adopt a D_2-symmetric geometry; these were not minima, and frequency analysis revealed two imaginary vibrational frequencies in each case. To generate the Walsh diagram for $[Re(ONO)_2]^-$ (Figure 5), structures were energy-minimized with the N–Re–N angle constrained to values ranging from 110º to 180º in 5º intervals. Plots of calculated Kohn-Sham orbitals were generated using the program GaussView (v. 5.0.8) with an isovalue of 0.04.

X-ray Crystallography. Crystals of $Ru(DOPO)_2$ were grown by slow evaporation from $CDCl_3$, while $Os(DOPO)_2$ was crystallized by liquid-liquid diffusion of acetonitrile into a chloroform solution of the compound. Crystals of $Ru(ONO)_2 \cdot CHCl_3 \cdot 1.31\ CH_3CN$ and $Os(ONO)_2 \cdot 2\ CHCl_3$ were crystallized by vapor diffusion of acetonitrile into chloroform. Crystals were placed in a perfluorinated polyether oil (PPFPE) before being transferred to the cold N_2 stream of a Bruker Apex II CCD diffractometer in a nylon loop. Data were reduced, correcting for absorption, using the program SADABS. The structures were solved using direct methods. Remaining nonhydrogen atoms were found on difference Fourier maps, and all nonhydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions, except those in $Os(DOPO)_2$, which were found on difference Fourier maps and refined isotropically. Calculations used SHELXTL (Bruker AXS),[S9] with scattering factors and anomalous dispersion terms taken from the literature.[S10]

In $Ru(ONO)_2 \cdot CHCl_3 \cdot 1.31\ CH_3CN$, two lattice acetonitriles and one chloroform in the asymmetric unit (which contained two metal complexes) were ordered. However, one region of solvent consisted of a disordered chloroform molecule next to a partially occupied acetonitrile, with one component of the disordered chloroform closer than van der Waals contact to the CH_3CN. This was modeled by allowing the occupancy of the minor component of the $CHCl_3$ to vary, with the occupancy of the acetonitrile set to the occupancy of the major (distant) component of the $CHCl_3$. The thermal parameters of the corresponding atoms in the two $CHCl_3$

sites were constrained to be equal. Two of the chlorine atoms were very close and were refined with identical coordinates. The site occupancy factor of the major component refined to 0.620(3), and was then fixed at 0.62 for the final refinement cycles. At this stage the *x*, *y*, *z* coordinates and thermal parameters of the two $CHCl_3$ components were allowed to vary independently, except that the spatially close chlorines (Cl5/Cl59 and Cl6/Cl69) were constrained to have equal thermal parameters.

$Os(ONO)_2$•2 $CHCl_3$ forms a structure containing alternating layers of metal complexes (two molecules per asymmetric unit) and of chloroform molecules perpendicular to the *a* axis. One chloroform is ordered in the metal-containing layers and was modeled explicitly. The chloroform in the solvent layers was severely disordered and was treated using the SQUEEZE routine[S11] in the program PLATON.[S12] A total of 3546 $Å^3$ of solvent-accessible void space, containing 1470 electrons, was detected per unit cell. This corresponds within 6% to the amount expected from 24 chloroform molecules per unit cell, corresponding to an overall formula of $Os(ONO)_2$•2 $CHCl_3$.

Further details may be found in Tables S1 and S2. Thermal ellipsoid plots of the DOPO compounds are given in Figure S1. Plots of overlays of the geometries of the crystallographically inequivalent complexes in $Ru(ONO)_2$•$CHCl_3$•1.31 CH_3CN and in $Os(ONO)_2$•2 $CHCl_3$ are shown in Figure S2. Summaries of bond distances and angles are given in Tables S3 and S4. In these tables, distances and angles are the averages of the two or four crystallographically inequivalent examples of each present in the crystal structures.

Table S1. Crystal data for $Ru(DOPO)_2$ and $Os(DOPO)_2$.

	$Ru(DOPO)_2$	$Os(DOPO)_2$
Molecular formula	$C_{56}H_{76}N_2O_6Ru$	$C_{56}H_{76}N_2O_6Os$
Formula weight	974.25	1063.38
T/K	120(2)	120(2)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
λ/Å	0.71073 (Mo Kα)	0.71073 (Mo Kα)
Total data collected	149553	117301
No. of indep. reflns.	11697	10557
R_{int}	0.0853	0.0739
Obsd refls [$I > 2\sigma(I)$]	8809	9028
a/Å	20.3495(11)	20.4119(19)
b/Å	19.7245(11)	19.7938(19)
c/Å	12.9833(7)	13.0487(12)
α/°	90	90
β/°	90.575(2)	90.3740(15)
γ/°	90	90
V/Å^3	5211.0(5)	5271.9(9)
Z	4	4
μ/mm^{-1}	0.350	2.468
Crystal size/mm	0.249 × 0.098 × 0.051	0.152 × 0.147 × 0.146
No. refined parameters	586	890
$R1$, $wR2$ [$I > 2\sigma(I)$]	0.0378, 0.0843	0.0246, 0.0536
$R1$, $wR2$ [all data]	0.0629, 0.0951	0.0331, 0.0568
Goodness of fit	1.026	1.030

Table S2. Crystal data for $Ru(ONO)_2$•$CHCl_3$•1.31 CH_3CN and $Os(ONO)_2$•2 $CHCl_3$.

	$Ru(ONO)_2$•$CHCl_3$•1.31 CH_3CN	$Os(ONO)_2$•2 $CHCl_3$
Molecular formula	$C_{59.62}H_{84.93}Cl_3N_{3.31}O_4Ru$	$C_{58}H_{82}Cl_6N_2O_4Os$
Formula weight	1119.43	1274.15
T/K	120(2)	120(2)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$C2/c$
λ/Å	0.71073 (Mo Kα)	1.54178 (Cu Kα)
Total data collected	215109	238998
No. of indep. reflns.	30196	23772
R_{int}	0.0457	0.0698
Obsd refls [$I > 2\sigma(I)$]	25253	20325
a/Å	14.2714(16)	59.4673(19)
b/Å	20.573(2)	21.5249(6)
c/Å	41.187(5)	19.0986(5)
α/°	90	90
β/°	93.0881(17)	95.211(3)
γ/°	90	90
V/Å^3	12075(2)	24345.7(12)
Z	8	16
μ/mm^{-1}	0.438	6.721
Crystal size/mm	0.352 × 0.184 × 0.180	0.161 × 0.037 × 0.018
No. refined parameters	1315	1171
$R1$, $wR2$ [$I > 2\sigma(I)$]	0.0478, 0.1229	0.0595, 0.1458
$R1$, $wR2$ [all data]	0.0598, 0.1310	0.0689, 0.1506
Goodness of fit	1.034	1.055

Figure S1. Thermal ellipsoid plot of (a) $Ru(DOPO)_2$ and (b) $Os(DOPO)_2$. Hydrogen atoms are omitted for clarity.

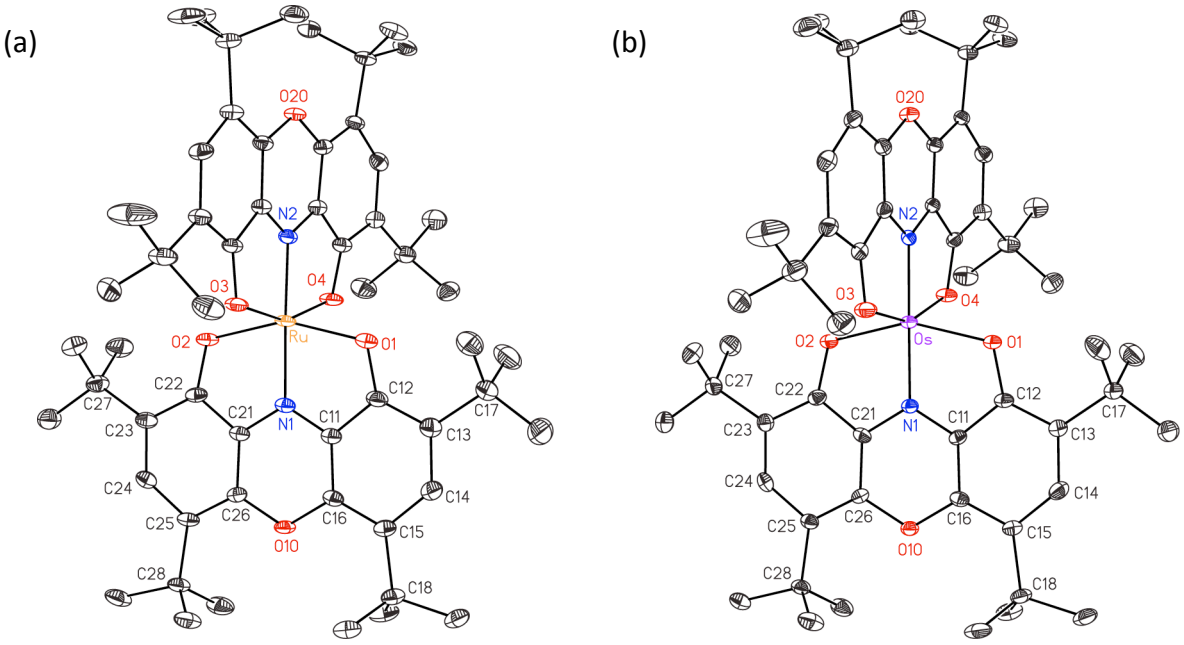


Figure S2. Overlays of the two crystallographically inequivalent metal complexes in the structures of (a) $Ru(ONO)_2 \cdot CHCl_3 \cdot 1.31\ CH_3CN$ and (b) $Os(ONO)_2 \cdot 2\ CHCl_3$. Hydrogen atoms and *tert*-butyl groups are omitted for clarity. Numbering scheme is given for molecule 1 (solid pink lines); molecule 2 is given by blue dashed lines.

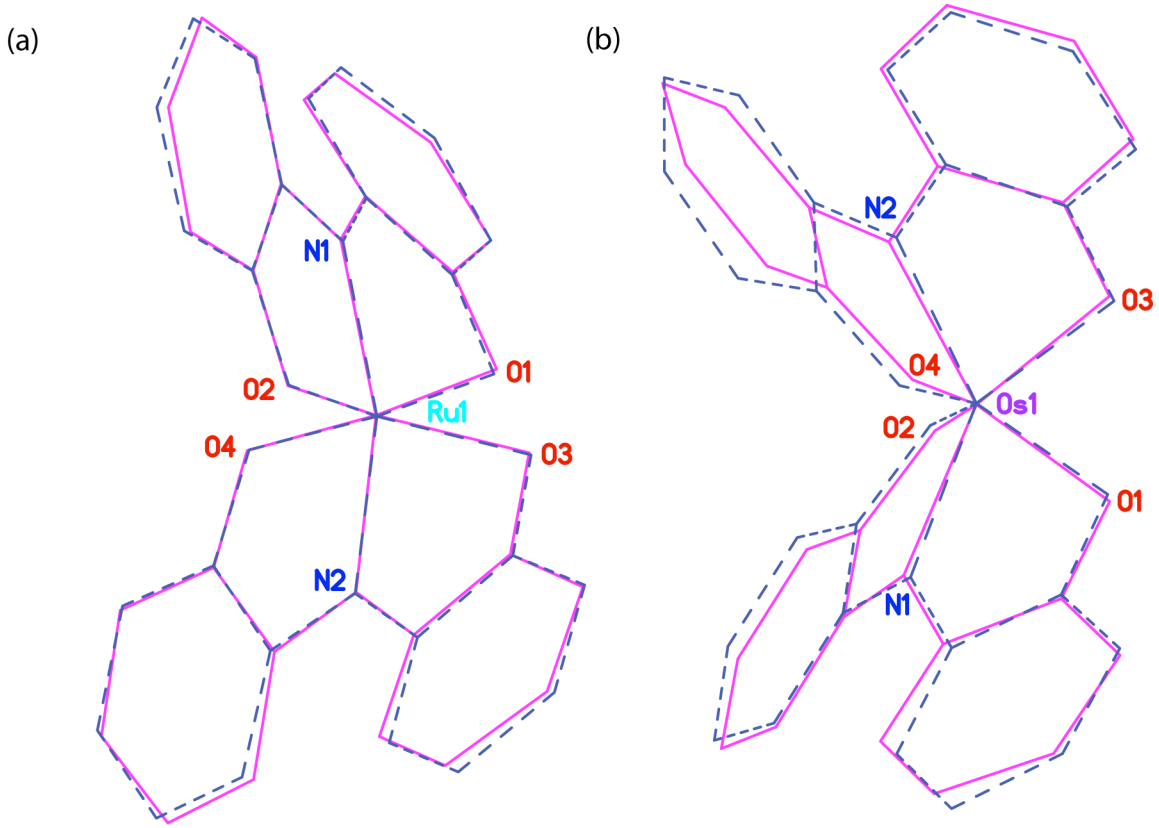


Table S3. Selected bond distances (Å), angles (deg), and metrical oxidation state (MOS) for $Ru(DOPO)_2$ and $Os(DOPO)_2$. Values given in Roman type are the averages over all chemically equivalent values from the crystal structures. Values given in italics are from DFT calculations.

Parameter	$Ru(DOPO)_2$	$Os(DOPO)_2$
M–O	2.076(7) *2.150*	2.064(8) *2.140*
M–N	1.9173(18) *1.938*	1.925(5) *1.945*
C1–N	1.342(4) *1.342*	1.358(4) *1.353*
C2–O	1.314(4) *1.302*	1.333(4) *1.313*
C1–C2	1.412(4) *1.431*	1.403(4) *1.422*
C2–C3	1.407(6) *1.416*	1.404(4) *1.411*
C3–C4	1.390(3) *1.393*	1.396(5) *1.396*
C4–C5	1.416(5) *1.420*	1.411(6) *1.416*
C5–C6	1.381(5) *1.380*	1.390(4) *1.383*
C1–C6	1.403(5) *1.412*	1.398(4) *1.406*
N–M–N	177.13(8) *180.0*	176.41(9) *180.0*
O–M–O (*cis*)	93(5) *92.8*	93(6) *93.0*
O–M–O (*trans*)	155.78(9) *154.7*	154.62(11) *153.4*
N–M–O (intraligand)	77.9(4) *77.3*	77.3(2) *76.7*
N–M–O (interligand)	102(3) *102.7*	103(3) *103.3*
Metrical Oxidation State (MOS)	–1.99(20) *–1.74(16)*	–2.35(18) *–2.00(15)*

Table S4. Selected bond distances (Å), metrical oxidation states (MOS), and angles (deg) for $Ru(ONO)_2$ and $Os(ONO)_2$. Values given in Roman type are the averages over all chemically equivalent values from the crystal structures of $Ru(ONO)_2$•$CHCl_3$•1.31 CH_3CN and $Os(ONO)_2$•2 $CHCl_3$, respectively. Values given in italics are from DFT calculations. "Ring 1" refers to the odd-numbered rings (e.g., those containing C11, C32, etc.) in the crystal structures, while "Ring 2" refers to the even-numbered rings.

	$Ru(ONO)_2$		**$Os(ONO)_2$**	
Parameter	Ring 1	Ring 2	Ring 1	Ring 2
M–O	2.023(6) *2.060*	1.988(8) *2.026*	1.975(11) *2.026*	1.954(8) *1.994*
M–N	1.951(4) *1.986*		1.974(8) *1.993*	
C1–N	1.392(6) *1.384*	1.373(3) *1.372*	1.403(8) *1.398*	1.393(10) *1.398*
C2–O	1.334(4) *1.307*	1.321(5) *1.305*	1.347(9) *1.333*	1.350(8) *1.333*
C1–C2	1.425(3) *1.442*	1.422(5) *1.441*	1.418(12) *1.426*	1.401(8) *1.421*
C2–C3	1.418(5) *1.415*	1.425(4) *1.416*	1.409(13) *1.403*	1.411(8) *1.402*
C3–C4	1.389(6) *1.382*	1.379(5) *1.379*	1.392(19) *1.389*	1.385(8) *1.388*
C4–C5	1.410(9) *1.414*	1.426(4) *1.417*	1.414(16) *1.406*	1.416(10) *1.408*
C5–C6	1.384(5) *1.383*	1.374(4) *1.380*	1.376(10) *1.390*	1.385(11) *1.388*
C1–C6	1.402(6) *1.415*	1.411(4) *1.419*	1.390(11) *1.406*	1.394(8) *1.409*
N–M–N	162.05(13) *166.4*		131(3) *154.0*	
O(1)–M–O(2) (intraligand)	154.1(8) *155.7*		124(3) *142.0*	
O(*n*)–M–O(*n*') (interligand)	84.5(7) *84.1*	106.50(9) *103.4*	87.1(6) *82.9*	144(4) *124.3*
O(1)–M–O(2') (interligand)	89.2(11) *90.5*		83.6(5) *84.9*	
N–M–O (intraligand)	80.05(18) *80.0*	79.66(17) *79.9*	78.3(2) *78.3*	77.9(3) *78.3*
N–M–O (interligand)	113.8(4) *110.5*	89.6(5) *91.7*	144(3) *122.7*	87.3(11) *89.5*
Metrical Oxidation State (MOS)	–2.33(8) *–1.94(12)*	–1.97(10) *–1.81(9)*	–2.56(12) *–2.44(10)*	–2.59(14) *–2.38(7)*

Figure S3. Optical spectra of $Ru(DOPO)_2$, $Os(DOPO)_2$, $Ru(ONO)_2$ and $Os(ONO)_2$ (CH_2Cl_2 solution).

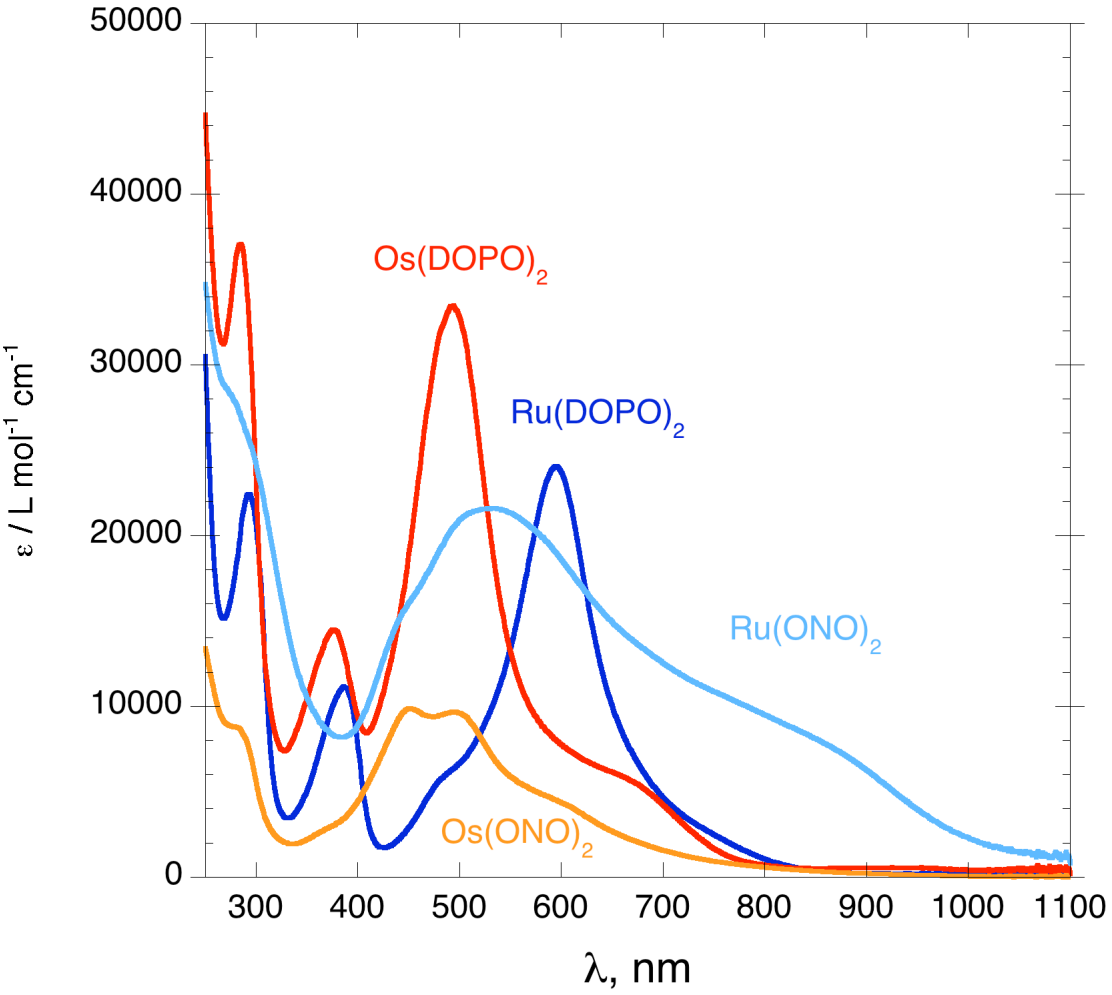


Figure S4. Cyclic voltammograms (CH_2Cl_2, 1 mM analyte, 100 mM $[Bu_4N]PF_6$ supporting electrolyte, scan rate 120 mV s^{-1}) of $Ru(DOPO)_2$, $Os(DOPO)_2$, $Ru(ONO)_2$ and $Os(ONO)_2$.

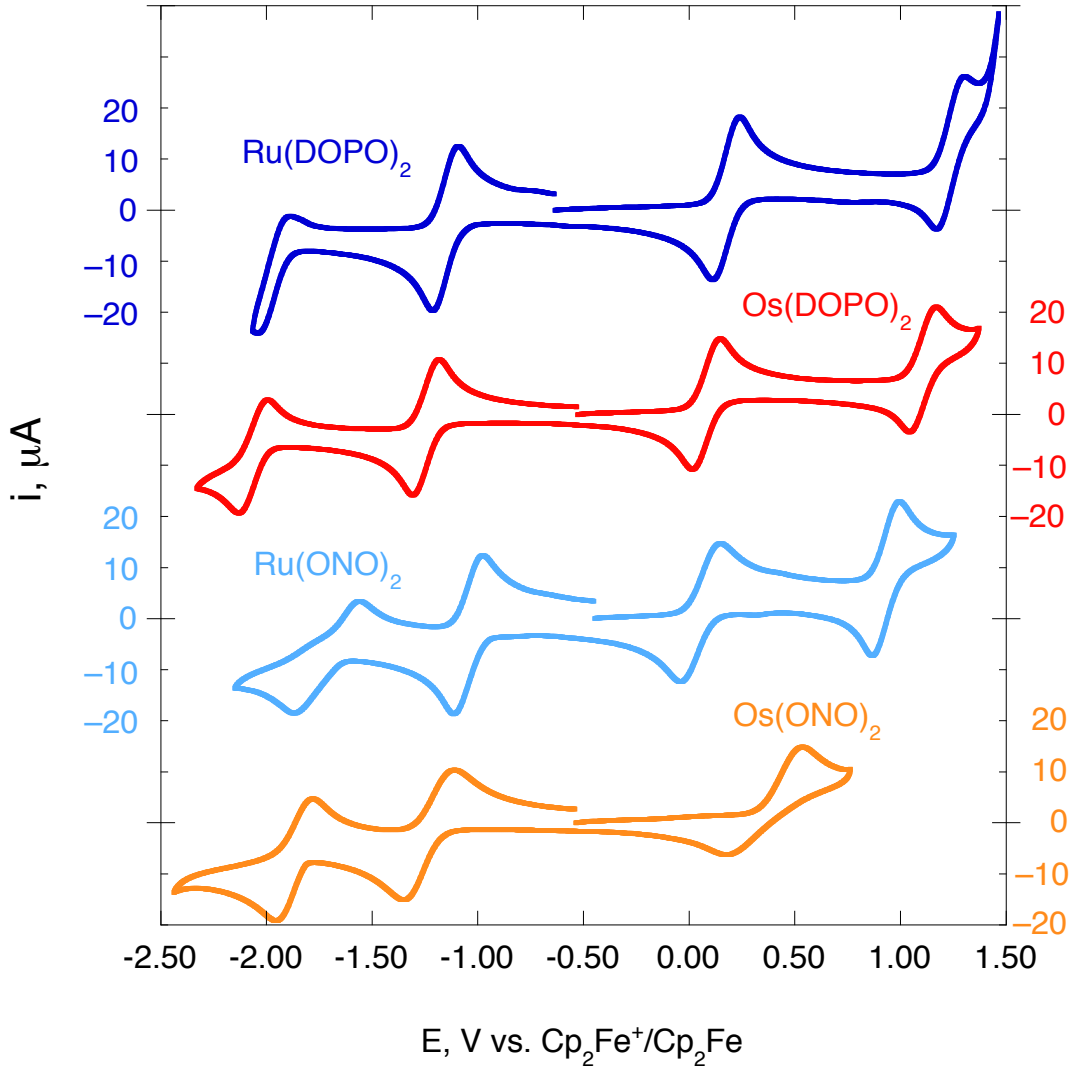


Table S5. Redox potentials of $Ru(DOPO)_2$, $Os(DOPO)_2$, $Ru(ONO)_2$ and $Os(ONO)_2$ (V vs. Cp_2Fe^+/Cp_2Fe).

Compound	E^o_1 (2d reduction)	E^o_2 (1st reduction)	E^o_3 (1st oxidation)	E^o_4 (2d oxidation)
$Ru(DOPO)_2$	–1.965	–1.154	0.176	1.237
$Os(DOPO)_2$	–2.063	–1.246	0.081	1.106
$Ru(ONO)_2$	–1.714	–1.047	0.055	0.930
$Os(ONO)_2$	–1.868	–1.231	0.358	0.852[a]

[a]Redox wave is partially irreversible.

Figure S5. Variable-temperature ^{1}H NMR spectra of $Os(ONO)_2$ (δ 6.0 – 8.5 ppm, CD_2Cl_2, 500 MHz).

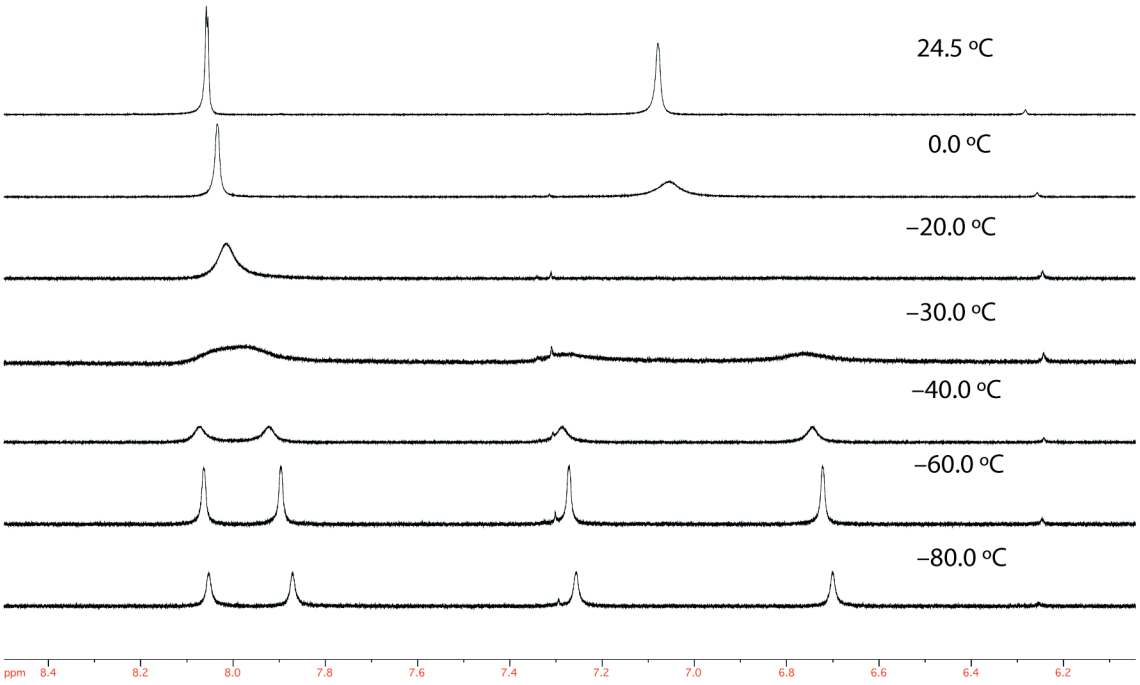
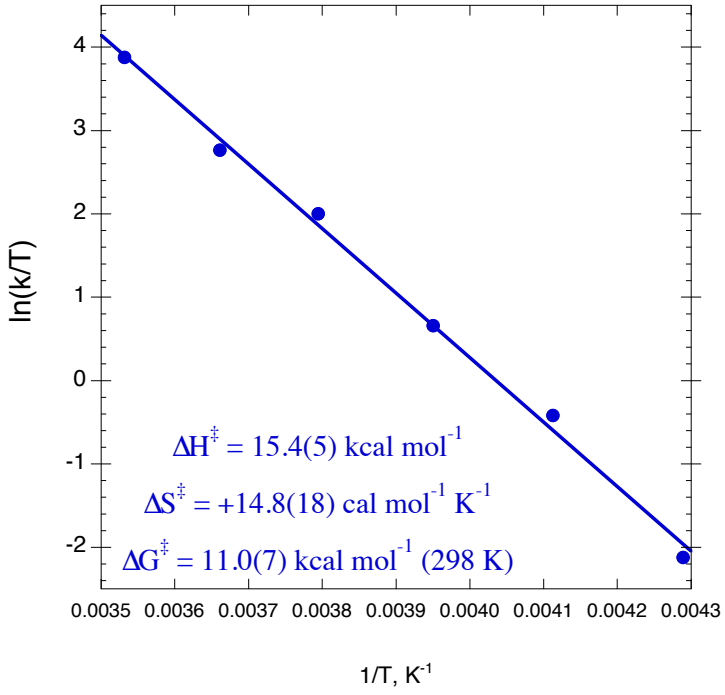


Figure S6. Eyring plot of symmetrization reaction of $Os(ONO)_2$ (CD_2Cl_2, –40° C to 10 °C).



DFT Calculations

(a) $Fe(ONO)_2$

Energy of optimized structure = –2598.26989830 a.u.

Cartesian coordinates of the optimized structure:

Centre Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	26	-0.000039	-0.000054	-0.000127
2	7	1.889094	0.000148	-0.000009
3	7	-1.889208	-0.000172	-0.000037
4	8	0.215431	1.381371	1.348911
5	6	2.456733	0.998650	0.729630
6	6	1.444170	1.725792	1.478709
7	6	1.859264	2.783187	2.341790
8	1	1.098939	3.305359	2.913282
9	6	3.188436	3.123343	2.409567
10	1	3.500908	3.937400	3.058896
11	6	4.170315	2.452580	1.626263
12	1	5.203816	2.782380	1.667943
13	6	3.816290	1.409972	0.801886
14	1	4.564899	0.948038	0.172250
15	8	0.215863	-1.381160	-1.349389
16	6	2.456987	-0.998291	-0.729520
17	6	1.444666	-1.725474	-1.478893
18	6	1.860063	-2.782780	-2.341940
19	1	1.099924	-3.304973	-2.913659
20	6	3.189276	-3.122840	-2.409386
21	1	3.501977	-3.936838	-3.058680
22	6	4.170904	-2.452053	-1.625785
23	1	5.204439	-2.781779	-1.667214
24	6	3.816595	-1.409512	-0.801448
25	1	4.565011	-0.947560	-0.171595
26	8	-0.215490	-1.381329	1.348795
27	6	-2.456827	-0.998693	0.729570
28	6	-1.444225	-1.725799	1.478621
29	6	-1.859257	-2.783204	2.341712
30	1	-1.098903	-3.305352	2.913187
31	6	-3.188420	-3.123403	2.409518
32	1	-3.500851	-3.937470	3.058855
33	6	-4.170342	-2.452664	1.626247
34	1	-5.203835	-2.782485	1.667968
35	6	-3.816374	-1.410040	0.801865
36	1	-4.565014	-0.948104	0.172266
37	8	-0.215813	1.381170	-1.349184
38	6	-2.457013	0.998318	-0.729549
39	6	-1.444600	1.725510	-1.478792
40	6	-1.859895	2.782867	-2.341822
41	1	-1.099695	3.305073	-2.913448
42	6	-3.189096	3.122962	-2.409370
43	1	-3.501716	3.937001	-3.058651
44	6	-4.170815	2.452160	-1.625898
45	1	-5.204340	2.781906	-1.667415
46	6	-3.816603	1.409571	-0.801577
47	1	-4.565084	0.947592	-0.171819

(b) **$[Co(ONO)_2]^+$**

Energy of optimized structure = –2717.10314636 a.u.

Cartesian coordinates of the optimized structure:

Centre Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	27	0.000000	0.000000	0.000000
2	7	-1.899134	0.000000	-0.000001
3	7	1.899135	0.000000	0.000000
4	8	-0.130748	1.334200	1.332992
5	8	-0.130747	-1.334199	-1.332993
6	8	0.130748	1.334217	-1.332975
7	8	0.130747	-1.334216	1.332975
8	6	-2.417194	0.933402	0.823313
9	6	-1.363173	1.635924	1.555829
10	6	-1.725834	2.632861	2.504457
11	1	-0.935941	3.135958	3.051074
12	6	-3.051280	2.932865	2.687216
13	1	-3.332368	3.697976	3.405193
14	6	-4.083313	2.275992	1.944054
15	1	-5.116141	2.567829	2.102472
16	6	-3.782534	1.299154	1.033384
17	1	-4.574644	0.838338	0.460613
18	6	-2.417194	-0.933402	-0.823314
19	6	-1.363172	-1.635924	-1.555830
20	6	-1.725833	-2.632861	-2.504458
21	1	-0.935940	-3.135958	-3.051074
22	6	-3.051278	-2.932866	-2.687216
23	1	-3.332366	-3.697976	-3.405194
24	6	-4.083312	-2.275993	-1.944055
25	1	-5.116139	-2.567830	-2.102473
26	6	-3.782533	-1.299155	-1.033385
27	1	-4.574643	-0.838338	-0.460614
28	6	2.417196	0.933407	-0.823309
29	6	1.363173	1.635939	-1.555813
30	6	1.725833	2.632886	-2.504432
31	1	0.935938	3.135992	-3.051039
32	6	3.051278	2.932887	-2.687195
33	1	3.332365	3.698004	-3.405166
34	6	4.083313	2.276000	-1.944048
35	1	5.116141	2.567832	-2.102471
36	6	3.782536	1.299154	-1.033386
37	1	4.574648	0.838325	-0.460629
38	6	2.417195	-0.933407	0.823310
39	6	1.363172	-1.635939	1.555814
40	6	1.725830	-2.632886	2.504433
41	1	0.935935	-3.135991	3.051039
42	6	3.051275	-2.932888	2.687196
43	1	3.332362	-3.698005	3.405167
44	6	4.083311	-2.276001	1.944050
45	1	5.116139	-2.567834	2.102473
46	6	3.782535	-1.299155	1.033388
47	1	4.574648	-0.838327	0.460631

(c) **$[Tc(ONO)_2]^-$**

Energy of optimized structure = –1415.60087072 a.u.

Cartesian coordinates of the optimized structure:

Centre Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	43	0.000048	0.000063	-0.478584
2	7	-1.877418	-0.435124	0.116132
3	7	1.877603	0.435420	0.115747
4	8	0.196352	-1.796471	0.369847
5	6	-2.077047	-1.574634	0.874989
6	6	-0.858764	-2.297136	1.010330
7	6	-0.810577	-3.486550	1.747025
8	1	0.138332	-4.007574	1.837550
9	6	-1.980862	-3.981273	2.322378
10	1	-1.951595	-4.906921	2.892836
11	6	-3.193920	-3.299649	2.156304
12	1	-4.106356	-3.702639	2.590049
13	6	-3.251965	-2.105214	1.436357
14	1	-4.204424	-1.610195	1.293477
15	8	-1.120584	0.750663	-1.993161
16	6	-2.822568	0.456631	-0.395954
17	6	-2.332596	1.101205	-1.571450
18	6	-3.145997	2.020452	-2.251412
19	1	-2.758328	2.493219	-3.149463
20	6	-4.418157	2.312260	-1.761561
21	1	-5.045645	3.028046	-2.288778
22	6	-4.887017	1.707310	-0.588151
23	1	-5.869013	1.963646	-0.197451
24	6	-4.093483	0.785313	0.098049
25	1	-4.446812	0.359712	1.030162
26	8	1.120363	-0.751117	-1.992964
27	6	2.822621	-0.456632	-0.396075
28	6	2.332396	-1.101611	-1.571276
29	6	3.145588	-2.021189	-2.251034
30	1	2.757712	-2.494241	-3.148850
31	6	4.417793	-2.312961	-1.761273
32	1	5.045122	-3.029015	-2.288320
33	6	4.886904	-1.707614	-0.588180
34	1	5.868945	-1.963896	-0.197550
35	6	4.093593	-0.785263	0.097813
36	1	4.447172	-0.359378	1.029668
37	8	-0.196288	1.796614	0.369692
38	6	2.077216	1.574935	0.874602
39	6	0.858869	2.297386	1.010012
40	6	0.810650	3.486786	1.746732
41	1	-0.138286	4.007751	1.837315
42	6	1.980928	3.981569	2.322030
43	1	1.951633	4.907213	2.892498
44	6	3.194019	3.300007	2.155914
45	1	4.106448	3.703048	2.589630
46	6	3.252112	2.105584	1.435969
47	1	4.204598	1.610651	1.293073

(d) **$Ru(ONO)_2$**

Energy of optimized structure = –1429.55791531 a.u.

Cartesian coordinates of the optimized structure:

Centre Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	44	0.000024	-0.000115	-0.262163
2	7	-1.951127	-0.290515	-0.027919
3	7	1.951188	0.290409	-0.027707
4	8	0.024521	-1.589885	0.992780
5	6	-2.314325	-1.334072	0.785012
6	6	-1.163976	-2.015623	1.323002
7	6	-1.345121	-3.128894	2.179940
8	1	-0.464036	-3.618555	2.581731
9	6	-2.622313	-3.563459	2.465410
10	1	-2.765069	-4.420025	3.118535
11	6	-3.754791	-2.927402	1.898249
12	1	-4.746813	-3.319739	2.100418
13	6	-3.611830	-1.831197	1.072238
14	1	-4.483592	-1.397037	0.602430
15	8	-0.724242	1.174011	-1.792538
16	6	-2.731351	0.687165	-0.620257
17	6	-1.987590	1.445640	-1.595520
18	6	-2.659993	2.444296	-2.339502
19	1	-2.098692	2.989719	-3.091121
20	6	-3.989560	2.717368	-2.077930
21	1	-4.495710	3.495300	-2.643776
22	6	-4.696762	2.026017	-1.067941
23	1	-5.725643	2.293473	-0.848078
24	6	-4.077209	1.024088	-0.344106
25	1	-4.610415	0.538444	0.462333
26	8	0.724482	-1.174530	-1.792166
27	6	2.731548	-0.687191	-0.619994
28	6	1.987887	-1.445889	-1.595157
29	6	2.660362	-2.444573	-2.339030
30	1	2.099063	-2.990180	-3.090519
31	6	3.989992	-2.717399	-2.077567
32	1	4.496220	-3.495321	-2.643358
33	6	4.697161	-2.025771	-1.067756
34	1	5.726125	-2.292978	-0.847976
35	6	4.077507	-1.023860	-0.343988
36	1	4.610782	-0.538039	0.462304
37	8	-0.024735	1.589943	0.992422
38	6	2.314190	1.334133	0.785169
39	6	1.163699	2.015749	1.322798
40	6	1.344599	3.129195	2.179560
41	1	0.463390	3.618888	2.581045
42	6	2.621704	3.563869	2.465269
43	1	2.764272	4.420560	3.118276
44	6	3.754332	2.927728	1.898501
45	1	4.746301	3.320100	2.100862
46	6	3.611602	1.831369	1.072646
47	1	4.483544	1.397174	0.603183

(e) $Ru(DOPO)_2$

Energy of optimized structure = –1577.59515354 a.u.

Cartesian coordinates of the optimized structure:

Centre Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	44	0.000000	0.000000	0.000000
2	7	0.000000	0.000000	1.938067
3	8	0.000000	0.000000	4.719087
4	8	0.000000	2.098134	0.471492
5	6	0.000000	1.162691	2.609218
6	6	0.000000	2.311256	1.755737
7	6	0.000000	3.559354	2.424550
8	1	0.000000	4.481437	1.853674
9	6	0.000000	3.574765	3.817288
10	1	0.000000	4.541312	4.315331
11	6	0.000000	2.420822	4.644021
12	1	0.000000	2.502343	5.724259
13	6	0.000000	1.189824	4.020426
14	8	0.000000	-2.098134	0.471492
15	6	0.000000	-1.162691	2.609218
16	6	0.000000	-2.311256	1.755737
17	6	0.000000	-3.559354	2.424550
18	1	0.000000	-4.481437	1.853674
19	6	0.000000	-3.574765	3.817288
20	1	0.000000	-4.541312	4.315331
21	6	0.000000	-2.420822	4.644021
22	1	0.000000	-2.502343	5.724259
23	6	0.000000	-1.189824	4.020426
24	7	0.000000	0.000000	-1.938067
25	8	0.000000	0.000000	-4.719087
26	8	-2.098134	0.000000	-0.471492
27	6	-1.162691	0.000000	-2.609218
28	6	-2.311256	0.000000	-1.755737
29	6	-3.559354	0.000000	-2.424550
30	1	-4.481437	0.000000	-1.853674
31	6	-3.574765	0.000000	-3.817288
32	1	-4.541312	0.000000	-4.315331
33	6	-2.420822	0.000000	-4.644021
34	1	-2.502343	0.000000	-5.724259
35	6	-1.189824	0.000000	-4.020426
36	8	2.098134	0.000000	-0.471492
37	6	1.162691	0.000000	-2.609218
38	6	2.311256	0.000000	-1.755737
39	6	3.559354	0.000000	-2.424550
40	1	4.481437	0.000000	-1.853674
41	6	3.574765	0.000000	-3.817288
42	1	4.541312	0.000000	-4.315331
43	6	2.420822	0.000000	-4.644021
44	1	2.502343	0.000000	-5.724259
45	6	1.189824	0.000000	-4.020426

(f) **$[Rh(ONO)_2]^+$**

Energy of optimized structure = –1444.98299077 a.u.

Cartesian coordinates of the optimized structure:

Centre Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	45	-0.000042	-0.000221	-0.000026
2	7	-2.006408	-0.000054	-0.000171
3	7	2.006390	-0.000097	0.000194
4	8	-0.263740	-1.432516	1.433231
5	6	-2.534265	-0.977333	0.777712
6	6	-1.523845	-1.700309	1.558063
7	6	-1.954282	-2.701577	2.473867
8	1	-1.199522	-3.208088	3.065377
9	6	-3.287199	-3.012849	2.564982
10	1	-3.609156	-3.787892	3.254472
11	6	-4.266452	-2.362772	1.751196
12	1	-5.303281	-2.675311	1.815677
13	6	-3.905625	-1.369654	0.880441
14	1	-4.651144	-0.925378	0.236402
15	8	-0.263256	1.432533	-1.432937
16	6	-2.533964	0.977283	-0.778126
17	6	-1.523295	1.700363	-1.558088
18	6	-1.953443	2.701834	-2.473824
19	1	-1.198493	3.208422	-3.065024
20	6	-3.286315	3.013162	-2.565270
21	1	-3.608055	3.788338	-3.254713
22	6	-4.265829	2.362962	-1.751869
23	1	-5.302630	2.675542	-1.816600
24	6	-3.905285	1.369695	-0.881178
25	1	-4.651007	0.925338	-0.237430
26	8	0.263791	-1.432164	-1.433560
27	6	2.534260	-0.977223	-0.777820
28	6	1.523880	-1.699955	-1.558409
29	6	1.954377	-2.700986	-2.474432
30	1	1.199672	-3.207321	-3.066163
31	6	3.287296	-3.012292	-2.565466
32	1	3.609291	-3.787172	-3.255122
33	6	4.266493	-2.362521	-1.751371
34	1	5.303299	-2.675153	-1.815767
35	6	3.905609	-1.369602	-0.880413
36	1	4.650998	-0.925564	-0.236078
37	8	0.263286	1.431983	1.433415
38	6	2.533949	0.977156	0.778222
39	6	1.523294	1.699935	1.558509
40	6	1.953487	2.701161	2.474496
41	1	1.198593	3.207496	3.065983
42	6	3.286341	3.012623	2.565766
43	1	3.608114	3.787639	3.255372
44	6	4.265793	2.362828	1.751952
45	1	5.302547	2.675598	1.816532
46	6	3.905234	1.369751	0.881054
47	1	4.650823	0.925719	0.236952

(g) **$[Re(ONO)_2]^+$**

Energy of optimized structure = –1412.79441304 a.u.

Cartesian coordinates of the optimized structure:

Centre Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	75	0.000000	0.000000	0.000000
2	7	0.000000	0.000000	2.030141
3	7	0.000000	0.000000	-2.030141
4	8	-1.359147	1.357123	0.392067
5	6	-0.825989	0.948466	2.646433
6	6	-1.584070	1.667718	1.678260
7	6	-2.499188	2.657178	2.042419
8	1	-3.062390	3.171766	1.271525
9	6	-2.640238	2.958347	3.391928
10	1	-3.341942	3.726904	3.700194
11	6	-1.866155	2.293715	4.359087
12	1	-1.966006	2.564673	5.405066
13	6	-0.962252	1.299565	4.002728
14	1	-0.356131	0.846729	4.771945
15	8	1.359147	-1.357123	0.392067
16	6	0.825989	-0.948466	2.646433
17	6	1.584070	-1.667718	1.678260
18	6	2.499188	-2.657178	2.042419
19	1	3.062390	-3.171766	1.271525
20	6	2.640238	-2.958347	3.391928
21	1	3.341942	-3.726904	3.700194
22	6	1.866155	-2.293715	4.359087
23	1	1.966006	-2.564673	5.405066
24	6	0.962252	-1.299565	4.002728
25	1	0.356131	-0.846729	4.771945
26	8	1.359147	1.357123	-0.392067
27	6	0.825989	0.948466	-2.646433
28	6	1.584070	1.667718	-1.678260
29	6	2.499188	2.657178	-2.042419
30	1	3.062390	3.171766	-1.271525
31	6	2.640238	2.958347	-3.391928
32	1	3.341942	3.726904	-3.700194
33	6	1.866155	2.293715	-4.359087
34	1	1.966006	2.564673	-5.405066
35	6	0.962252	1.299565	-4.002728
36	1	0.356131	0.846729	-4.771945
37	8	-1.359147	-1.357123	-0.392067
38	6	-0.825989	-0.948466	-2.646433
39	6	-1.584070	-1.667718	-1.678260
40	6	-2.499188	-2.657178	-2.042419
41	1	-3.062390	-3.171766	-1.271525
42	6	-2.640238	-2.958347	-3.391928
43	1	-3.341942	-3.726904	-3.700194
44	6	-1.866155	-2.293715	-4.359087
45	1	-1.966006	-2.564673	-5.405066
46	6	-0.962252	-1.299565	-4.002728
47	1	-0.356131	-0.846729	-4.771945

(h) $[Re(ONO)_2]^-$ minimum-energy (C_2) structure

Energy of optimized structure = –1413.10935399 a.u.

Cartesian coordinates of the optimized structure:

Centre Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	75	-0.000002	0.000013	-0.425483
2	7	1.883075	0.409134	0.211206
3	7	-1.883079	-0.409070	0.211294
4	8	-0.165262	1.827498	0.356597
5	6	2.088273	1.571112	0.944193
6	6	0.887641	2.325684	1.022469
7	6	0.840317	3.534084	1.719582
8	1	-0.098789	4.078505	1.762501
9	6	2.003770	4.020414	2.320778
10	1	1.977051	4.962347	2.863862
11	6	3.202130	3.306420	2.213972
12	1	4.109778	3.698013	2.667910
13	6	3.254672	2.089084	1.528880
14	1	4.198565	1.566582	1.436089
15	8	1.153550	-0.735317	-1.927536
16	6	2.840273	-0.473966	-0.308124
17	6	2.368644	-1.098269	-1.498603
18	6	3.185165	-2.003453	-2.186482
19	1	2.807696	-2.458493	-3.098011
20	6	4.452738	-2.306331	-1.686689
21	1	5.085809	-3.013167	-2.219084
22	6	4.906192	-1.721688	-0.498979
23	1	5.884363	-1.982541	-0.101544
24	6	4.103692	-0.810983	0.194887
25	1	4.447270	-0.400498	1.137437
26	8	-1.153615	0.735314	-1.927591
27	6	-2.840315	0.473925	-0.308151
28	6	-2.368716	1.098229	-1.498653
29	6	-3.185279	2.003393	-2.186508
30	1	-2.807852	2.458444	-3.098047
31	6	-4.452850	2.306248	-1.686680
32	1	-5.085947	3.013075	-2.219057
33	6	-4.906255	1.721615	-0.498951
34	1	-5.884413	1.982467	-0.101483
35	6	-4.103710	0.810941	0.194910
36	1	-4.447193	0.400529	1.137481
37	8	0.165194	-1.827593	0.356271
38	6	-2.088230	-1.571118	0.944220
39	6	-0.887615	-2.325707	1.022352
40	6	-0.840224	-3.534065	1.719535
41	1	0.098877	-4.078500	1.762372
42	6	-2.003610	-4.020333	2.320915
43	1	-1.976837	-4.962235	2.864066
44	6	-3.201975	-3.306337	2.214195
45	1	-4.109570	-3.697882	2.668275
46	6	-3.254578	-2.089035	1.529045
47	1	-4.198438	-1.566494	1.436369

(i) $[Re(ONO)_2]^-$ constrained to D_2 symmetry

Energy of optimized structure = –1413.06961135 a.u.

Cartesian coordinates of the optimized structure:

Centre Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	75	0.000000	0.000000	0.000000
2	7	0.000000	0.000000	2.033481
3	7	0.000000	0.000000	-2.033481
4	8	-1.453452	1.366818	0.478627
5	6	-0.770632	0.986313	2.678884
6	6	-1.584768	1.694222	1.746063
7	6	-2.460495	2.698131	2.194474
8	1	-3.087032	3.204461	1.465824
9	6	-2.478237	3.041723	3.543187
10	1	-3.147403	3.827794	3.887250
11	6	-1.623339	2.404845	4.452537
12	1	-1.611406	2.706839	5.496746
13	6	-0.769928	1.385508	4.024522
14	1	-0.080871	0.944294	4.731807
15	8	1.453452	-1.366818	0.478627
16	6	0.770632	-0.986313	2.678884
17	6	1.584768	-1.694222	1.746063
18	6	2.460495	-2.698131	2.194474
19	1	3.087032	-3.204461	1.465824
20	6	2.478237	-3.041723	3.543187
21	1	3.147403	-3.827794	3.887250
22	6	1.623339	-2.404845	4.452537
23	1	1.611406	-2.706839	5.496746
24	6	0.769928	-1.385508	4.024522
25	1	0.080871	-0.944294	4.731807
26	8	1.453452	1.366818	-0.478627
27	6	0.770632	0.986313	-2.678884
28	6	1.584768	1.694222	-1.746063
29	6	2.460495	2.698131	-2.194474
30	1	3.087032	3.204461	-1.465824
31	6	2.478237	3.041723	-3.543187
32	1	3.147403	3.827794	-3.887250
33	6	1.623339	2.404845	-4.452537
34	1	1.611406	2.706839	-5.496746
35	6	0.769928	1.385508	-4.024522
36	1	0.080871	0.944294	-4.731807
37	8	-1.453452	-1.366818	-0.478627
38	6	-0.770632	-0.986313	-2.678884
39	6	-1.584768	-1.694222	-1.746063
40	6	-2.460495	-2.698131	-2.194474
41	1	-3.087032	-3.204461	-1.465824
42	6	-2.478237	-3.041723	-3.543187
43	1	-3.147403	-3.827794	-3.887250
44	6	-1.623339	-2.404845	-4.452537
45	1	-1.611406	-2.706839	-5.496746
46	6	-0.769928	-1.385508	-4.024522
47	1	-0.080871	-0.944294	-4.731807

(j) $Os(ONO)_2$ minimum-energy (C_2) structure

Energy of optimized structure = –1425.37051482 a.u.

Cartesian coordinates of the optimized structure:

Centre Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	76	0.000059	-0.000010	-0.344421
2	7	1.898557	0.407344	0.104769
3	7	-1.898447	-0.407311	0.104771
4	8	-0.173482	1.754567	0.586096
5	6	2.147019	1.541923	0.860874
6	6	0.943945	2.254394	1.114472
7	6	0.953533	3.446278	1.853413
8	1	0.016128	3.961966	2.034639
9	6	2.167446	3.934694	2.315917
10	1	2.191744	4.857812	2.887833
11	6	3.369244	3.257546	2.035557
12	1	4.312317	3.671019	2.380411
13	6	3.371809	2.072032	1.313051
14	1	4.309276	1.588882	1.072862
15	8	0.985453	-0.911256	-1.862694
16	6	2.795155	-0.539144	-0.398712
17	6	2.220288	-1.250772	-1.492278
18	6	2.968934	-2.228777	-2.164317
19	1	2.519163	-2.750561	-3.002693
20	6	4.259207	-2.507507	-1.730983
21	1	4.843378	-3.265492	-2.245614
22	6	4.812095	-1.840642	-0.623375
23	1	5.808665	-2.099432	-0.278543
24	6	4.087952	-0.862340	0.047988
25	1	4.504285	-0.390613	0.929046
26	8	-0.985578	0.910934	-1.863083
27	6	-2.795054	0.539119	-0.398795
28	6	-2.220291	1.250596	-1.492522
29	6	-2.969012	2.228588	-2.164534
30	1	-2.519350	2.750267	-3.003036
31	6	-4.259192	2.507431	-1.731017
32	1	-4.843401	3.265400	-2.245628
33	6	-4.811946	1.840729	-0.623225
34	1	-5.808424	2.099656	-0.278235
35	6	-4.087751	0.862458	0.048110
36	1	-4.503955	0.390814	0.929381
37	8	0.173503	-1.754604	0.586453
38	6	-2.147024	-1.541859	0.860844
39	6	-0.943983	-2.254312	1.114735
40	6	-0.953752	-3.446117	1.853831
41	1	-0.016394	-3.961797	2.035321
42	6	-2.167770	-3.934491	2.316080
43	1	-2.192198	-4.857557	2.888075
44	6	-3.369528	-3.257405	2.035336
45	1	-4.312680	-3.670887	2.379965
46	6	-3.371930	-2.071965	1.312726
47	1	-4.309375	-1.588825	1.072190

(k) $Os(ONO)_2$ constrained to D_2 symmetry

Energy of optimized structure = –1425.35423815 a.u.

Cartesian coordinates of the optimized structure:

Centre Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	76	0.000000	0.000000	0.000000
2	7	0.000000	0.000000	1.997827
3	7	0.000000	0.000000	-1.997827
4	8	-1.463952	1.403593	0.385371
5	6	-0.783948	0.972778	2.607654
6	6	-1.588522	1.687479	1.653703
7	6	-2.487255	2.681528	2.106521
8	1	-3.106123	3.188123	1.373281
9	6	-2.528639	3.000971	3.449133
10	1	-3.208068	3.775908	3.794034
11	6	-1.676792	2.361219	4.378823
12	1	-1.686104	2.667722	5.420119
13	6	-0.814030	1.362601	3.968355
14	1	-0.128473	0.930270	4.682807
15	8	1.463952	-1.403593	0.385371
16	6	0.783948	-0.972778	2.607654
17	6	1.588522	-1.687479	1.653703
18	6	2.487255	-2.681528	2.106521
19	1	3.106123	-3.188123	1.373281
20	6	2.528639	-3.000971	3.449133
21	1	3.208068	-3.775908	3.794034
22	6	1.676792	-2.361219	4.378823
23	1	1.686104	-2.667722	5.420119
24	6	0.814030	-1.362601	3.968355
25	1	0.128473	-0.930270	4.682807
26	8	1.463952	1.403593	-0.385371
27	6	0.783948	0.972778	-2.607654
28	6	1.588522	1.687479	-1.653703
29	6	2.487255	2.681528	-2.106521
30	1	3.106123	3.188123	-1.373281
31	6	2.528639	3.000971	-3.449133
32	1	3.208068	3.775908	-3.794034
33	6	1.676792	2.361219	-4.378823
34	1	1.686104	2.667722	-5.420119
35	6	0.814030	1.362601	-3.968355
36	1	0.128473	0.930270	-4.682807
37	8	-1.463952	-1.403593	-0.385371
38	6	-0.783948	-0.972778	-2.607654
39	6	-1.588522	-1.687479	-1.653703
40	6	-2.487255	-2.681528	-2.106521
41	1	-3.106123	-3.188123	-1.373281
42	6	-2.528639	-3.000971	-3.449133
43	1	-3.208068	-3.775908	-3.794034
44	6	-1.676792	-2.361219	-4.378823
45	1	-1.686104	-2.667722	-5.420119
46	6	-0.814030	-1.362601	-3.968355
47	1	-0.128473	-0.930270	-4.682807

(l) $Os(DOPO)_2$

Energy of optimized structure = –1573.39276804 a.u.

Cartesian coordinates of the optimized structure:

Centre Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	76	0.000000	0.000000	0.000000
2	7	0.000000	0.000000	1.945096
3	8	0.000000	0.000000	4.740787
4	8	0.000000	2.082279	0.491457
5	6	0.000000	1.165418	2.631643
6	6	0.000000	2.308296	1.785260
7	6	0.000000	3.556680	2.442331
8	1	0.000000	4.477073	1.868805
9	6	0.000000	3.575359	3.838101
10	1	0.000000	4.542693	4.334226
11	6	0.000000	2.423293	4.661046
12	1	0.000000	2.502714	5.741553
13	6	0.000000	1.188390	4.037502
14	8	0.000000	-2.082279	0.491457
15	6	0.000000	-1.165418	2.631643
16	6	0.000000	-2.308296	1.785260
17	6	0.000000	-3.556680	2.442331
18	1	0.000000	-4.477073	1.868805
19	6	0.000000	-3.575359	3.838101
20	1	0.000000	-4.542693	4.334226
21	6	0.000000	-2.423293	4.661046
22	1	0.000000	-2.502714	5.741553
23	6	0.000000	-1.188390	4.037502
24	7	0.000000	0.000000	-1.945096
25	8	0.000000	0.000000	-4.740787
26	8	-2.082279	0.000000	-0.491457
27	6	-1.165418	0.000000	-2.631643
28	6	-2.308296	0.000000	-1.785260
29	6	-3.556680	0.000000	-2.442331
30	1	-4.477073	0.000000	-1.868805
31	6	-3.575359	0.000000	-3.838101
32	1	-4.542693	0.000000	-4.334226
33	6	-2.423293	0.000000	-4.661046
34	1	-2.502714	0.000000	-5.741553
35	6	-1.188390	0.000000	-4.037502
36	8	2.082279	0.000000	-0.491457
37	6	1.165418	0.000000	-2.631643
38	6	2.308296	0.000000	-1.785260
39	6	3.556680	0.000000	-2.442331
40	1	4.477073	0.000000	-1.868805
41	6	3.575359	0.000000	-3.838101
42	1	4.542693	0.000000	-4.334226
43	6	2.423293	0.000000	-4.661046
44	1	2.502714	0.000000	-5.741553
45	6	1.188390	0.000000	-4.037502

(m) **$[Ir(ONO)_2]^+$**

Energy of optimized structure = –1438.79213747 a.u.

Cartesian coordinates of the optimized structure:

Centre Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	77	0.000012	-0.000200	-0.000137
2	7	-2.011089	-0.000253	-0.000195
3	7	2.011122	0.000005	0.000199
4	8	-0.296095	-1.438298	1.447213
5	6	-2.557508	-0.983016	0.771541
6	6	-1.562741	-1.709110	1.560074
7	6	-2.001098	-2.709897	2.466416
8	1	-1.254445	-3.218755	3.066162
9	6	-3.337110	-3.021182	2.539654
10	1	-3.667767	-3.797830	3.223145
11	6	-4.302643	-2.370699	1.714191
12	1	-5.340184	-2.684049	1.760183
13	6	-3.928183	-1.374207	0.850535
14	1	-4.663270	-0.932394	0.193478
15	8	-0.295992	1.438123	-1.447434
16	6	-2.557466	0.982709	-0.771878
17	6	-1.562666	1.708979	-1.560196
18	6	-2.001022	2.709989	-2.466283
19	1	-1.254349	3.219011	-3.065866
20	6	-3.337044	3.021284	-2.539513
21	1	-3.667664	3.798110	-3.222822
22	6	-4.302605	2.370587	-1.714268
23	1	-5.340158	2.683893	-1.760249
24	6	-3.928133	1.373895	-0.850831
25	1	-4.663243	0.931878	-0.193929
26	8	0.296390	-1.438466	-1.447298
27	6	2.557695	-0.982802	-0.771412
28	6	1.563116	-1.709102	-1.559910
29	6	2.001690	-2.710008	-2.465980
30	1	1.255143	-3.219084	-3.065672
31	6	3.337751	-3.021154	-2.539081
32	1	3.668528	-3.797913	-3.222387
33	6	4.303123	-2.370396	-1.713713
34	1	5.340728	-2.683550	-1.759599
35	6	3.928417	-1.373809	-0.850262
36	1	4.663401	-0.931775	-0.193272
37	8	0.295681	1.438499	1.446795
38	6	2.557325	0.983056	0.771895
39	6	1.562286	1.709390	1.559924
40	6	2.000329	2.710527	2.466074
41	1	1.253461	3.219530	3.065430
42	6	3.336297	3.021922	2.539581
43	1	3.666729	3.798821	3.222897
44	6	4.302101	2.371197	1.714574
45	1	5.339613	2.684613	1.760760
46	6	3.927955	1.374401	0.851131
47	1	4.663275	0.932458	0.194449

References

S1 S. Shekar and S. N. Brown, *Organometallics*, 2013, **32**, 556-564.

S2 B. R. McGarvey, A. Ozarowski, Z. Tian and D. G. Tuck, *Can. J. Chem.*, 1995, **73**, 1213-1222.

S3 A. J. Godó, A. C. Bényei, B. Duff, D. A. Egan and P. Buglyó, *RSC Advances*, 2012, **2**, 1486-1495.

S4 L. G. Ranis, K. Werellapatha, N. J. Pietrini, B. A. Bunker and S. N. Brown, submitted.

S5 N. G. Connelly and W. E. Geiger, *Chem. Rev.*, 1996, **96**, 877-910.

S6 D. Lionetti, A. J. Medvecz, V. Ugrinova, M. Quiroz-Guzman, B. C. Noll and S. N. Brown, *Inorg. Chem.*, 2010, **49**, 4687-4697.

S7 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Gaussian 09, Revision A.02*, Gaussian, Inc., Wallingford CT, 2009.

S8 C. L. Simpson, S. R. Boone and C. G. Pierpont, *Inorg. Chem.*, 1989, **28**, 4379-4385.

S9 G. M. Sheldrick, *Acta Cryst. A*, 2008, **A64**, 112-122.

S10 *International Tables for Crystallography*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1992, Vol C.

S11 P. van der Sluis and A. L. Spek, *Acta Cryst. A*, 1990, **A46**, 194-201.

S12 A. L. Spek, *Acta Cryst. D*, 2009, **D65**, 148-155.