Electronic Supplementary Information

Structural Isomers and Low-Lying Electronic States of Gas–Phase $M^+(N_2O)_n$ (M = Co, Rh, Ir) Ion–Molecule Complexes

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Contents

Computational Methodology

To support assignment and interpretation of the experimental IR-REPD spectra, density functional theory and harmonic vibrational frequency calculations are performed using the B3P86 hybrid density functional[1] coupled with the Def2TZVP basis set[2,3] using the Gaussian09 suite of programs.[4] Each structure shown below has been geometry optimised with each figure showing Cartesian coordinates. The calculated energies of each structure relative to the putative global minimum are given, inclusive of zero point energy.

In every case the fully N-bound geometries are the global minimum structures, the energies of the higher local minima increase upon addition of an O–bound nitrous oxide molecule.

In common with the main article, isomeric structures with *x* N–bound ligands and *y* O–bound ligands are labelled N^xO^y structures.

Structures and Cartesian coordinates of complexes occupying a higher multiplicity other than the ground state are available upon request.

A. $Co^+(N_2O)_n$ Calculated Structures

Atom labels for the structures that follow:
Light Blue: Cobalt (Co^+)
Blue: Nitrogen (N)
Red: Oxygen (O)

Structures occupying the ground-state multiplicity are shown here, along with Cartesian coordinates.

i. $Co^+(N_2O)$

N	0.02176500	-1.63457000	0.00000000
N	0.00000000	-0.51069400	0.00000000
Co	-0.01810100	1.38222200	0.00000000
O	0.04204600	-2.78789200	0.00000000

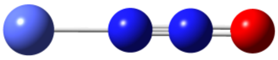

Fig. S1 N-bound global minimum structure of the triplet $Co^+(N_2O)$ molecule.

Co	0.00000000	1.30404400	0.00000000
N	0.05729500	-1.66662600	0.00000000
N	0.54944100	-2.65980400	0.00000000
O	-0.53089400	-0.61552100	0.00000000

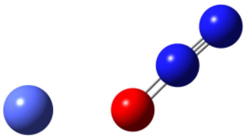

Fig. S2 Lowest energy O-bound minimum structure of the triplet $Co^+(N_2O)$ molecule at $E_{rel.}$ = 0.54 eV.

ii. $Co^+(N_2O)_2$

N	0.72127600	-0.33023600	0.00024400
N	1.80809000	-0.61582000	0.00005200
O	-0.39604600	-0.03727700	0.00044200
Co	3.63474600	-1.10082100	-0.00028300
N	6.54466400	-1.88095500	-0.00084200
N	5.46018500	-1.58657600	-0.00060400
O	7.65994900	-2.18164600	-0.00106800

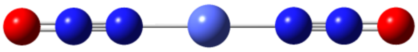

Fig. S3 Putative global minimum of the doubly N-bound, N^2, triplet structure of $Co^+(N_2O)_2$.

N	-0.81187800	-0.32391100	-0.00601400
N	0.31071600	-0.38060800	-0.00906300
O	-1.96537200	-0.26961600	-0.00220400
Co	2.18283600	-0.58098400	0.00088600
N	5.13161800	-0.43831600	0.00300900
N	6.11134500	0.07988400	-0.03335500
O	4.10068700	-1.05687500	0.04755100

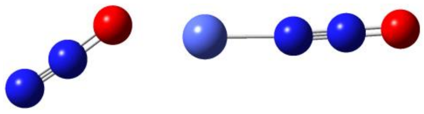

Fig. S4 Lowest energy minima of the N^1O^1 triplet structure of $Co^+(N_2O)_2$ at $E_{rel.}$ = 0.85 eV.

N	-2.01454400	0.06587500	-0.12398800
Co	0.90505500	-0.16282100	-0.06835800
N	3.82453600	-0.39101700	-0.00591200
N	4.78137900	-0.94707100	0.05956700
O	2.81880600	0.26804700	-0.08170800
N	-2.97147800	0.62220400	-0.18568000
O	-1.00871700	-0.59350500	-0.05233300

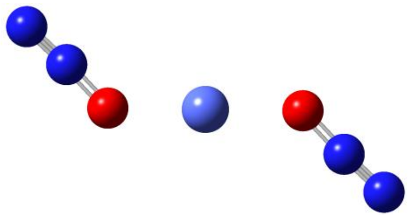

Fig. S5 Lowest energy minima of the O^2 triplet structure of $Co^+(N_2O)_2$ at $E_{rel.}$ = 1.01 eV.

iii. $Co^+(N_2O)_3$

N	0.70029700	-0.60950700	-0.09697600
N	1.81827700	-0.58285800	0.01323900
O	-0.45185500	-0.63367900	-0.20944500
Co	3.74448700	-0.69371800	0.14980600
N	6.42548800	-2.13774300	-0.09954300
N	5.46965800	-1.55741800	0.01161100
O	7.41218700	-2.73293100	-0.21295200
N	4.50558400	2.15594700	1.19032800
N	4.23232000	1.13298000	0.81700700
O	4.78782000	3.21251500	1.57595100

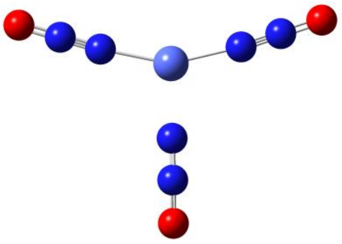

Fig. S6 The putative global minimum of the N^3 triplet structure of $Co^+(N_2O)_3$.

N	3.21792400	-0.50727300	0.00035700
N	2.09530600	-0.46882100	0.00034400
O	4.37510400	-0.54605600	0.00090300
N	-2.71374300	-1.34198000	0.00078900
N	-1.66089300	-0.94683800	-0.00050300
O	-3.80065700	-1.74155400	0.00133100
Co	0.18490100	-0.47941900	-0.00136600
N	-0.80080300	2.50616600	0.00020500
N	-1.61859500	3.25957500	-0.00098700
O	0.09721700	1.71742500	0.00219800

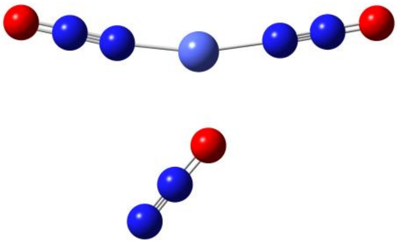

Fig. S7 The lowest minimum N^2O^1 triplet structure of $Co^+(N_2O)_3$ at $E_{rel.}$ = 0.27 eV

N	-0.90245000	-0.54076900	0.00162200
N	0.19843300	-0.31413900	0.00347000
O	-2.03849200	-0.76947500	-0.00027000
Co	2.10791700	-0.09134700	0.00588000
N	5.11533800	-0.54401100	0.00514600
N	6.16881800	-0.19207800	0.00747700
O	3.99157700	-0.95911800	0.00246700
N	2.61523700	2.95540200	0.02544800
N	2.46472100	1.84161700	0.01829000
O	2.77307400	4.10452300	0.03283700

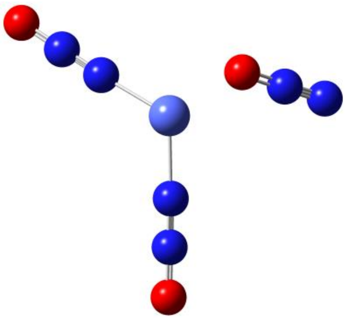

Fig. S8 A higher energy minimum N^2O^1, triplet structure of $Co^+(N_2O)_3$ at $E_{rel.}$ = 0.38 eV.

N	-1.09221300	2.47428300	-0.00274700
N	-1.97687700	3.14761900	0.00027700
O	-0.12073700	1.77723900	-0.00271600
N	3.20377000	-0.40397000	-0.00097900
N	2.08073000	-0.36175700	0.00010800
O	4.36291100	-0.44471200	-0.00201500
Co	0.19260200	-0.36584200	0.00206600
N	-2.52002400	-1.65754100	-0.00059600
N	-3.20164600	-2.53392900	-0.00696900
O	-1.82422800	-0.67942600	0.00729900

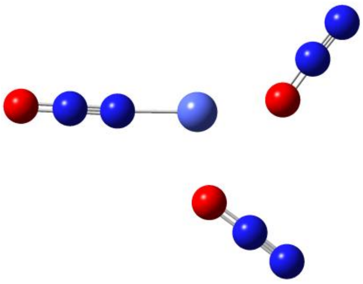

Fig. S9 The lowest minimum N^1O^2 triplet structure of $Co^+(N_2O)_3$ at $E_{rel.}$ = 0.70 eV.

N	-2.20855600	-0.30829000	-0.11628500
Co	0.71710200	0.12158300	-0.07275100
N	3.68502100	-0.09981400	-0.01587600
N	4.63397900	-0.67383500	0.02169100
O	2.68452900	0.56577000	-0.05791800
N	-3.25337700	0.06373700	-0.15431500
O	-1.09497700	-0.75700800	-0.07366700
N	0.49280300	3.21247500	-0.20559600
N	0.95533400	4.22245600	-0.24309000
O	-0.03059600	2.13747300	-0.16580800

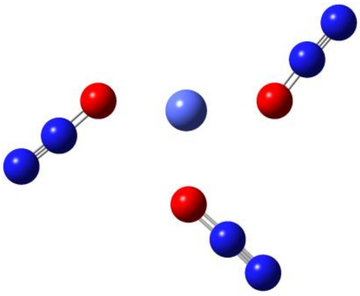

Fig. S10 The lowest minimum O^3 triplet structure of $Co^+(N_2O)_3$ at $E_{rel.}$ = 1.22 eV.

iv. $Co^+(N_2O)_4$

N	-2.74607900	-0.29554500	-1.48822400
N	-1.73179700	-0.21381900	-1.00998500
O	-3.79507600	-0.37964900	-1.97649700
Co	0.13020300	-0.14109300	-0.43318100
N	0.43427200	2.83045000	0.50415200
O	0.57413800	3.93439600	0.83801800
N	0.29703300	1.76346700	0.18316100
N	3.05913600	-1.04603200	-0.69846000
N	2.01127100	-0.66617800	-0.55950500
O	4.14261100	-1.43484300	-0.84109500
N	-0.98219800	-1.36153500	2.27248000
O	-0.05845000	-1.17783000	1.54022300
N	-1.83039200	-1.54325000	2.96933900

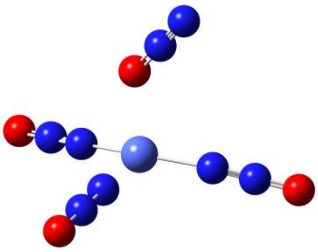

Fig. S11 The putative global minimum N^3O^1 triplet structure of $Co^+(N_2O)_4$.

N	-2.05627800	1.51267700	-1.79515200
N	-1.37506700	0.90935300	-1.13656300
O	-2.75724500	2.13568000	-2.47864600
Co	0.00170400	-0.00098600	-0.01423300
N	2.06813900	-1.64653000	-1.66277500
O	2.76818000	-2.31755400	-2.30019400
N	1.38813100	-0.99730400	-1.04805500
N	-1.72012600	-1.85159400	1.80320900
N	-1.17717000	-1.15149700	1.11259100
O	-2.27858400	-2.57515400	2.51825800
N	1.70649900	1.98652100	1.66975900
O	2.25845300	2.76232900	2.33321300
N	1.16981000	1.23611700	1.02887800

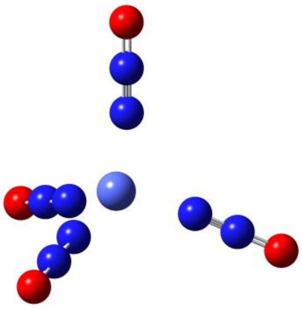

Fig. S12 The lowest minimum N^4 triplet structure of $Co^+(N_2O)_4$ at $E_{rel.}$ = 0.08 eV.

N	-2.88720300	0.75158200	-1.15078100
N	-1.84806600	0.43880900	-0.85727300
O	-3.96178300	1.07056300	-1.45014000
Co	-0.00033100	0.00212100	-0.54922500
N	1.14986400	2.03585700	1.56398500
N	2.89057800	-0.72506100	-1.15919900
N	1.84927600	-0.42396400	-0.86114800
O	3.96731500	-1.03223100	-1.46316400
N	-1.15293000	-2.06616700	1.52724600
O	-0.21049300	-1.65658400	0.91981600
N	-2.01835200	-2.46335700	2.10253500
O	0.20485700	1.62643600	0.96036800
N	2.01822900	2.43476600	2.13378200

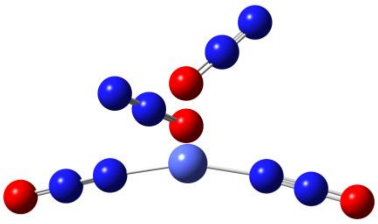

Fig. S13 The lowest minimum N^2O^2 triplet structure of $Co^+(N_2O)_4$ at $E_{rel.}$ = 0.25 eV.

N	2.52959600	-1.82427700	-0.02027100
N	1.60503200	-1.18443600	-0.01134700
O	3.48919500	-2.47620100	-0.02921300
Co	-0.04190000	-0.16669000	-0.00111800
N	-2.10125300	2.06564900	-0.02865300
N	-2.47262600	-2.08049200	0.02290500
N	2.03097000	2.17787900	0.02875100
O	0.88593300	1.83466700	0.02208500
N	3.09117900	2.51219500	0.03361400
O	-1.84259600	0.89518200	-0.02296100
N	-2.37305300	3.14247100	-0.03175300
N	-3.57271500	-2.24100900	0.02959600
O	-1.28610500	-1.93805300	0.01387800

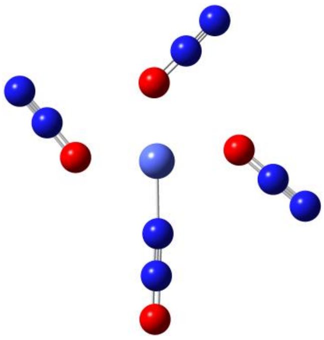

Fig. S14 The lowest minimum N^1O^3 triplet structure of $Co^+(N_2O)_4$ at $E_{rel.}$ = 0.98 eV.

Co	-0.00104800	-0.00064300	-0.45684700
N	2.97381900	0.40501900	-0.92890900
N	0.49604900	-2.52553800	1.22988100
N	-0.49179600	2.52656900	1.22923800
O	0.28307400	1.79501500	0.68691500
N	-1.19285600	3.22179900	1.74087900
O	2.04853300	-0.32762000	-0.73077100
N	3.85298300	1.05932900	-1.11628600
N	1.19941300	-3.21908700	1.74064200
O	-0.28126000	-1.79571400	0.68871200
N	-2.97664700	-0.40512700	-0.92584000
O	-2.05098100	0.32676000	-0.72666200
N	-3.85619900	-1.05870100	-1.11398700

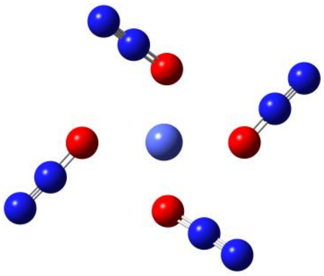

Fig. S15 The lowest minimum O^4 triplet structure of $Co^+(N_2O)_4$ at $E_{rel.}$ = 1.08 eV.

B. $Rh^+(N_2O)_n$ Calculated Structures

Atom labels for the structures that follow:
Turquoise: Rhodium (Rh^+)
Blue: Nitrogen (N)
Red: Oxygen (O)

Structures occupying the ground-state multiplicity are shown here, along with Cartesian coordinates.

i. $Rh^+(N_2O)$

N	0.62579400	-0.40545700	-0.00005200
N	1.74814300	-0.40543800	-0.00003300
O	-0.52838000	-0.40535100	0.00005400
Rh	3.78824100	-0.40537300	0.00003200

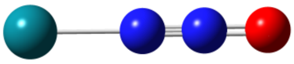

Fig. S16 N-bound global minimum structure of the triplet $Rh^+(N_2O)$ molecule.

N	1.09104400	-1.18302100	-0.77761600
N	0.39522200	-1.79417000	-1.38876500
O	1.81192100	-0.50223500	-0.09682900
Rh	4.02014100	-0.23757700	0.16782800

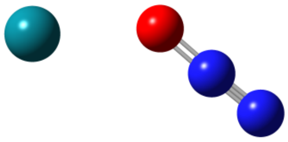

Fig. S17 O-bound minimum structure of the triplet $Rh^+(N_2O)$ molecule at $E_{rel.}$ = 0.62 eV.

ii. $Rh^+(N_2O)_2$

N	0.61998500	-0.40441800	-0.00000400
N	1.74198400	-0.40690700	0.00001500
O	-0.53592000	-0.40185400	-0.00003400
Rh	3.77093400	-0.41143800	0.00002800
N	6.92212900	-0.41750400	0.00007400
N	5.80013500	-0.41526400	0.00005800
O	8.07806400	-0.41974100	0.00008300

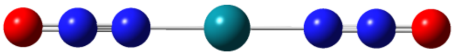

Fig. S18 Putative global minimum doubly N-bound, N^2, structure of triplet $Rh^+(N_2O)_2$.

N	-1.36275300	-0.52916500	0.00176300
N	-0.24958000	-0.38927300	-0.00124200
O	-2.51093600	-0.67299600	0.00487900
N	4.82424200	-0.42723800	0.00047900
N	5.74454700	-1.04725200	0.00982600
O	3.86250600	0.29429500	-0.01008600
Rh	1.75239600	-0.14564800	-0.00528800

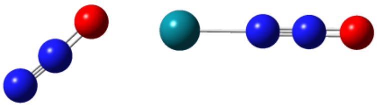

Fig. S19 Minimum N^{1}O^1 geometry of the triplet structure of Rh$^+$(N$_2$O)$_2$ at $E_{\text{rel.}}$ = 0.48 eV.

N	-0.25831500	-0.91426200	0.90517100
N	-0.84074400	-1.64922900	1.50029400
O	0.34905600	-0.08805300	0.28179700
N	4.74213300	-0.61724400	0.15984700
N	5.52108800	-0.25302100	0.86279500
O	3.92593700	-1.04611900	-0.60802400
Rh	1.94307800	-0.27154300	-1.26487200

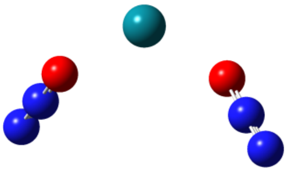

Fig. S20 Minimum O^2 geometry of the triplet structure of Rh$^+$(N$_2$O)$_2$ at $E_{\text{rel.}}$ = 1.16 eV.

iii. Rh$^+$(N$_2$O)$_3$

N	-1.42952400	-0.21497600	-0.00020100
N	-0.31918800	-0.37710400	-0.00005700
O	-2.57637200	-0.04943500	-0.00036000
N	4.89980300	-0.21803400	-0.00034600
O	6.04681400	-0.05362700	-0.00046400
N	3.78931000	-0.37908200	-0.00023100
Rh	1.73497100	-0.59596900	-0.00006400
N	1.73211400	-3.94437000	0.00078700
O	1.73090800	-5.10407700	0.00109700
N	1.73321500	-2.82207000	0.00049100

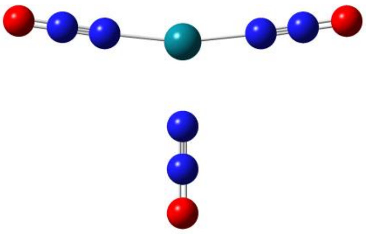

Fig. S21 Putative global minimum N^3 geometry of the triplet structure of Rh$^+$(N$_2$O)$_3$.

N	-1.33884800	-0.49807500	0.00113100
N	-0.21804300	-0.56076300	0.00036900
O	-2.49567700	-0.43973600	0.00117000
N	4.96167500	-0.09946200	0.00102300
O	6.10994300	0.05144200	0.00051400
N	3.84945800	-0.24477200	0.00149500
Rh	1.82178000	-0.50741100	0.00100600
N	1.52948300	-3.84739800	-0.00204100
O	2.25443200	-2.89921400	-0.00133100
N	0.86844200	-4.74268500	-0.00268300

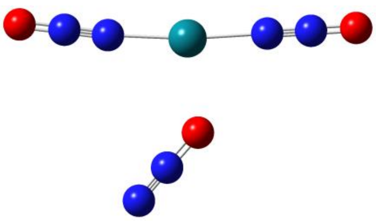

Fig. S22 Lowest energy minimum N^{2}O^1 geometry of the triplet structure of Rh$^+$(N$_2$O)$_3$ at $E_{\text{rel.}}$ = 0.19 eV.

N	-1.47280000	-0.23622200	-0.07665900
N	-0.36071400	-0.36639800	-0.00003300
O	-2.62189000	-0.10302000	-0.15589800
N	4.83992200	-0.76000100	0.38428800
O	3.87338800	-0.05770000	0.30835300
N	5.75673800	-1.38408200	0.45614200
Rh	1.69187900	-0.54662100	0.14303000
N	1.86878200	-3.82707800	0.05106400
O	1.82555100	-4.98497400	0.00961900
N	1.91717500	-2.70567100	0.09174200

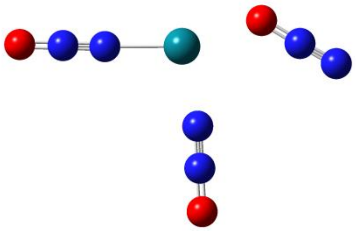

Fig. S23 Higher-lying minimum N^2O^1 geometry of the triplet structure of $Rh^+(N_2O)_3$ at $E_{rel.}$ = 0.40 eV.

N	-1.45922000	-0.26761500	-0.08753500
N	-0.34250900	-0.35703700	-0.01728000
O	-2.61341600	-0.18059400	-0.15947000
N	4.74408100	-0.83842900	0.32651300
O	3.85066600	-0.05627000	0.15693400
N	5.60126000	-1.52761100	0.47966800
Rh	1.68465000	-0.38351800	0.09266300
N	1.52426000	-3.67094200	0.54503400
O	2.20856700	-2.69527900	0.45637600
N	0.90088800	-4.58805800	0.62979700

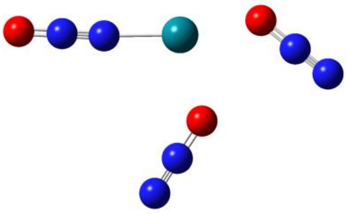

Fig. S24 Lowest energy minimum N^1O^2 geometry of the triplet structure of $Rh^+(N_2O)_3$ at $E_{rel.}$ = 0.62 eV.

N	-0.53531800	0.22061700	-0.18415800
N	-1.00983900	0.76451900	0.66130400
O	-0.04992200	-0.35708100	-1.11263200
N	4.11293000	-0.07428300	0.59066400
O	3.03121500	-0.04443100	0.07898400
N	5.11239500	-0.07725600	1.07724000
Rh	1.91220000	-1.53477100	-1.29128400
N	1.59406100	-4.40826000	0.05403900
O	1.46677900	-5.46802200	0.50769500
N	1.71847200	-3.38079400	-0.38122900

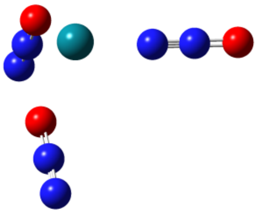

Fig. S25 Higher-lying minimum N^1O^2 geometry of the triplet structure of $Rh^+(N_2O)_3$ at $E_{rel.}$ = 0.80 eV.

N	-0.67011300	0.28808800	-0.16406900
N	-1.09047600	1.26922600	0.14639300
O	-0.24783900	-0.78274900	-0.49286500
N	4.17095500	-0.14894000	0.56475500
O	3.12010100	0.01145400	0.01407200
N	5.14579800	-0.26748700	1.08565800
Rh	1.82809800	-1.42397400	-1.20858800
N	1.26151400	-4.11078900	0.43026200
O	2.07625400	-3.37939200	-0.05363000
N	0.52849000	-4.80889500	0.88969000

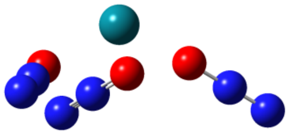

Fig. S26 Lowest energy minimum O^3 geometry of the triplet structure of $Rh^+(N_2O)_3$ at $E_{rel.}$ = 1.19 eV.

iv. Rh$^+$(N$_2$O)$_4$

N	-1.36043500	-0.41384000	-0.00125600
N	-0.24037700	-0.41841100	-0.00119800
O	-2.52215300	-0.40757500	-0.00132100
N	4.84107300	-0.42969700	-0.00085400
O	6.00279400	-0.43186600	-0.00075500
N	3.72100400	-0.42653100	-0.00093200
Rh	1.74025500	-0.42206500	-0.00106500
N	1.73363000	-3.52286100	0.00778400
O	1.73119200	-4.68458900	0.01225000
N	1.73594400	-2.40268400	0.00330900
N	1.74692700	2.67866500	-0.00538200
O	1.74942500	3.84033000	-0.00554600
N	1.74458700	1.55848800	-0.00503100

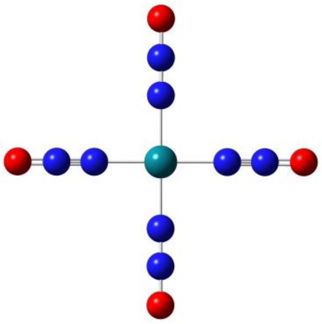

Fig. S27 Putative global minimum N^4 geometry of the singlet structure of Rh$^+$(N$_2$O)$_4$.

N	-1.23436800	-0.27236600	0.03220700
N	-0.11427000	-0.30612300	0.01076700
O	-2.39565000	-0.22995300	0.04890700
N	4.94598700	-0.53667300	0.21387300
O	6.10363700	-0.59421400	0.29866100
N	3.83024800	-0.47480100	0.12704100
Rh	1.85737500	-0.41586200	0.05306000
N	1.73246600	-3.47845400	-0.16016000
O	1.68471500	-4.63813200	-0.24425900
N	1.77807300	-2.36231000	-0.07868100
N	1.99991300	2.44031400	-0.66176100
O	1.94049500	1.69189200	0.27996400
N	2.05570900	3.18425200	-1.48395100

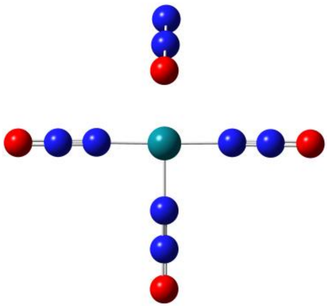

Fig. S28 Lowest energy minimum N^{3}O^1 geometry of the singlet structure of Rh$^+$(N$_2$O)$_4$ at E$_{rel.}$ = 0.48 eV.

N	-1.33942600	-0.27754500	0.74765900
N	-0.24229500	-0.37996800	0.54292800
O	-2.48091900	-0.17968900	0.95560500
N	4.56953700	-0.62622400	0.76478000
O	3.74875000	-0.72437100	-0.11190800
N	5.37571800	-0.54787000	1.52382400
Rh	1.67815600	-0.50142900	0.25489500
N	1.41527400	-3.37927400	-0.27751300
O	1.62792600	-2.58628600	0.60449400
N	1.22503800	-4.16131900	-1.04198900
N	1.85216000	2.52330600	-0.21341200
N	1.80956500	1.42059800	-0.01764100
O	1.90508300	3.66940900	-0.41210100

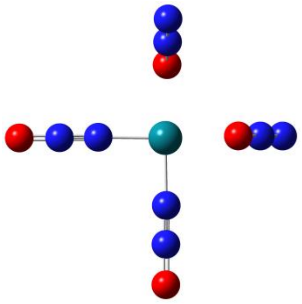

Fig. S29 Lowest energy minimum N^{2}O^2 geometry of the singlet structure of Rh$^+$(N$_2$O)$_4$ at E$_{rel.}$ = 0.95 eV.

N	-0.50606200	-0.80318000	-1.76363600
N	-1.46824500	-0.25884700	-1.65833700
O	0.50385700	-1.43764600	-1.93740000
N	4.96297600	-1.35329400	0.18158300
O	3.95290500	-0.71925400	0.35598600
N	5.92549000	-1.89702600	0.07608800
Rh	2.22847500	-1.07843100	-0.79064500
N	1.29327100	-3.18862700	1.26375900
O	0.94014800	-3.98356600	2.03609900
N	1.63428300	-2.42243300	0.51935300
N	3.16454100	1.03060000	-2.84540600
O	3.51851600	1.82469800	-3.61829700
N	2.82296400	0.26491300	-2.10074700

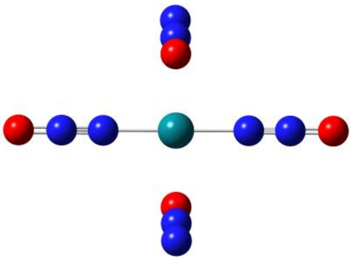

Fig. S30 Higher-lying minimum N^{2}O^2 geometry of the singlet structure of Rh$^+$(N$_2$O)$_4$ at E$_{rel.}$ = 1.02 eV.

N	-1.30385100	-0.17224200	0.96695900
N	-0.21041000	-0.22133900	0.72233600
O	-2.44278100	-0.12071000	1.21092200
N	4.57844400	-0.50091400	0.94645100
O	3.77657500	-0.40697700	0.05151500
N	5.36800600	-0.58763900	1.72188600
Rh	1.70172100	-0.31211900	0.42609100
N	1.41889300	-3.01164000	-0.61340400
O	1.66016400	-2.40612100	0.40065000
N	1.20330300	-3.63287800	-1.50820100
N	1.73194200	2.49131300	-0.34017200
N	1.60029000	3.21759700	-1.16978600
O	1.88895900	1.76606900	0.60986400

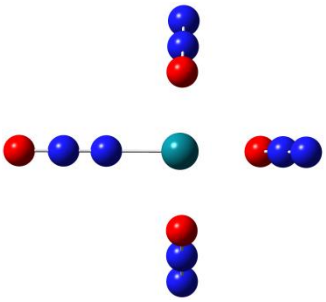

Fig. S31 Lowest energy minimum N^{1}O^3 geometry of the singlet structure of Rh$^+$(N$_2$O)$_4$ at E$_{rel.}$ = 1.49 eV.

N	-0.30862400	-0.02770900	0.43698800
N	-1.26549200	0.52161700	0.31030300
O	0.72008600	-0.61754000	0.65567500
N	3.85790000	0.73270600	-0.31170800
O	2.88858700	0.52926800	-0.99945700
N	4.75430400	0.98934200	0.29161800
Rh	1.90085600	-1.31101100	-0.92328600
N	1.12414600	-4.02072300	-0.26453000
O	0.80551300	-3.09082600	-0.96289100
N	1.35945800	-4.91555000	0.34972400
N	2.93132600	-1.92736600	-3.55703800
N	2.75834500	-1.83747100	-4.65037600
O	3.18852300	-2.06508000	-2.38701600

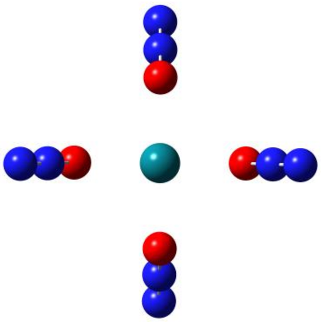

Fig. S32 Lowest energy minimum O^4 geometry of the singlet structure of Rh$^+$(N$_2$O)$_4$ at E$_{rel.}$ = 2.06 eV.

C. $Ir^+(N_2O)_n$ Calculated Structures

Atom labels for the structures that follow:
Dark Blue: Iridium (Ir^+)
Blue: Nitrogen (N)
Red: Oxygen (O)

Structures occupying the ground-state multiplicity are shown here, along with Cartesian coordinates.

i. $Ir^+(N_2O)$

N	0.63183700	-0.40514000	0.00026500
N	1.75391500	-0.40528800	0.00011700
O	-0.52172600	-0.40565100	-0.00024600
Ir	3.68967400	-0.40554300	-0.00013800

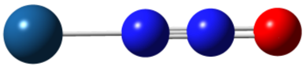

Fig. S33 N-bound global minimum structure of the triplet $Ir^+(N_2O)$ molecule.

N	0.88077500	-1.18573500	-0.78033000
N	0.21115700	-1.80928700	-1.40388200
O	1.54454800	-0.46325000	-0.05784400
Ir	3.61619200	-0.38645100	0.01895400

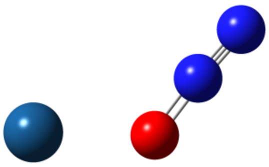

Fig. S34 O-bound minimum structure of the triplet $Ir^+(N_2O)$ molecule at $E_{rel.}$ = 0.36 eV.

ii. $Ir^+(N_2O)_2$

N	0.67955500	-0.40371000	-0.00026700
N	1.80333200	-0.40698400	0.00006600
O	-0.47321300	-0.40033900	-0.00066400
N	6.86235200	-0.41794000	0.00028900
N	5.73850900	-0.41561700	0.00028900
O	8.01513700	-0.42038600	0.00029700
Ir	3.77089100	-0.41155200	0.00022500

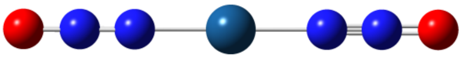

Fig. S35 Putative global minimum N^2 geometry of the triplet structure of $Ir^+(N_2O)_2$.

N	-1.36394000	-0.56471300	0.00231200
N	-0.25025800	-0.40267000	0.00009200
O	-2.50558600	-0.73169900	0.00459900
N	4.58988300	-0.45090800	0.00052500
N	5.48591800	-1.10052400	0.01048100
O	3.66806800	0.34207900	-0.01168400
Ir	1.66527800	-0.10267400	-0.00443500

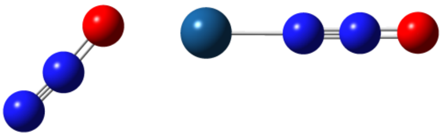

Fig. S36 Minimum N^1O^1 geometry of the triplet structure of $Ir^+(N_2O)_2$ at $E_{rel.}$ = 0.57 eV.

N	-0.60717900	0.21061600	0.20139200
N	0.32611300	0.63017500	-0.22492300
O	-1.57778300	-0.28707300	0.72647500
N	-6.46863400	-0.24456400	-0.02384400
N	-7.40193900	-0.66404400	0.40252100
O	-5.49801900	0.25311200	-0.54891800
Ir	-3.53790400	-0.01700600	0.08877600

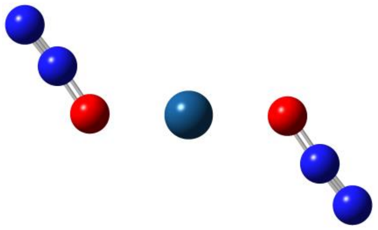

Fig. S37 Minimum O^2 geometry of the triplet structure of Ir$^+$(N$_2$O)$_2$ at E$_{rel.}$ = 1.04 eV.

iii. Ir$^+$(N$_2$O)$_3$

N	0.70545800	-0.38186700	-0.00034600
N	1.82623200	-0.44758000	-0.00028700
O	-0.45230900	-0.29967600	-0.00040400
N	6.84581700	-0.38453800	0.00034000
N	5.72498300	-0.44919300	0.00047400
O	8.00367200	-0.30357700	0.00019100
Ir	3.77556300	-0.54289900	0.00012500
N	3.77409700	-3.55274400	0.00017500
N	3.77482600	-2.43209400	0.00015600
O	3.77277700	-4.71740100	0.00019400

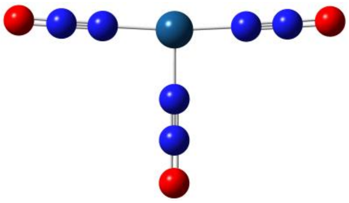

Fig. S38 Putative global minimum N^3 geometry of the singlet structure of Ir$^+$(N$_2$O)$_3$.

N	-1.24636300	-0.48994600	0.19525800
N	-0.13851800	-0.44922300	0.01972800
O	-2.39496500	-0.51397200	0.38099600
N	4.63489500	-0.19790500	0.16207900
N	5.47894500	-0.27612600	0.87597700
O	3.77872900	-0.08753800	-0.69120300
Ir	1.75749300	-0.38928400	-0.28635400
N	1.92731700	-3.37732000	-0.51139700
N	1.91663200	-2.26029100	-0.40596500
O	1.96507700	-4.53826800	-0.61200700

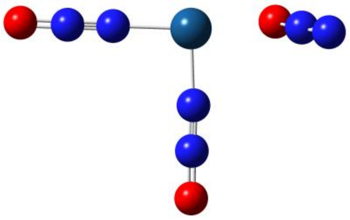

Fig. S39 Minimum N^{2}O^1 geometry of the singlet structure of Ir$^+$(N$_2$O)$_3$ at E$_{rel.}$ = 0.66 eV.

N	-0.93612500	-0.14272200	0.41039700
N	-0.05102700	0.36475300	0.84377000
O	-1.83749200	-0.77064500	-0.11195300
N	-6.66018700	-0.24027900	-0.12070300
N	-7.55882100	-0.82581400	-0.40062400
O	-5.74161900	0.48627200	0.20777400
Ir	-3.79935300	-0.20200500	0.16300400
N	-4.02253500	-1.57087200	2.81779300
N	-3.93895700	-1.05783300	1.82261400
O	-4.10963100	-2.10517800	3.85371400

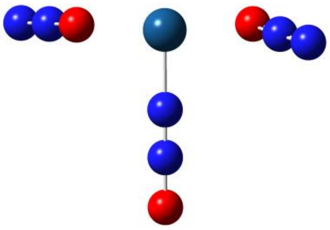

Fig. S40 Minimum N^{1}O^2 geometry of the singlet structure of Ir$^+$(N$_2$O)$_3$ at E$_{rel.}$ = 1.42 eV.

N	-1.20933100	-0.55527200	0.25020600
N	-0.10855200	-0.57644400	0.02954800
O	-2.35397500	-0.52709100	0.47386700
N	4.63120500	-0.13802500	0.06789100
N	5.44659900	0.13135900	0.76891100
O	3.80853400	-0.43787500	-0.77194300
Ir	1.77546100	-0.55321900	-0.31048300
N	1.88319000	-3.31446600	-0.52094300
N	1.75255000	-4.19410600	-1.18359300
O	2.05776600	-2.44268400	0.32104700

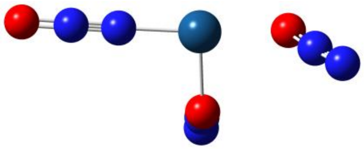

Fig. S41 Higher-energy minimum N^{1}O^2 geometry of the singlet structure of Ir$^+$(N$_2$O)$_3$ at E$_{rel.}$ = 1.49 eV.

N	-0.92670000	-0.17362200	0.44492200
N	-0.03751500	0.48187500	0.54200300
O	-1.83235600	-0.97685900	0.32989200
N	-6.63998600	-0.30618200	-0.13930200
N	-7.54509300	-0.88690800	-0.41227900
O	-5.71386100	0.41790800	0.16188300
Ir	-3.78165600	-0.30140500	0.28328000
N	-4.07525000	-1.51344800	2.75829700
N	-4.23522500	-2.46070400	3.31446400
O	-3.89018200	-0.39968000	2.28642800

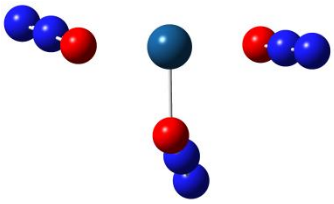

Fig. S42 Minimum O^3 geometry of the singlet structure of Ir$^+$(N$_2$O)$_3$ at E$_{rel.}$ = 2.33 eV.

iv. Ir$^+$(N$_2$O)$_4$

N	-1.25308000	-0.53515300	0.26623100
N	-0.15361200	-0.46315300	0.06007100
O	-2.39414600	-0.60992000	0.48017100
N	4.79136800	-0.13879100	-0.86702000
N	3.69193300	-0.21115400	-0.66081400
O	5.93246300	-0.06397500	-1.08103000
Ir	1.76919100	-0.33715200	-0.30041800
N	1.91794100	-3.40211700	-0.57908400
N	1.86376200	-2.28708700	-0.47755700
O	1.97427500	-4.55935300	-0.68437200
N	1.62066300	2.72786200	-0.02208500
N	1.67462500	1.61279200	-0.12328200
O	1.56458000	3.88512300	0.08304000

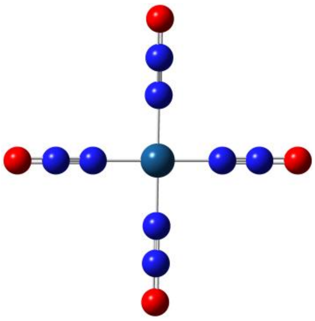

Fig. S43 Putative global minimum N^4 geometry of the singlet structure of Ir$^+$(N$_2$O)$_4$.

N	-1.24377500	-0.53417000	0.26840300
N	-0.14119400	-0.46404900	0.08084300
O	-2.39112100	-0.60816000	0.46548400
N	4.62931600	-0.24562100	0.22693600
N	5.44052600	-0.27411400	0.98252800
O	3.81346100	-0.20511800	-0.66684500
Ir	1.75482100	-0.34280800	-0.24173800
N	1.92372000	-3.39296900	-0.59061400
N	1.87856500	-2.28206600	-0.44045500
O	1.97908000	-4.54619500	-0.74014100
N	1.62582000	2.72169600	-0.03451700
N	1.68999400	1.60281300	-0.08667500
O	1.56804600	3.88295900	0.02539900

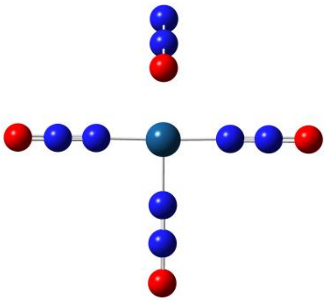

Fig. S44 Lowest energy minimum N^{3}O^1 geometry of the singlet structure of Ir$^+$(N$_2$O)$_4$ at E$_{rel.}$ = 0.64 eV.

N	-1.23421500	-0.61507600	0.22305900
N	-0.13963500	-0.59341100	-0.02082500
O	-2.37376700	-0.64931500	0.47640600
N	4.58913300	-0.11016600	-0.00443100
N	5.38140900	0.23226000	0.69174800
O	3.79488000	-0.50349100	-0.83050500
Ir	1.73876100	-0.49951400	-0.40105800
N	1.87170400	-3.40032400	-0.43709000
N	1.76412100	-4.31734500	-1.05117400
O	2.00995900	-2.45704200	0.31063600
N	1.46397900	2.35201700	-1.41820400
N	1.58391300	1.30749800	-1.02749800
O	1.35075700	3.44159300	-1.82305700

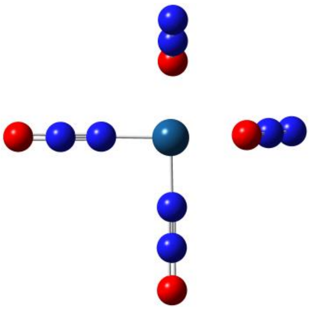

Fig. S45 Lowest energy minimum N^{2}O^2 geometry of the singlet structure of Ir$^+$(N$_2$O)$_4$ at E$_{rel.}$ = 1.28 eV.

N	-0.95319600	-0.17534000	0.38121500
N	-0.07450100	0.40213000	0.73430100
O	-1.84571200	-0.88330900	-0.03688200
N	-6.66437200	-0.26643200	-0.11785000
N	-7.54312600	-0.84391400	-0.47076400
O	-5.77190800	0.44204200	0.29950200
Ir	-3.80877100	-0.22049300	0.13125200
N	-4.02780400	-1.56579700	2.87996500
N	-3.94763200	-1.07352800	1.87398700
O	-4.11103900	-2.07672600	3.92497200
N	-3.59006000	1.12453800	-2.61739100
N	-3.67020300	0.63219800	-1.61145200
O	-3.50675300	1.63628100	-3.66201600

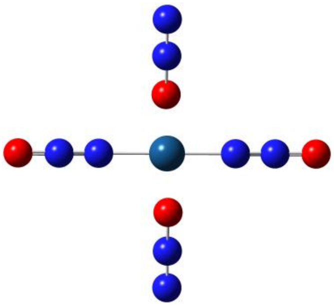

Fig. S46 Higher-energy minimum N^{2}O^2 geometry of the singlet structure of Ir$^+$(N$_2$O)$_4$ at E$_{rel.}$ = 1.38 eV.

N	-0.94264500	-0.19406600	0.42751900
N	-0.05872600	0.47490000	0.46450200
O	-1.84118200	-1.01066300	0.39042400
N	-6.63449900	-0.29036600	-0.19899700
N	-7.51484200	-0.83716100	-0.59578300
O	-5.73762500	0.38798500	0.25288500
Ir	-3.78850100	-0.31731300	0.24475300
N	-4.04564900	-1.51334800	2.88907300
N	-4.15652600	-2.44887400	3.47525800
O	-3.92197200	-0.44447800	2.33558300
N	-3.54959200	-0.02539600	-2.76217100
N	-3.64771900	-0.13200800	-1.64844900
O	-3.45074100	0.08401600	-3.92382400

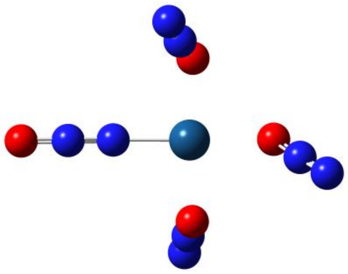

Fig. S47 Lowest energy minimum N^1O^3 geometry of the singlet structure of $Ir^+(N_2O)_4$ at $E_{rel.}$ = 2.08 eV.

N	-0.95511700	0.07064900	0.47934500
N	-0.11526700	0.74574400	0.74411900
O	-1.79863800	-0.74927700	0.17334400
N	-6.64555500	-0.14760900	-0.08777900
N	-7.55529000	-0.73372800	-0.33800600
O	-5.72012500	0.57602200	0.20334500
Ir	-3.77051800	-0.12125600	0.17708200
N	-4.01490200	-1.76201500	2.51211000
N	-4.09380700	-2.79723500	2.90548200
O	-3.92707000	-0.59747200	2.18685800
N	-3.55466500	-0.29371200	-2.67403600
N	-3.51890200	-0.96812500	-3.55524000
O	-3.57662600	0.52601700	-1.78114700

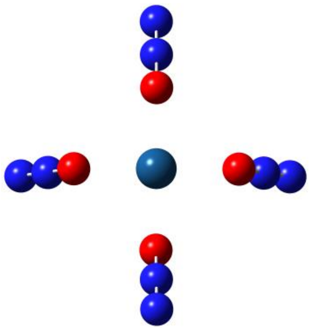

Fig. S48 Lowest energy minimum O^4 geometry of the singlet structure of $Ir^+(N_2O)_4$ at $E_{rel.}$ = 2.94 eV.

D. Calculated Relative Energies

Table S1 Zero-point corrected energies of structural isomers of $Co^+(N_2O)_n$ complexes calculated at the B3P86/Def2TZVP level of theory. Energies are relative to the global minimum geometry and electronic state for each complex size.

Species	Isomer	Relative Energy / eV
$^3Co^+(N_2O)$	N^1	0.00
	O^1	0.54
$^1Co^+(N_2O)$	N^1	2.28
	O^1	2.57
$^5Co^+(N_2O)$	N^1	2.67
	O^1	2.74
$^3Co^+(N_2O)_2$	N^2	0.00
	N^1O^1	0.85
	O^2	1.01
$^1Co^+(N_2O)_2$	N^2	2.14
	N^1O^1	2.60
	O^2	3.09
$^5Co^+(N_2O)_2$	N^2	2.28
	N^1O^1	2.36
	O^2	2.48
$^3Co^+(N_2O)_3$	N^3	0.00
	N^2O^1	0.27
	$^*N^2O^1$	0.38
	N^1O^2	0.70
	O^3	1.22
$^1Co^+(N_2O)_3$	N^3	1.62
	N^2O^1	2.02
	$^*N^2O^1$	2.07
	N^1O^2	2.48
	O^3	2.98
$^5Co^+(N_2O)_3$	N^3	2.40
	N^2O^1	2.54
	N^1O^2	2.64
	O^3	2.74
$^3Co^+(N_2O)_4$	N^4	0.08
	N^3O^1	0.00
	N^2O^2	0.25
	N^1O^3	0.98
	O^4	1.08
$^1Co^+(N_2O)_4$	N^4	0.88
	N^3O^1	1.26
	N^2O^2	1.68
	N^1O^3	2.05
	O^4	2.51
$^5Co^+(N_2O)_4$	N^4	2.50
	N^3O^1	2.56
	N^2O^2	2.76
	N^1O^3	2.78
	O^4	2.83

Table S2 Zero-point corrected energies of structural isomers of $Rh^+(N_2O)_n$ complexes calculated at the B3P86/Def2TZVP level of theory. Energies are relative to the global minimum geometry and electronic state for each complex size.

Species	Isomer	Relative Energy / eV
$^3Rh^+(N_2O)$	N^1	0.00
	O^1	0.62
$^1Rh^+(N_2O)$	N^1	1.17
	O^1	1.73
$^5Rh^+(N_2O)$	N^1	2.93
	O^1	3.48
$^3Rh^+(N_2O)_2$	N^2	0.00
	N^1O^1	0.48
	O^2	1.16
$^1Rh^+(N_2O)_2$	N^2	0.83
	N^1O^1	1.36
	O^2	1.93
$^5Rh^+(N_2O)_2$	N^2	3.38
	N^1O^1	3.65
	O^2	3.52
$^3Rh^+(N_2O)_3$	N^3	0.00
	N^2O^1	0.19
	*N^2O^1	0.40
	N^1O^2	0.62
	*N^1O^2	0.80
	O^3	1.19
$^1Rh^+(N_2O)_3$	N^3	0.30
	N^2O^1	0.79
	*N^2O^1	0.83
	N^1O^2	1.32
	*N^1O^2	1.34
	O^3	1.92
$^5Rh^+(N_2O)_3$	N^3	3.40
	N^2O^1	3.52
	N^1O^2	3.61
	O^3	3.70
$^1Rh^+(N_2O)_4$	N^4	0.00
	N^3O^1	0.48
	N^2O^2	0.95
	*N^2O^2	1.02
	N^1O^3	1.49
	O^4	2.06
$^3Rh^+(N_2O)_4$	N^4	0.63
	N^3O^1	0.77
	N^2O^2	0.89
	*N^2O^2	1.04
	N^1O^3	1.28
	O^4	1.71

Species	**Isomer**	**Relative Energy / eV**
${}^5Rh^+(N_2O)_4$	N^4	4.16
	N^3O^1	4.21
	$*N^3O^1$	4.27
	N^2O^2	4.27
	N^1O^3	4.48
	O^4	4.42

Table S3 Zero-point corrected energies of structural isomers of $\mathrm{Ir^+(N_2O)}_n$ complexes calculated at the B3P86/Def2TZVP level of theory. Energies are relative to the global minimum geometry and electronic state for each complex size.

Species	**Isomer**	**Relative Energy / eV**
$^{3}\mathrm{Ir^+(N_2O)}$	$\mathrm{N^1}$	0.00
	$\mathrm{O^1}$	0.36
$^{5}\mathrm{Ir^+(N_2O)}$	$\mathrm{N^1}$	0.53
	$\mathrm{O^1}$	0.63
$^{1}\mathrm{Ir^+(N_2O)}$	$\mathrm{N^1}$	1.10
	$\mathrm{O^1}$	1.35
$^{3}\mathrm{Ir^+(N_2O)_2}$	$\mathrm{N^2}$	0.00
	$\mathrm{N^1O^1}$	0.57
	$\mathrm{O^2}$	1.04
$^{1}\mathrm{Ir^+(N_2O)_2}$	$\mathrm{N^2}$	0.84
	$\mathrm{N^1O^1}$	1.40
	$\mathrm{O^2}$	2.21
$^{5}\mathrm{Ir^+(N_2O)_2}$	$\mathrm{N^2}$	2.12
	$\mathrm{N^1O^1}$	2.28
	$\mathrm{O^2}$	2.35
$^{1}\mathrm{Ir^+(N_2O)_3}$	$\mathrm{N^3}$	0.00
	$\mathrm{N^2O^1}$	0.66
	$\mathrm{N^1O^2}$	1.42
	$^*\mathrm{N^1O^2}$	1.49
	$\mathrm{O^3}$	2.33
$^{3}\mathrm{Ir^+(N_2O)_3}$	$\mathrm{N^3}$	0.15
	$\mathrm{N^2O^1}$	0.82
	$\mathrm{N^1O^2}$	1.55
	$\mathrm{O^3}$	1.99
$^{5}\mathrm{Ir^+(N_2O)_3}$	$\mathrm{N^3}$	2.75
	$\mathrm{N^2O^1}$	2.85
	$\mathrm{N^1O^2}$	2.97
	$\mathrm{O^3}$	3.09
$^{1}\mathrm{Ir^+(N_2O)_4}$	$\mathrm{N^4}$	0.00
	$\mathrm{N^3O^1}$	0.64
	$\mathrm{N^2O^2}$	1.28
	$^*\mathrm{N^2O^2}$	1.38
	$\mathrm{N^1O^3}$	2.08
	$\mathrm{O^4}$	2.94
$^{3}\mathrm{Ir^+(N_2O)_4}$	$\mathrm{N^4}$	1.43
	$\mathrm{N^3O^1}$	1.61
	$^*\mathrm{N^3O^1}$	2.00
	$\mathrm{N^2O^2}$	1.85
	$\mathrm{N^1O^3}$	2.45
	$\mathrm{O^4}$	3.48
$^{5}\mathrm{Ir^+(N_2O)_4}$	$\mathrm{N^4}$	4.24
	$\mathrm{N^3O^1}$	4.28
	$\mathrm{N^2O^2}$	4.37
	$\mathrm{N^1O^3}$	4.49
	$\mathrm{O^4}$	4.54

E. Time-of-Flight Mass Spectra

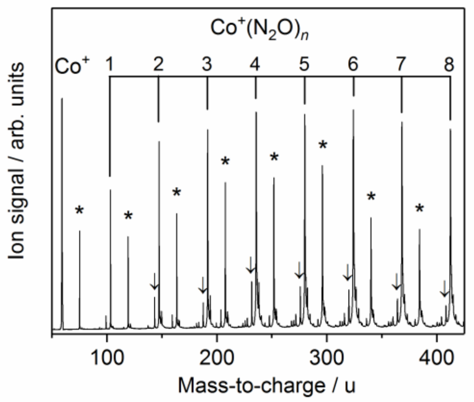

Fig. S49 Time-of-flight mass spectrum of $Co^+(N_2O)_n$ complexes produced by ablation of a cobalt target in an argon carrier gas seeded with 0.6% N_2O. Ar-tagged peaks are indicated by arrows with $CoO^+(N_2O)_n$ (*) complexes also being formed.

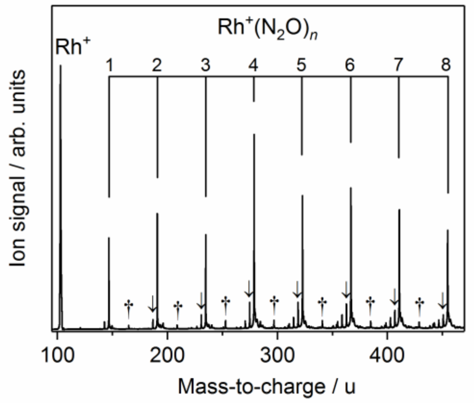

Fig. S50 Time-of-flight mass spectrum of $Rh^+(N_2O)_n$ complexes produced by ablation of a rhodium target in an argon carrier gas seeded with 0.6% N_2O. Ar-tagged peaks are indicated by arrows with $Rh^+(N_2O)_n(H_2O)$ (†) complexes also being formed.

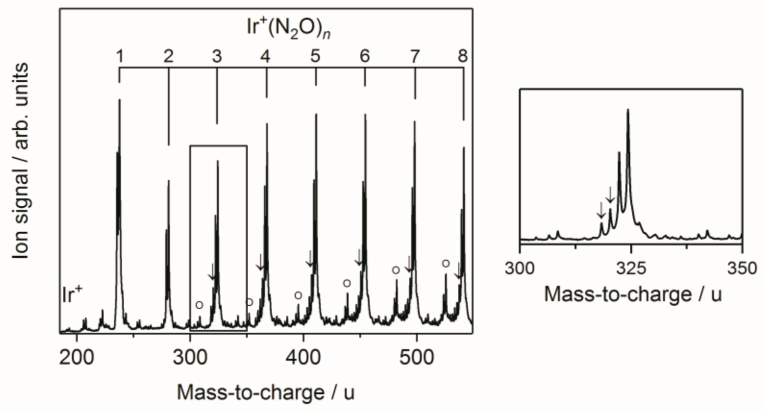

Fig. S51 *Left* Time-of-flight mass spectrum of $Ir^+(N_2O)_n$ complexes produced by ablation of an iridium target in an argon carrier gas seeded with 0.6% N_2O. Ar-tagged peaks are indicated by arrows with $Ir^+(N_2O)_n(N_2)$ (°) complexes also being formed. *Right* Inlet between 350-300 mass units to show the ion signals of $^{193}Ir^+(N_2O)_3$ & $^{191}Ir^+(N_2O)_3$ along with $^{193}Ir^+(N_2O)_2$-Ar & $^{191}Ir^+(N_2O)_2$-Ar (marked by arrows).

F. Combined Simulated Infrared Spectra

i. $Co^+(N_2O)_2$-Ar

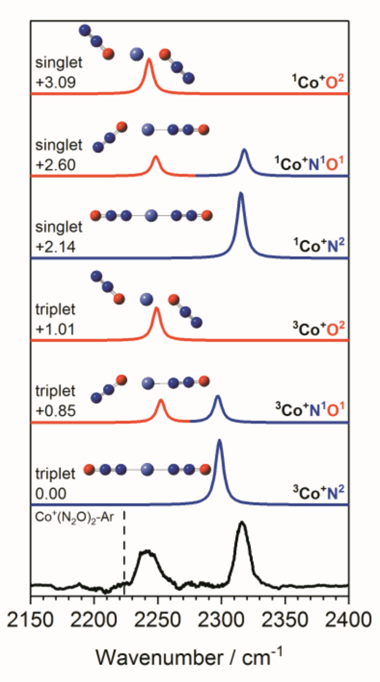

Fig. S52 Experimental infrared depletion spectrum of $Co^+(N_2O)_2$-Ar complex along with simulated IR spectra of low-lying triplet and singlet isomers in the region of the N_2O asymmetric (N=N) stretch. Blue: Simulated IR bands correspond to N-bound N_2O ligands. Red: Simulated IR bands correspond to O-bound ligands. The relative energies of the isomers concerned are given in eV. The vertical dashed line indicates the wavenumber of the ν_3 (N=N) mode in isolated N_2O at 2223.5 cm^{-1}.[5]

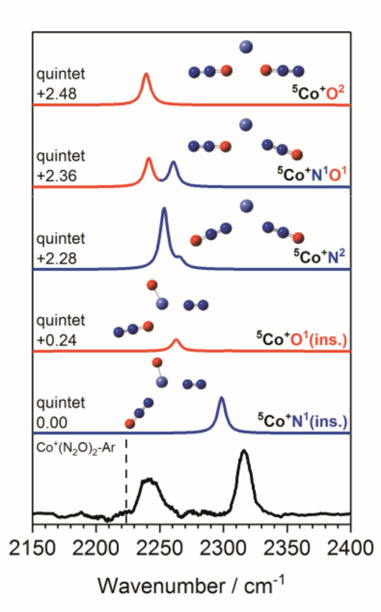

Fig. S53 Experimental infrared depletion spectrum of $Co^+(N_2O)_2$-Ar complex along with simulated IR spectra of low-lying quintet isomers along with inserted quintet isomers in the region of the N_2O asymmetric (N=N) stretch. Blue: Simulated IR bands correspond to N-bound N_2O ligands. Red: Simulated IR bands correspond to O-bound ligands. The relative energies of the isomers concerned are given in eV. The vertical dashed line indicates the wavenumber of the ν_3 (N=N) mode in isolated N_2O at 2223.5 cm^{-1}.[5]

The N-bound inserted quintet isomer, $^5Co^+N^1$(ins.), is isoenergetic with the doubly N-bound triplet isomer, $^3Co^+N^2$, so both could be regarded as the ground state structure of $Co^+(N_2O)_2$. However, as discussed in the main article, these inserted structures occupy a barrier to O-atom transfer (see Fig. 2) and are strongly exothermic so it is unlikely that the N_2 molecule could remain bound once significant energy is released upon formation of the strong M^+-O bond.

ii. $Co^+(N_2O)_3$-Ar

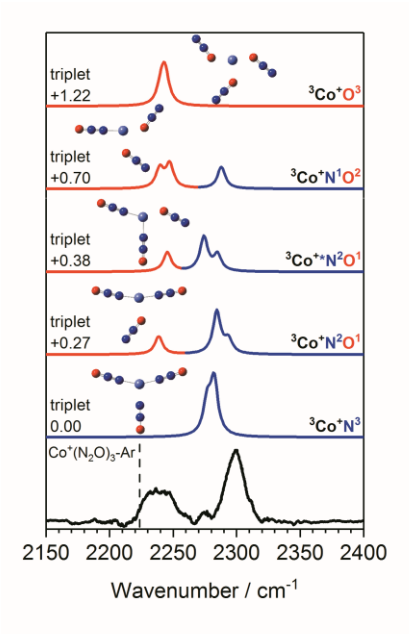

Fig. S54 Experimental infrared depletion spectrum of $Co^+(N_2O)_3$-Ar complex along with simulated IR spectra of low-lying triplet isomers in the region of the N_2O asymmetric (N=N) stretch. Blue: Simulated IR bands correspond to N-bound N_2O ligands. Red: Simulated IR bands correspond to O-bound ligands. The relative energies of the isomers concerned are given in eV. The vertical dashed line indicates the wavenumber of the ν_3 (N=N) mode in isolated N_2O at 2223.5 cm^{-1}.[5]

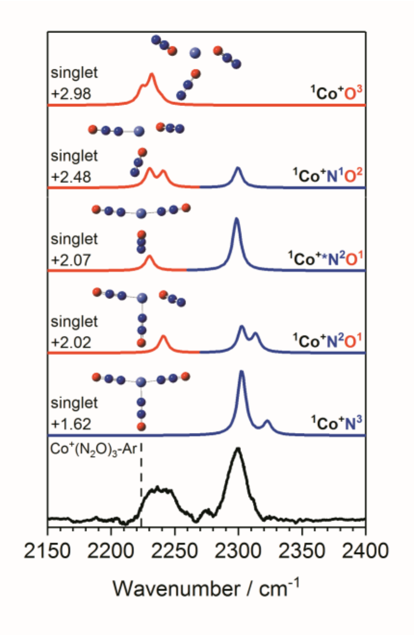

Fig. S55 Experimental infrared depletion spectrum of $Co^+(N_2O)_3$-Ar complex along with simulated IR spectra of low-lying singlet isomers in the region of the N_2O asymmetric (N=N) stretch. Blue: Simulated IR bands correspond to N-bound N_2O ligands. Red: Simulated IR bands correspond to O-bound ligands. The relative energies of the isomers concerned are given in eV. The vertical dashed line indicates the wavenumber of the ν_3 (N=N) mode in isolated N_2O at 2223.5 cm^{-1}.[5]

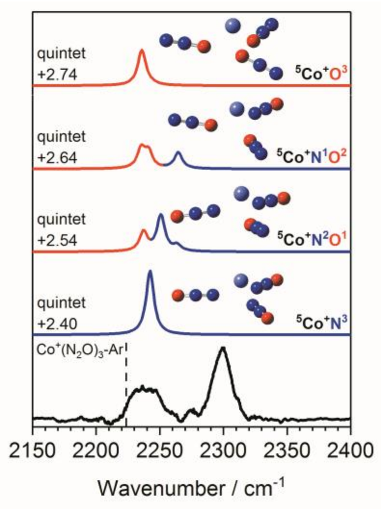

Fig. S56 Experimental infrared depletion spectrum of $Co^+(N_2O)_3$-Ar complex along with simulated IR spectra of low-lying quintet isomers in the region of the N_2O asymmetric (N=N) stretch. Blue: Simulated IR bands correspond to N-bound N_2O ligands. Red: Simulated IR bands correspond to O-bound ligands. The relative energies of the isomers concerned are given in eV. The vertical dashed line indicates the wavenumber of the ν_3 (N=N) mode in isolated N_2O at 2223.5 cm^{-1}.[5]

iii. $Co^+(N_2O)_4$-Ar

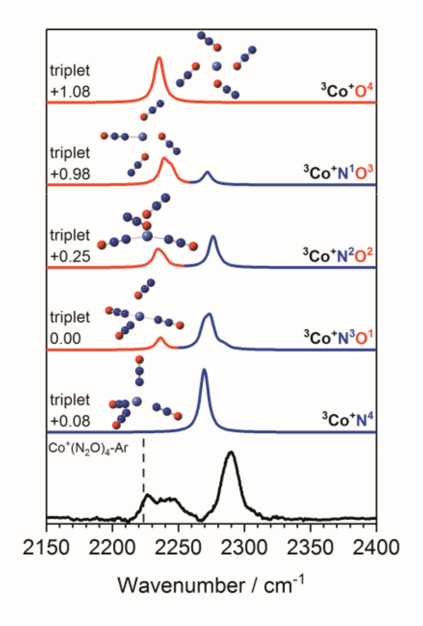

Fig. S57 Experimental infrared depletion spectrum of $Co^+(N_2O)_4$-Ar complex along with simulated IR spectra of low-lying triplet isomers in the region of the N_2O asymmetric (N=N) stretch. Blue: Simulated IR bands correspond to N-bound N_2O ligands. Red: Simulated IR bands correspond to O-bound ligands. The relative energies of the isomers concerned are given in eV. The vertical dashed line indicates the wavenumber of the ν_3 (N=N) mode in isolated N_2O at 2223.5 cm^{-1}.[5]

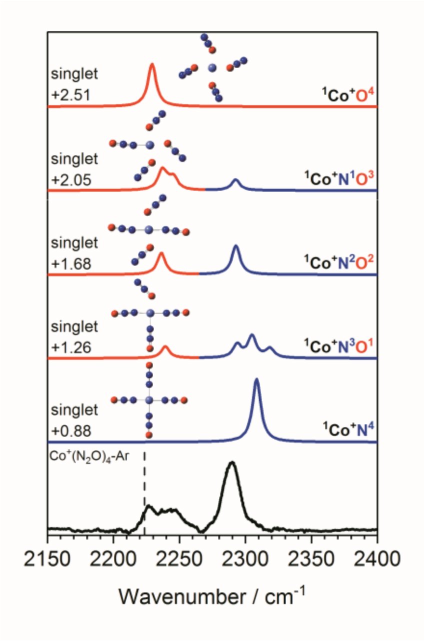

Fig. S58 Experimental infrared depletion spectrum of $Co^+(N_2O)_4$-Ar complex along with simulated IR spectra of low-lying singlet isomers in the region of the N_2O asymmetric (N=N) stretch. Blue: Simulated IR bands correspond to N-bound N_2O ligands. Red: Simulated IR bands correspond to O-bound ligands. The relative energies of the isomers concerned are given in eV. The vertical dashed line indicates the wavenumber of the ν_3 (N=N) mode in isolated N_2O at 2223.5 cm^{-1}.[5]

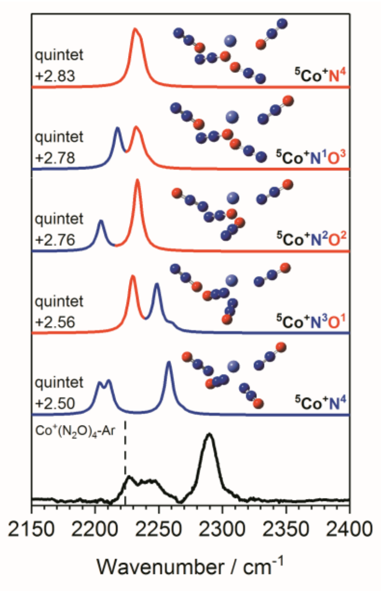

Fig. S59 Experimental infrared depletion spectrum of $Co^+(N_2O)_4$-Ar complex along with simulated IR spectra of low-lying singlet isomers in the region of the N_2O asymmetric (N=N) stretch. Blue: Simulated IR bands correspond to N-bound N_2O ligands. Red: Simulated IR bands correspond to O-bound ligands. The relative energies of the isomers concerned are given in eV. The vertical dashed line indicates the wavenumber of the ν_3 (N=N) mode in isolated N_2O at 2223.5 cm^{-1}.[5]

iv. $Rh^+(N_2O)_2$-Ar

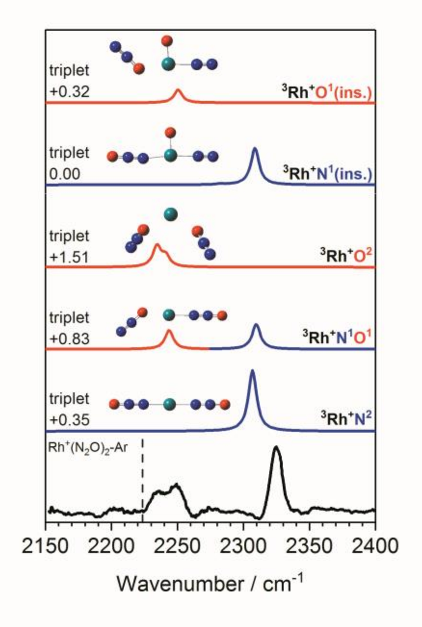

Fig. S60 Experimental infrared depletion spectrum of $Rh^+(N_2O)_2$-Ar complex along with simulated IR spectra of low-lying triplet isomers and inserted structures in the region of the N_2O asymmetric (N=N) stretch. Blue: Simulated IR bands correspond to N-bound N_2O ligands. Red: Simulated IR bands correspond to O-bound ligands. The relative energies of the isomers concerned are given in eV. The vertical dashed line indicates the wavenumber of the v_3 (N=N) mode in isolated N_2O at 2223.5 cm^{-1}.[5]

The N-bound inserted triplet isomer, $^3Rh^+N^1$(ins.), is the ground state structure of $Rh^+(N_2O)_2$. However, as discussed in the main article, these inserted structures occupy a barrier to O-atom transfer (see Fig. 2) and are strongly exothermic so it is unlikely that the N_2 molecule could remain bound once significant energy is released upon formation of the strong M^+-O bond.

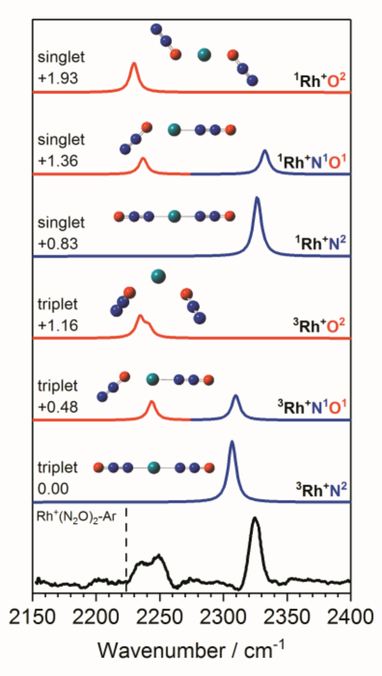

Fig. S61 Experimental infrared depletion spectrum of $Rh^+(N_2O)_2$-Ar complex along with simulated IR spectra of low-lying triplet and singlet isomers in the region of the N_2O asymmetric (N=N) stretch. Blue: Simulated IR bands correspond to N-bound N_2O ligands. Red: Simulated IR bands correspond to O-bound ligands. The relative energies of the isomers concerned are given in eV. The vertical dashed line indicates the wavenumber of the ν_3 (N=N) mode in isolated N_2O at 2223.5 cm^{-1}.[5]

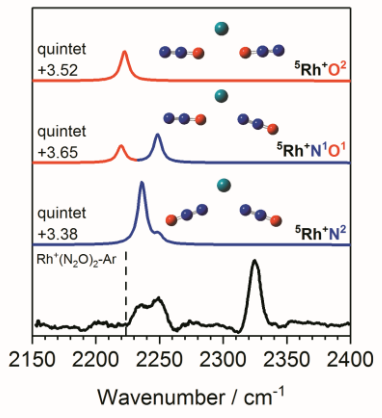

Fig. S62 Experimental infrared depletion spectrum of $Rh^+(N_2O)_2$-Ar complex along with simulated IR spectra of low-lying quintet isomers in the region of the N_2O asymmetric (N=N) stretch. Blue: Simulated IR bands correspond to N-bound N_2O ligands. Red: Simulated IR bands correspond to O-bound ligands. The relative energies of the isomers concerned are given in eV. The vertical dashed line indicates the wavenumber of the ν_3 (N=N) mode in isolated N_2O at 2223.5 cm^{-1}.[5]

v. $Rh^+(N_2O)_3$-Ar

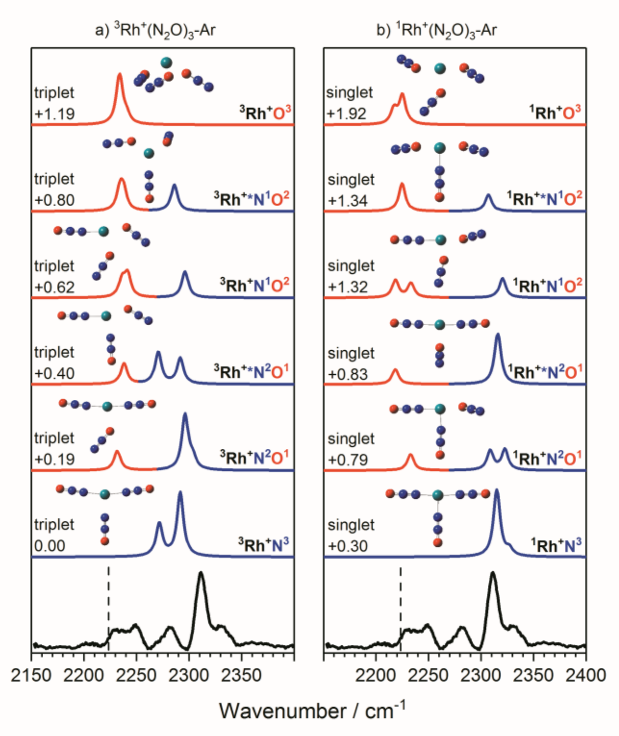

Fig. S63 Experimental infrared depletion spectrum of $Rh^+(N_2O)_3$-Ar complex along with simulated IR spectra of low-lying a) triplet and b) singlet structures in the region of the N_2O asymmetric (N=N) stretch. Blue: Simulated IR bands correspond to N-bound N_2O ligands. Red: Simulated IR bands correspond to O-bound ligands. The relative energies of the isomers concerned are given in eV. The vertical dashed line indicates the wavenumber of the v_3 (N=N) mode in isolated N_2O at 2223.5 cm^{-1}.[5]

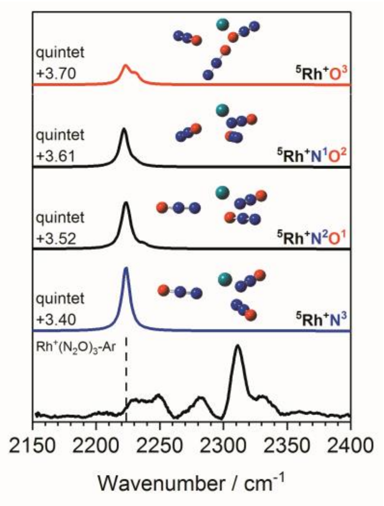

Fig. S64 Experimental infrared depletion spectrum of $Rh^+(N_2O)_3$-Ar complex along with simulated IR spectra of low-lying quintet structures in the region of the N_2O asymmetric (N=N) stretch. Blue: Simulated IR bands correspond to N-bound N_2O ligands. Red: Simulated IR bands correspond to O-bound ligands. Black: Simulated IR bands where N- and O-bound bands overlap. The relative energies of the isomers concerned are given in eV. The vertical dashed line indicates the wavenumber of the ν_3 (N=N) mode in isolated N_2O at 2223.5 cm^{-1}.[5]

vi. $Rh^+(N_2O)_4$-Ar

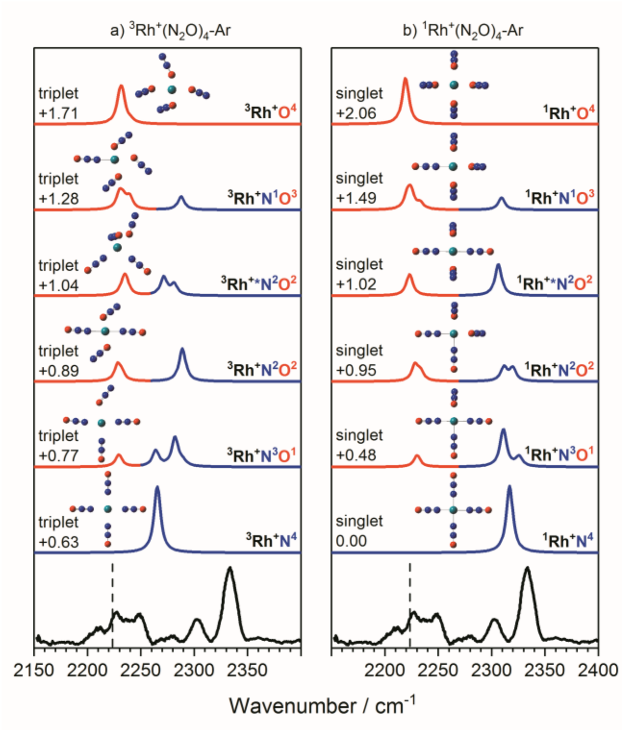

Fig. S65 Experimental infrared depletion spectrum of $Rh^+(N_2O)_4$-Ar complex along with simulated IR spectra of low-lying a) triplet and b) singlet structures in the region of the N_2O asymmetric (N=N) stretch. Blue: Simulated IR bands correspond to N-bound N_2O ligands. Red: Simulated IR bands correspond to O-bound ligands. The relative energies of the isomers concerned are given in eV. The vertical dashed line indicates the wavenumber of the ν_3 (N=N) mode in isolated N_2O at 2223.5 cm^{-1}.[5]

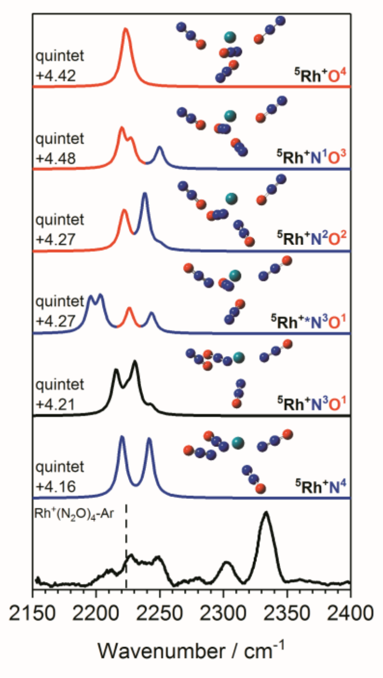

Fig. S66 Experimental infrared depletion spectrum of $Rh^+(N_2O)_4$-Ar complex along with simulated IR spectra of low-lying quintet structures in the region of the N_2O asymmetric (N=N) stretch. Blue: Simulated IR bands correspond to N-bound N_2O ligands. Red: Simulated IR bands correspond to O-bound ligands. Black: Simulated IR bands where N- and O-bound bands overlap. The relative energies of the isomers concerned are given in eV. The vertical dashed line indicates the wavenumber of the v_3 (N=N) mode in isolated N_2O at 2223.5 cm^{-1}.[5]

vii. $Ir^+(N_2O)_2$-Ar

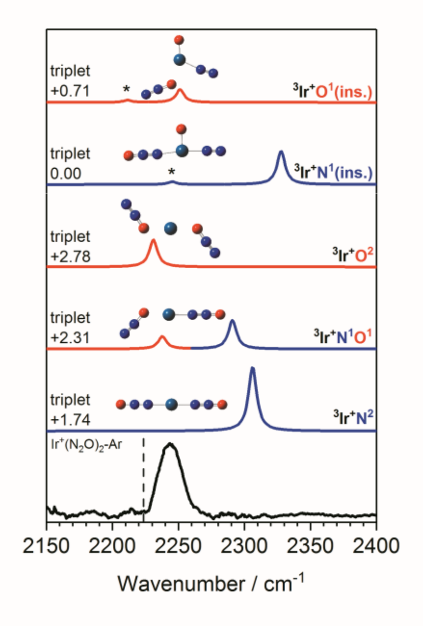

Fig. S67 Experimental infrared depletion spectrum of $Ir^+(N_2O)_2$-Ar complex along with simulated IR spectra of low-lying triplet isomers and inserted structures in the region of the N_2O asymmetric (N=N) stretch. Blue: Simulated IR bands correspond to N-bound N_2O ligands. Red: Simulated IR bands correspond to O-bound ligands. Asterisk: Simulated IR bands correspond to N_2 ligands. The relative energies of the isomers concerned are given in eV. The vertical dashed line indicates the wavenumber of the ν_3 (N=N) mode in isolated N_2O at 2223.5 cm^{-1}.[5]

The N-bound inserted triplet isomer, $^3Ir^+N^1$(ins.), is the ground state structure of $Rh^+(N_2O)_2$. However, as discussed in the main article, these inserted structures occupy a barrier to O-atom transfer (see Fig. 2) and are strongly exothermic so it is unlikely that the N_2 molecule could remain bound once significant energy is released upon formation of the strong M^+-O bond.

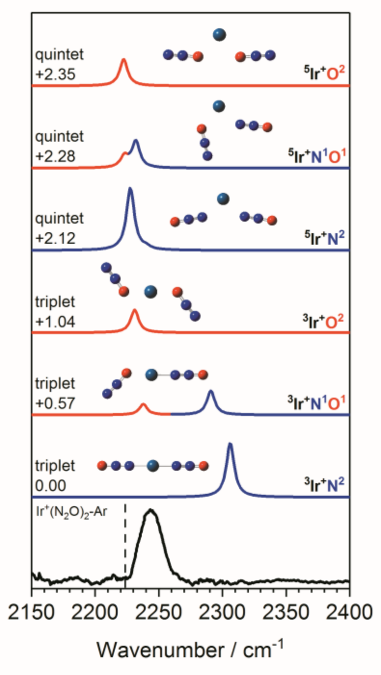

Fig. S68 Experimental infrared depletion spectrum of $Ir^+(N_2O)_2$-Ar complex along with simulated IR spectra of low-lying triplet and quintet structures in the region of the N_2O asymmetric (N=N) stretch. Blue: Simulated IR bands correspond to N-bound N_2O ligands. Red: Simulated IR bands correspond to O-bound ligands. The relative energies of the isomers concerned are given in eV. The vertical dashed line indicates the wavenumber of the ν_3 (N=N) mode in isolated N_2O at 2223.5 cm^{-1}.[5]

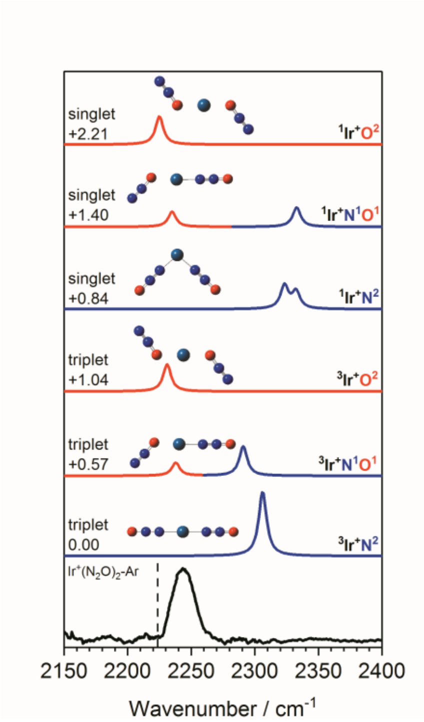

Fig. S69 Experimental infrared depletion spectrum of $Ir^+(N_2O)_2$-Ar complex along with simulated IR spectra of low-lying triplet and singlet structures in the region of the N_2O asymmetric (N=N) stretch. Blue: Simulated IR bands correspond to N-bound N_2O ligands. Red: Simulated IR bands correspond to O-bound ligands. The relative energies of the isomers concerned are given in eV. The vertical dashed line indicates the wavenumber of the v_3 (N=N) mode in isolated N_2O at 2223.5 cm^{-1}.[5]

viii. $Ir^+(N_2O)_3$-Ar

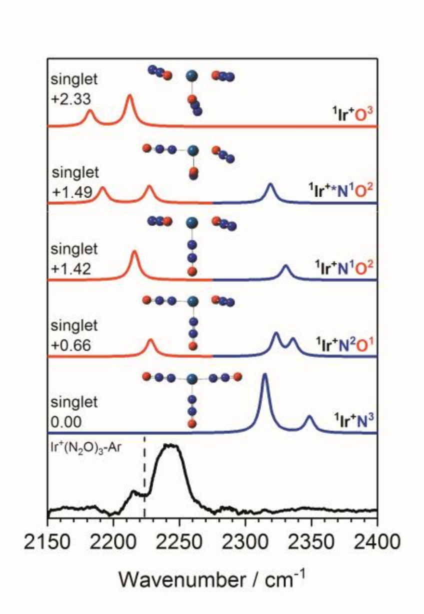

Fig. S70 Experimental infrared depletion spectrum of $Ir^+(N_2O)_3$-Ar complex along with simulated IR spectra of low-lying singlet isomers in the region of the N_2O asymmetric (N=N) stretch. Blue: Simulated IR bands correspond to N-bound N_2O ligands. Red: Simulated IR bands correspond to O-bound ligands. The relative energies of the isomers concerned are given in eV. The vertical dashed line indicates the wavenumber of the ν_3 (N=N) mode in isolated N_2O at 2223.5 cm^{-1}.[5]

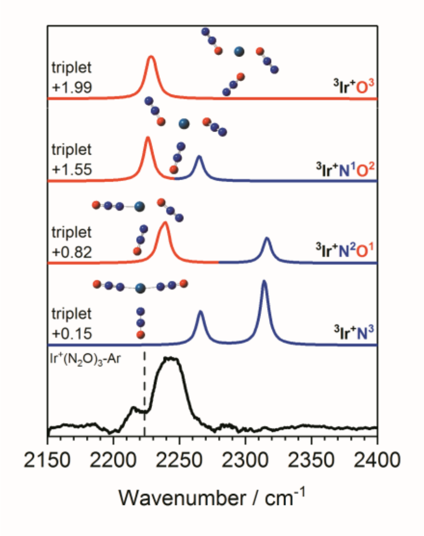

Fig. S71 Experimental infrared depletion spectrum of $Ir^+(N_2O)_3$-Ar complex along with simulated IR spectra of low-lying triplet isomers in the region of the N_2O asymmetric (N=N) stretch. Blue: Simulated IR bands correspond to N-bound N_2O ligands. Red: Simulated IR bands correspond to O-bound ligands. The relative energies of the isomers concerned are given in eV. The vertical dashed line indicates the wavenumber of the ν_3 (N=N) mode in isolated N_2O at 2223.5 cm^{-1}.[5]

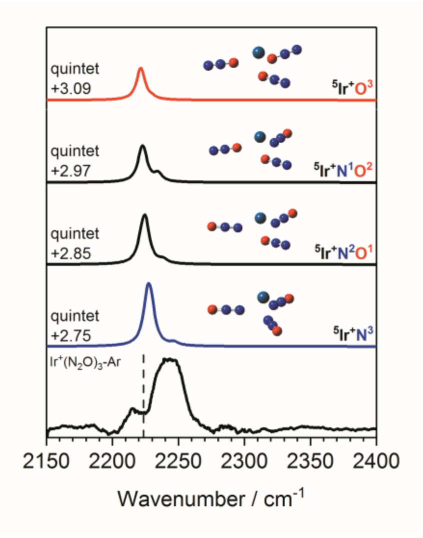

Fig. S72 Experimental infrared depletion spectrum of $Ir^+(N_2O)_3$-Ar complex along with simulated IR spectra of low-lying quintet isomers in the region of the N_2O asymmetric (N=N) stretch. Blue: Simulated IR bands correspond to N-bound N_2O ligands. Red: Simulated IR bands correspond to O-bound ligands. Black: Simulated IR bands where N- and O-bound bands overlap. The relative energies of the isomers concerned are given in eV. The vertical dashed line indicates the wavenumber of the ν_3 (N=N) mode in isolated N_2O at 2223.5 cm^{-1}.[5]

ix. $Ir^+(N_2O)_4$-Ar

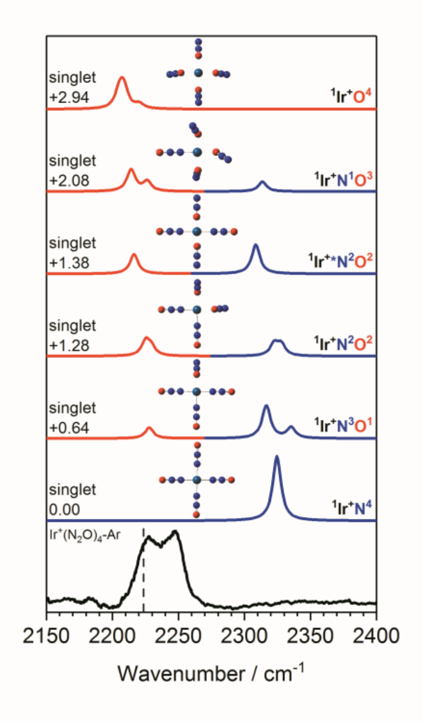

Fig. S73 Experimental infrared depletion spectrum of $Ir^+(N_2O)_4$-Ar complex along with simulated IR spectra of low-lying singlet isomers in the region of the N_2O asymmetric (N=N) stretch. Blue: Simulated IR bands correspond to N-bound N_2O ligands. Red: Simulated IR bands correspond to O-bound ligands. The relative energies of the isomers concerned are given in eV. The vertical dashed line indicates the wavenumber of the ν_3 (N=N) mode in isolated N_2O at 2223.5 cm^{-1}.[5]

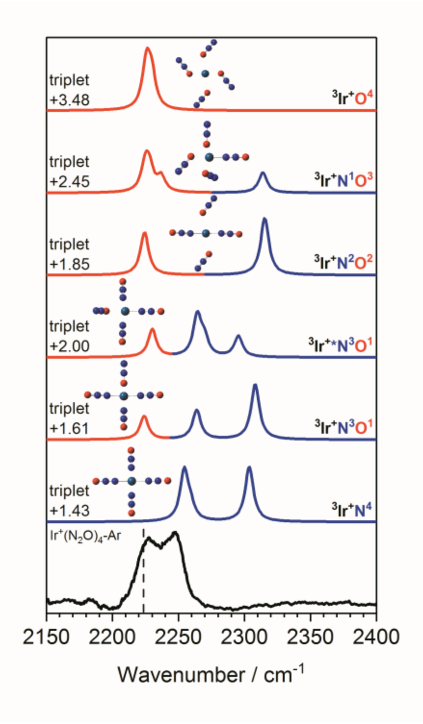

Fig. S74 Experimental infrared depletion spectrum of $Ir^+(N_2O)_4$-Ar complex along with simulated IR spectra of low-lying triplet isomers in the region of the N_2O asymmetric (N=N) stretch. Blue: Simulated IR bands correspond to N-bound N_2O ligands. Red: Simulated IR bands correspond to O-bound ligands. The relative energies of the isomers concerned are given in eV. The vertical dashed line indicates the wavenumber of the ν_3 (N=N) mode in isolated N_2O at 2223.5 cm^{-1}.[5]

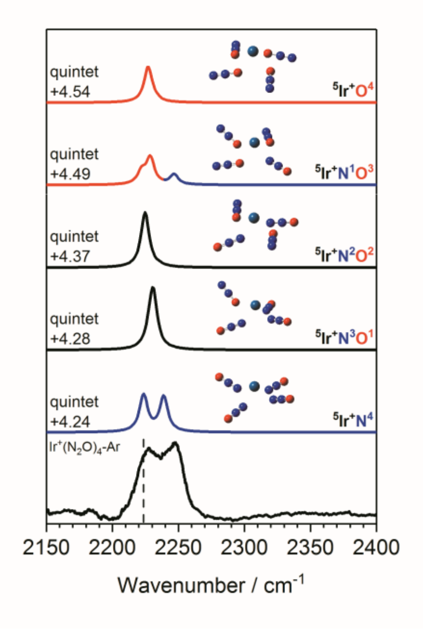

Fig. S75 Experimental infrared depletion spectrum of $Ir^+(N_2O)_4$-Ar complex along with simulated IR spectra of low-lying quintet isomers in the region of the N_2O asymmetric (N=N) stretch. Blue: Simulated IR bands correspond to N-bound N_2O ligands. Red: Simulated IR bands correspond to O-bound ligands. Black: Simulated IR bands where N- and O-bound bands overlap. The relative energies of the isomers concerned are given in eV. The vertical dashed line indicates the wavenumber of the ν_3 (N=N) mode in isolated N_2O at 2223.5 cm^{-1}.[5]

G. M^+-N_2O Relaxed Scans

The relaxed scans were performed by rotating the N_2O molecule about the metal centre, by 1° increments, and allowing the N_2O geometry to relax at each point between 0 and 180°.

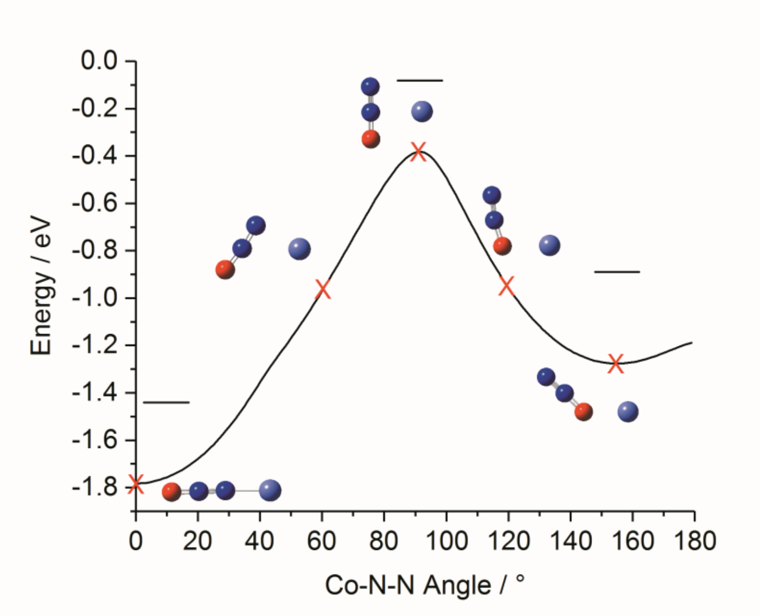

Fig. S76 Minimum energy pathway for the triplet Co^+N_2O complex as a function of Co-N-N angle illustrating the relative energies of N-bound and O-bound minima. Horizontal lines indicate the energy of the respective geometry-optimised structures including zero point correction.

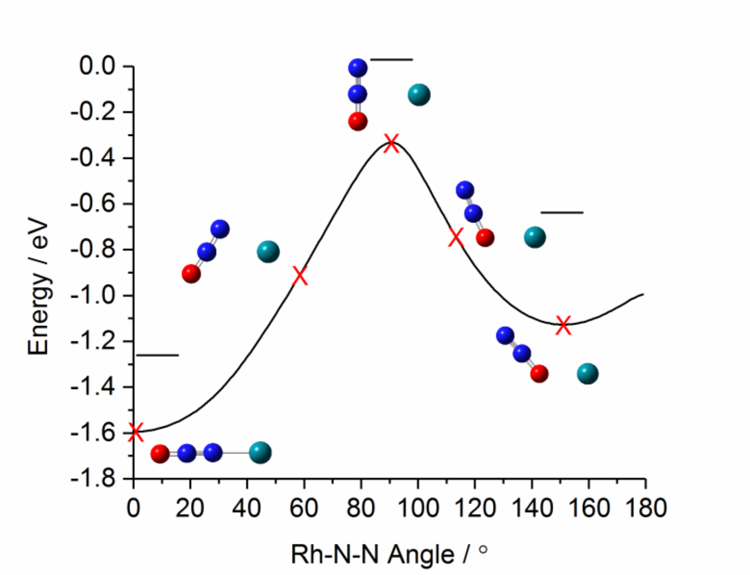

Fig. S77 Minimum energy pathway for the triplet Rh^+N_2O complex as a function of Rh-N-N angle illustrating the relative energies of N-bound and O-bound minima. Horizontal lines indicate the energy of the respective geometry-optimised structures including zero point correction.

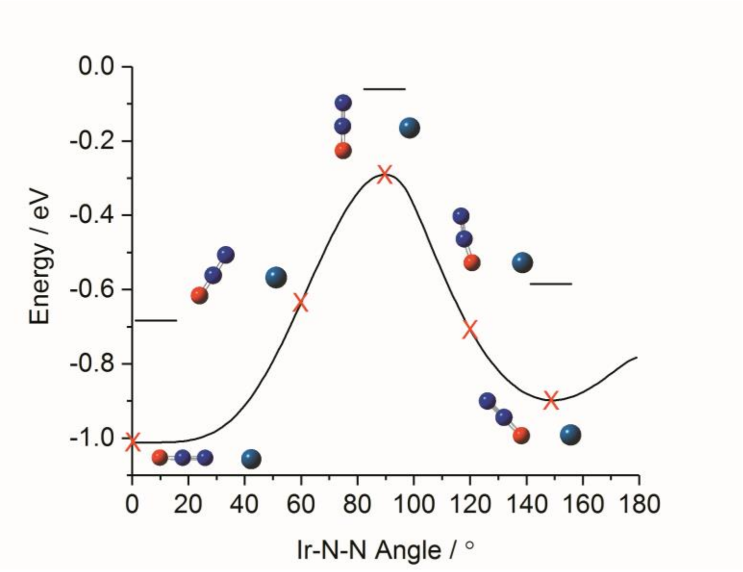

Fig. S78 Minimum energy pathway for the quintet Ir$^+$N$_2$O complex as a function of Ir-N-N angle illustrating the relative energies of N-bound and O-bound minima. Horizontal lines indicate the energy of the respective geometry-optimised structures including zero point correction.

References

1. J. P. Perdew, *Phys. Rev. B*, 1986, **33**, 8822-8824.
2. F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297-3305.
3. F. Weigend, *Phys. Chem. Chem. Phys.*, 2006, **8**, 1057-1065.
4. 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, 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, Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Gaussian 09, Revision B.01, Gaussian, Inc., Wallingford CT*, 2009.
5. G. Herzberg, *Molecular Spectra and Molecular Structure: II Infrared and Raman Spectra of Polyatomic Molecules*, Krieger, Malabar, Florida, 1991.