Electronic Supplementary Material (ESI) for Dalton Transactions

Synthesis, Spectroscopic Analysis and Photolabilization of Water Soluble Ruthenium(III)-Nitrosyl Complexes

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Supporting Information

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Figure S1. Plot of the concentration of the photoproduct of **4** versus time, taken in DMF solution. The data were fit to a line, the slope of which, m, was used to calculate the quantum yield (ϕ). In this experiment, **4** (0.15 mM) in DMF was irradiated with UV-light at 1 minute increments. Data for the first 8 minutes are shown.

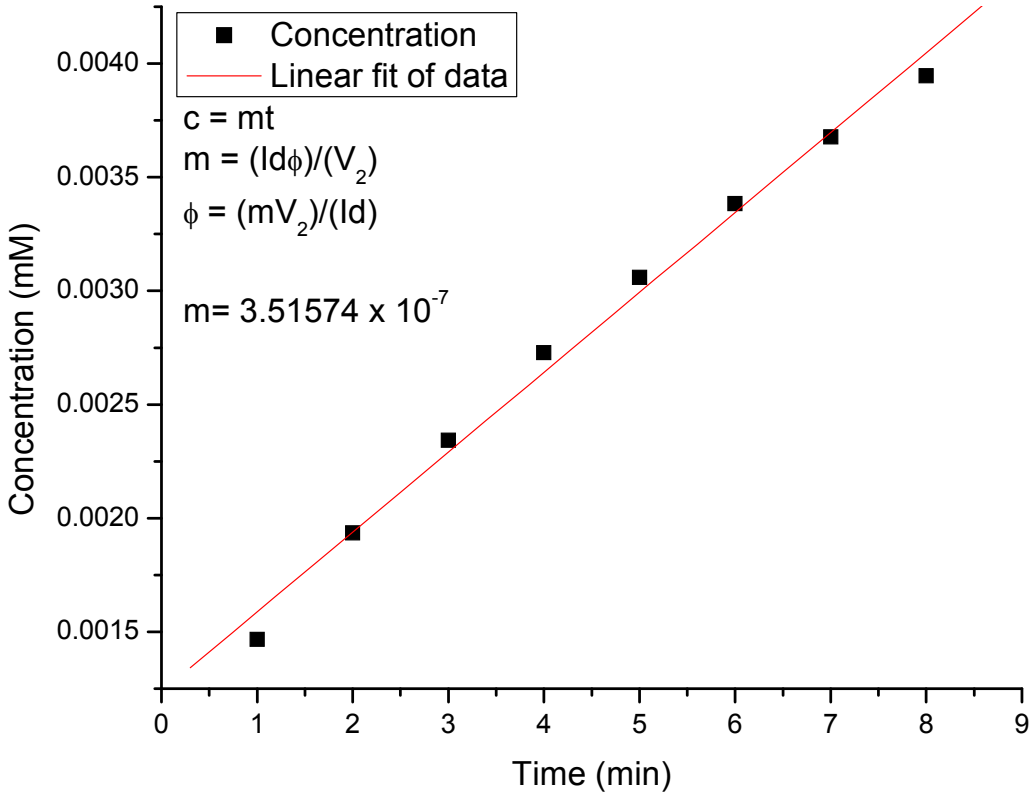


Figure S2. ^{1}H-NMR spectrum of **2** in deuterated dichloromethane. The aromatic protons are observed as a range of doublets and multiplets. The methylene hydrogens of the TPA coligand are found in a wide range between 5 and 6 ppm.

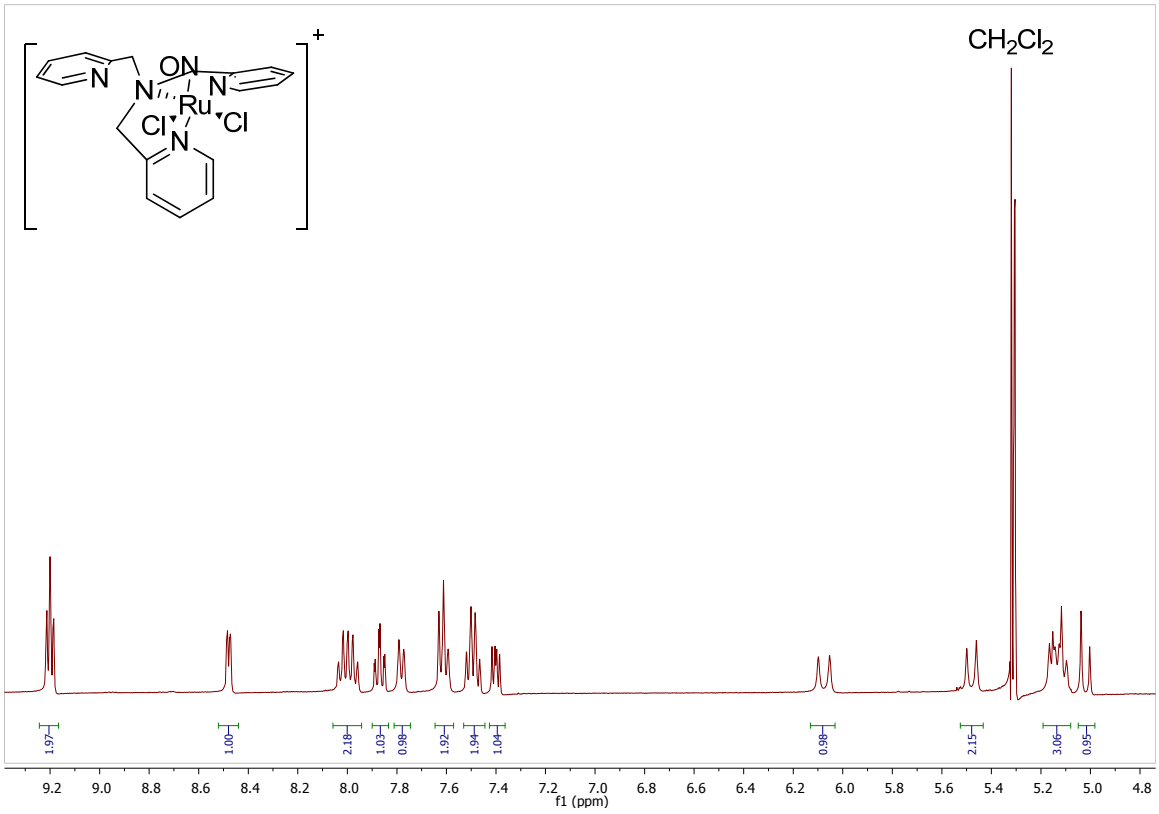


Figure S3. ^{1}H-NMR spectrum of **3** in deuterated methanol. The aromatic protons are observed as a range of doublets and triplets. The methylene hydrogens of the TPA coligand are found around ~5 ppm.

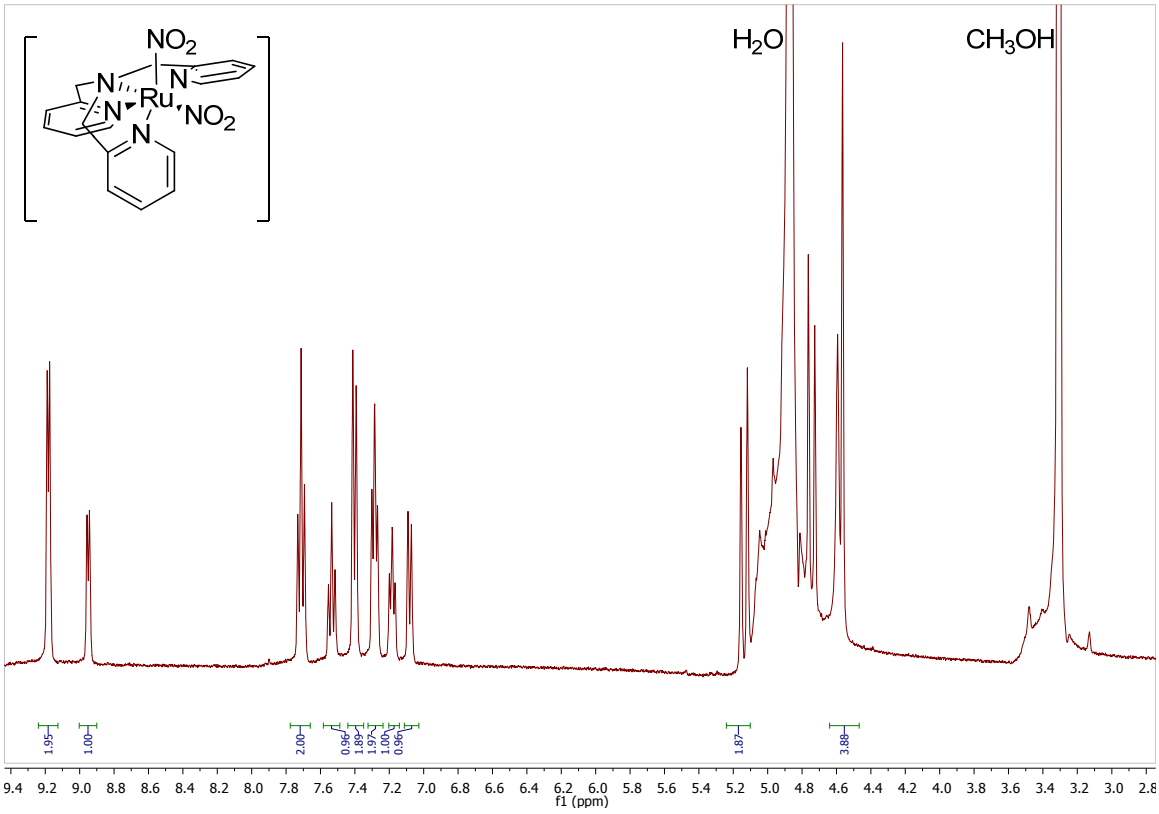


Figure S4. ^{1}H-NMR spectrum of **4** in deuterated acetonitrile. The aromatic protons are observed as a range of doublets and triplets. The methylene hydrogens of the TPA coligand are found around ~5 ppm.

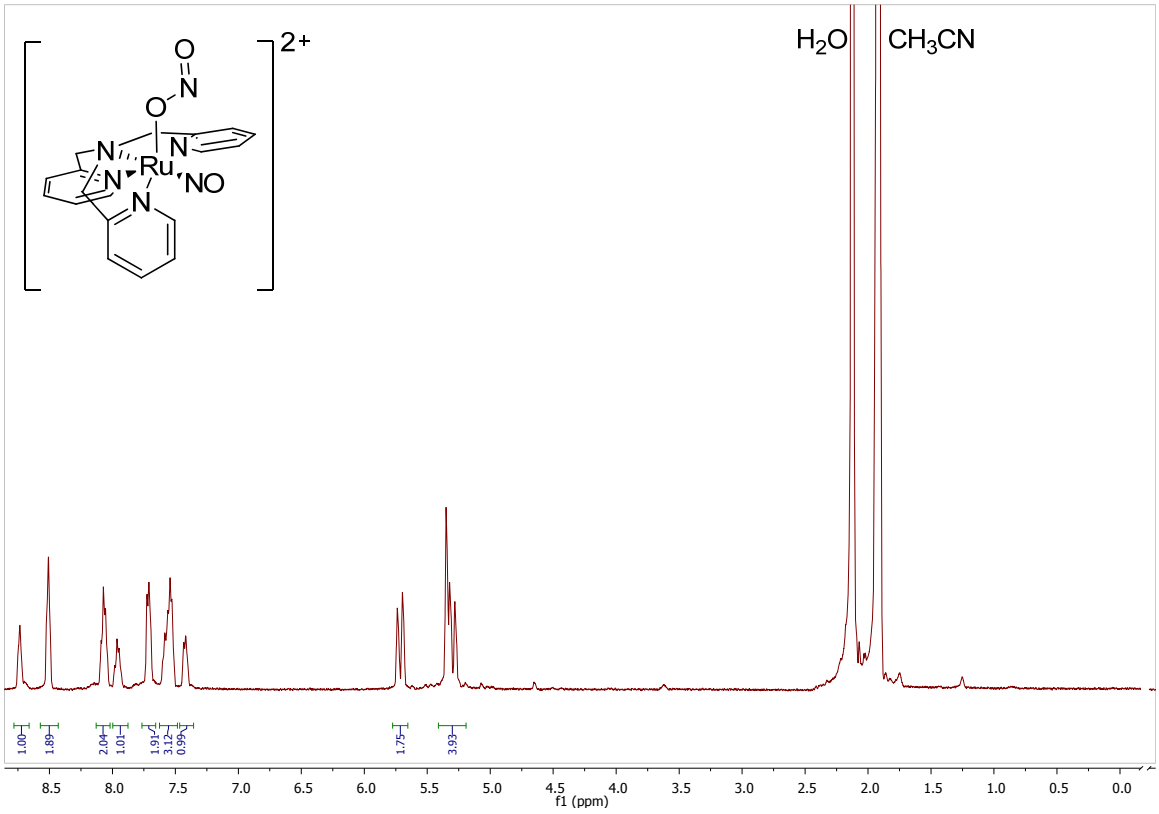


Figure S5. ^{1}H-NMR spectrum of **5** in deuterated dmso. The aromatic protons are observed as a range of doublets and triplets. The methylene hydrogens of the TPA coligand are found around ~5 ppm.

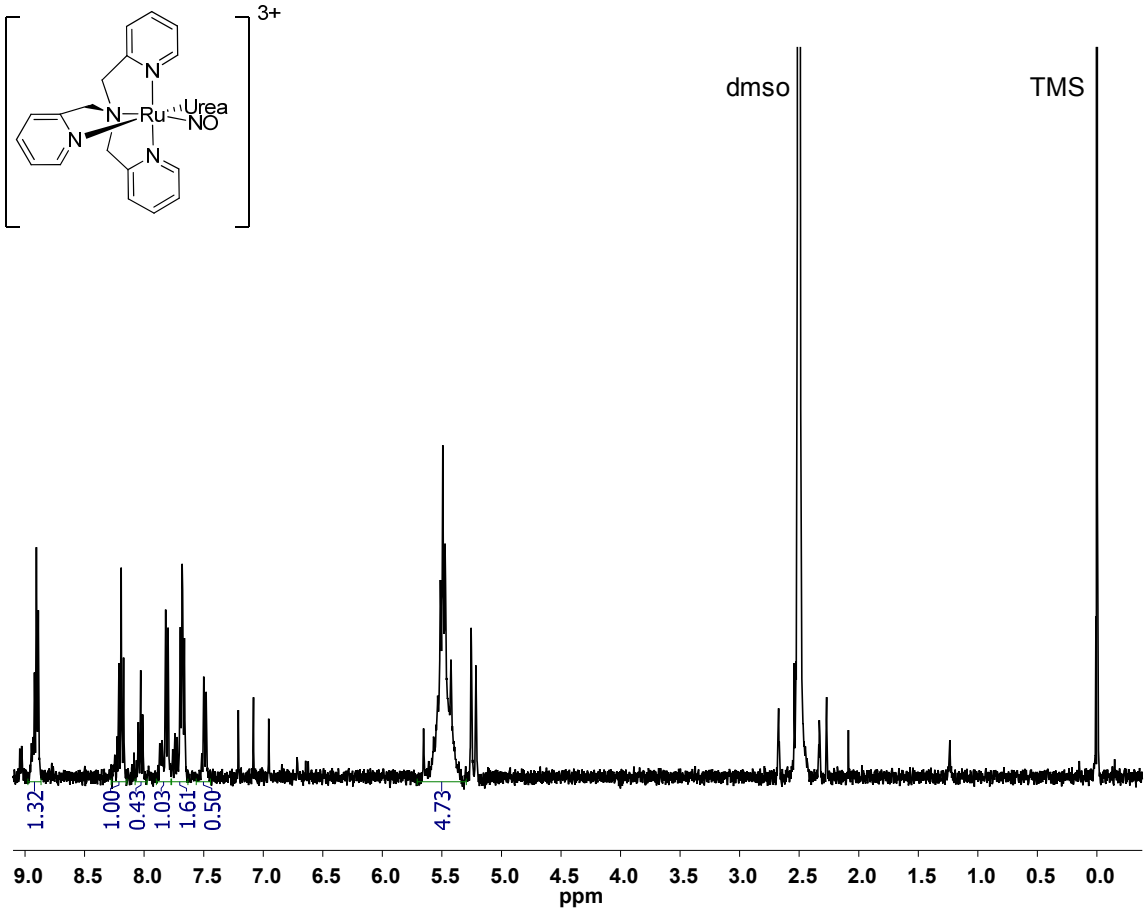
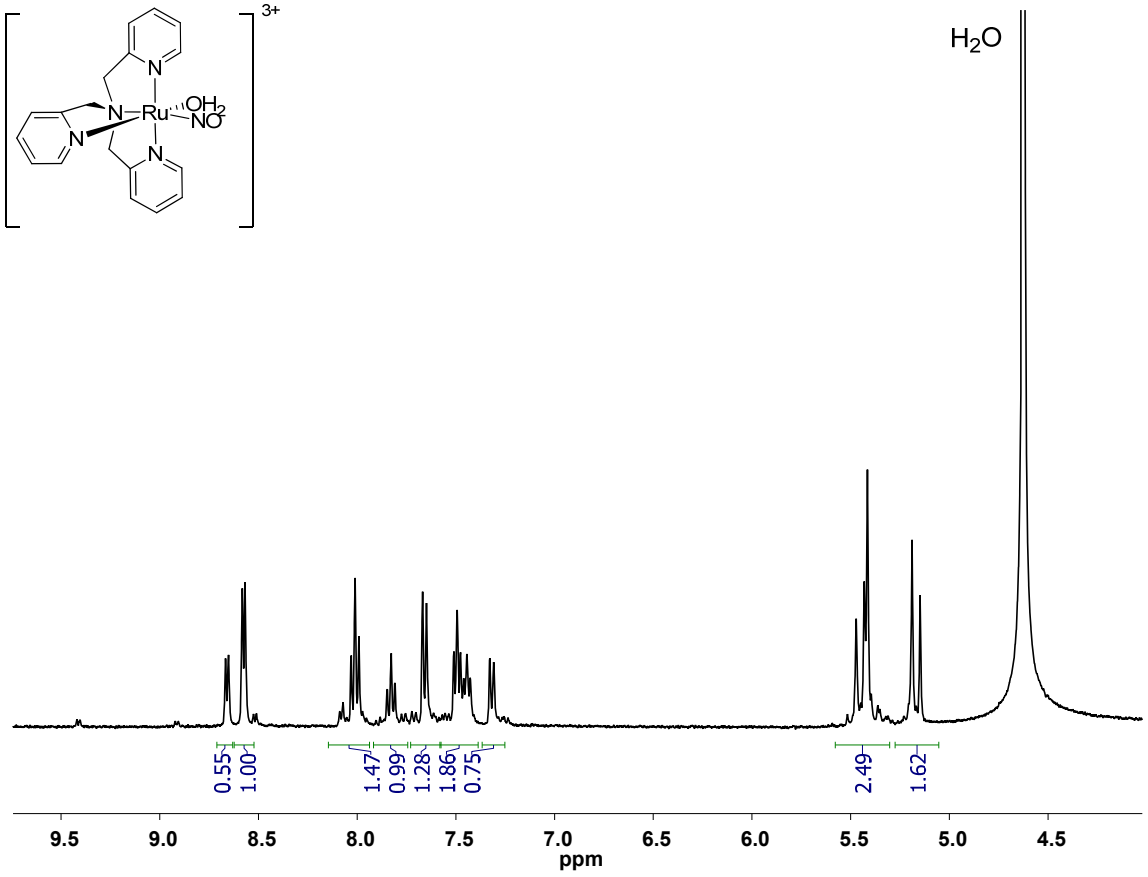


Figure S6. ^{1}H-NMR spectrum of **6** in D_2O. The aromatic protons are observed as a range of doublets and triplets. The methylene hydrogens of the TPA coligand are found around ~5 ppm.



Structure 2: The Cartesian coordinated of **2** were obtained from the cif file of the crystal structure and optimized with BP86/TZVP, resulting in the coordinates listed in Tables S1.

Figure S7. Optimized structure of **2** using BP86/TZVP.

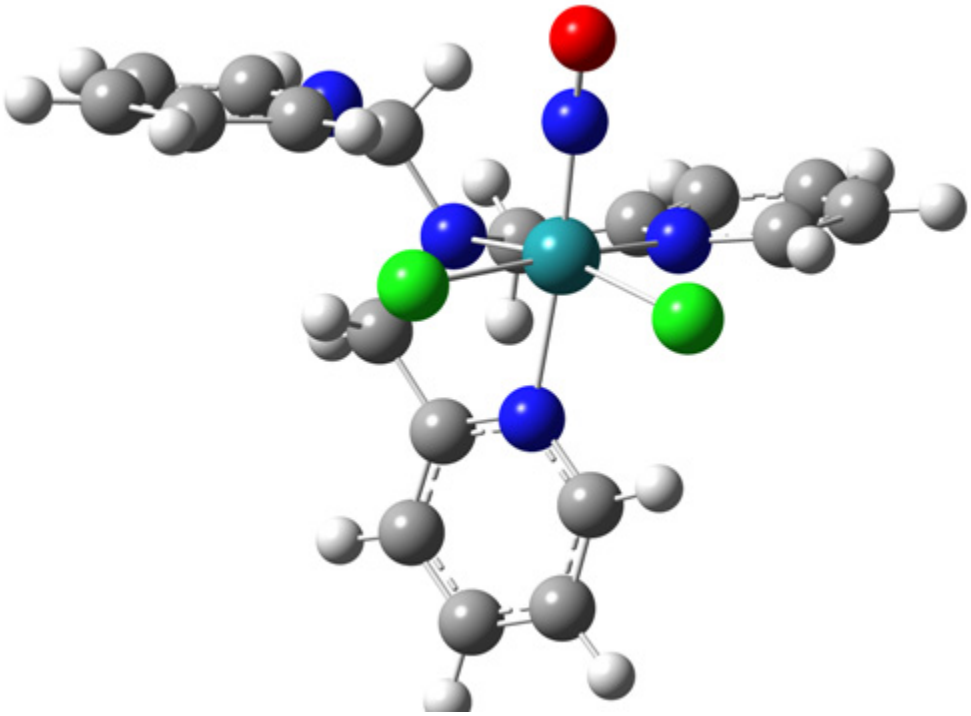


Table S1. Cartesian coordinates of **2** (BP86/TZVP).

Ru	-1.06465800	-0.09407900	-0.82514200
N	-0.85866300	0.85677200	-2.31878300
O	-0.78791200	1.38141100	-3.34118200
Cl	-0.49443400	-2.11520600	-2.00105400
Cl	-3.39465500	-0.38488500	-1.27506600
N	-1.23128400	-1.38436300	0.89912000
N	0.93229600	0.02860800	0.09576700
N	-1.37918500	1.59689200	0.44406200
C	-2.38731000	-1.82010500	1.44270400
H	-3.29841800	-1.45320200	0.96642000
C	-2.39754000	-2.70590000	2.51790000
H	-3.35171800	-3.04255700	2.92370400
C	-1.18323700	-3.14667900	3.04759700
H	-1.16300900	-3.84070300	3.88966400
C	0.01045600	-2.68779900	2.48379500
H	0.97737400	-3.01310600	2.87055700
C	-0.04131100	-1.81160800	1.39989000
C	1.17921300	-1.33701800	0.66449100
H	2.07109500	-1.33479900	1.31035800
H	1.34794000	-2.01118500	-0.19190100

C	0.89044600	1.05412300	1.21184200
H	0.83367000	0.50676000	2.16700100
H	1.84843200	1.60168200	1.21797400
C	-0.29063600	1.98670900	1.15463400
C	-0.30616200	3.18144300	1.88131700
H	0.58348200	3.48838700	2.43360900
C	-1.46242900	3.96366500	1.88992000
H	-1.48826400	4.89916500	2.45153100
C	-2.58123500	3.53586100	1.16913000
H	-3.50414200	4.11602300	1.15101600
C	-2.50370300	2.34835200	0.44749600
H	-3.33064500	1.95443200	-0.14803300
C	1.98458000	0.36138700	-0.94686500
H	1.80043000	-0.32242900	-1.78656200
H	1.78559800	1.39227000	-1.27253700
C	3.42413500	0.24654300	-0.48228300
C	4.26919700	-0.74061600	-1.00676700
C	5.12759700	1.11870600	0.80963100
C	5.60537700	-0.77174600	-0.59388500
H	3.89256600	-1.46195600	-1.73531200
H	5.43451400	1.87862700	1.53374800
H	6.29036900	-1.52143800	-0.99441900
C	6.04535700	0.17581200	0.33152100
H	7.08020900	0.19312700	0.67656900
N	3.84491000	1.16692500	0.41325200

Structure 4: The Cartesian coordinated of **4** were obtained from the cif file of the crystal structure and optimized with BP86/TZVP, resulting in the coordinates listed in Tables S2.

Figure S8. Optimized structure of **4** using BP86/TZVP.

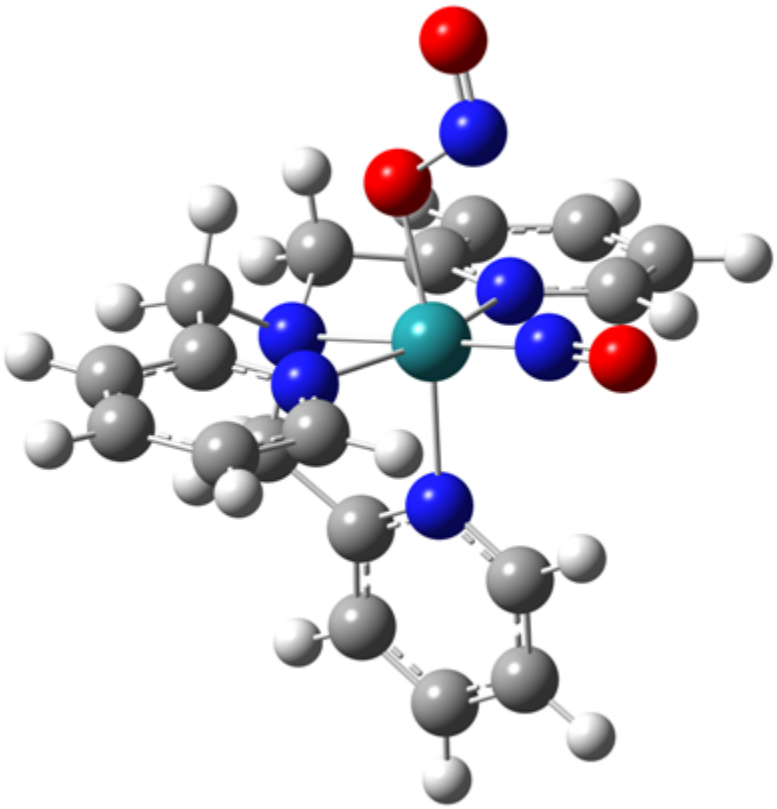


Table S2. Cartesian coordinates of **4** (BP86/TZVP).

Ru	0.11698800	-0.39555400	0.40523500
N	0.17865900	-0.84136700	2.16622200
O	0.21827100	-1.02318200	3.30307000
N	2.17944400	0.04543900	0.08670300
N	0.09057000	0.12973200	-1.65522600
N	-0.39937300	1.68924000	0.59549200
N	-1.94343300	-0.73161500	0.00352400
C	3.12304600	0.30813700	1.01979500
H	2.80456800	0.30340400	2.06178700
C	4.44723300	0.56680100	0.67357500
H	5.17764300	0.76057500	1.45986500
C	4.80777700	0.57532500	-0.67544700
H	5.83695200	0.78022400	-0.97506800
C	3.82828900	0.32061800	-1.64066600
H	4.07675800	0.32276900	-2.70340100
C	2.52264200	0.04744800	-1.23539800

C	1.42562900	-0.33427700	-2.19644300
H	1.59562400	0.07687600	-3.20360700
H	1.38066700	-1.43222100	-2.26112500
C	-0.05776400	1.62747700	-1.82613900
H	0.93688900	2.02766800	-2.07881400
H	-0.71291000	1.83239300	-2.68609400
C	-0.54557200	2.33906800	-0.58812800
C	-1.03226000	3.64713100	-0.64815600
H	-1.14498900	4.14195000	-1.61464500
C	-1.35933000	4.31112400	0.53566700
H	-1.73801600	5.33425300	0.50877000
C	-1.19097900	3.64388300	1.75258800
H	-1.42823800	4.12370900	2.70273900
C	-0.72034100	2.33508400	1.74410700
H	-0.59214500	1.78089600	2.67383800
C	-1.05187800	-0.65188000	-2.26223400
H	-0.68454500	-1.67981800	-2.40734700
H	-1.32153200	-0.23674400	-3.24523800
C	-2.23450000	-0.71100300	-1.32959000
C	-3.54588400	-0.85256700	-1.78283800
H	-3.75459800	-0.83054900	-2.85379700
C	-4.57592100	-1.04037300	-0.85658000
H	-5.60611100	-1.16305100	-1.19508400
C	-4.26520900	-1.07247000	0.50479200
H	-5.03562700	-1.22285800	1.26184700
C	-2.94118300	-0.90346700	0.90121500
H	-2.66305900	-0.91275900	1.95465700
O	0.49529800	-2.27268900	-0.24421200
N	0.65296100	-3.23449200	0.83210000
O	0.86275700	-4.32128400	0.44463700

Structure 4b: The Cartesian coordinates of **4b** (NO trans to py) were obtained by changing the position of NO and ONO^- in **4**, and re-optimizing the structure with BP86/TZVP.

Figure S9. Optimized structure of **4b** using BP86/TZVP.

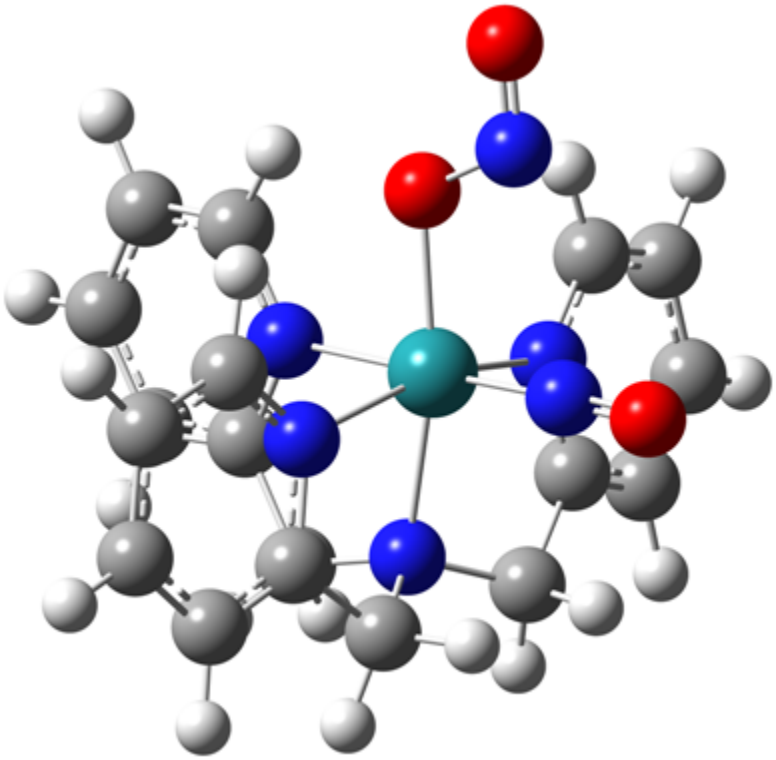


Table S3. Cartesian coordinates of **4b** (BP86/TZVP).

Ru	-0.06659400	-0.59814200	0.02556300
N	-0.17752500	-2.21385600	-0.80637300
O	-0.21951900	-3.20646800	-1.38718900
N	2.03528700	-0.47929700	-0.26855600
N	-0.05572100	0.71149500	-1.68443600
N	0.13845100	1.27589500	1.00169200
N	-2.15242500	-0.22274100	-0.13628300
C	3.01135800	-0.80866700	0.60256200
H	2.68367900	-1.22659900	1.55559200
C	4.35778300	-0.62818700	0.28689200
H	5.12316900	-0.91665200	1.00816800
C	4.69346400	-0.07533700	-0.95078800
H	5.73886100	0.08203100	-1.22230200
C	3.67476200	0.27802800	-1.84470400
H	3.91393400	0.71149700	-2.81742700
C	2.34553000	0.05914900	-1.48599300
C	1.18697300	0.31371000	-2.43837900
H	1.45701400	1.07268200	-3.18994800

H	0.95602800	-0.61614600	-2.98322800
C	-0.01839200	2.16674000	-1.26984600
H	0.74510900	2.69330900	-1.86245800
H	-0.98724200	2.62014900	-1.53202500
C	0.22190000	2.37078600	0.20507600
C	0.45607200	3.63707200	0.74411300
H	0.52454500	4.50567600	0.08652600
C	0.59238300	3.77457900	2.12749900
H	0.77431700	4.75728500	2.56645200
C	0.49142300	2.63988300	2.93898100
H	0.58802500	2.70498900	4.02320100
C	0.27162500	1.40115900	2.34624300
H	0.19688200	0.47255200	2.91570400
C	-1.35688800	0.39778700	-2.37968800
H	-1.23431700	-0.56820500	-2.89515400
H	-1.59112600	1.15164200	-3.14851300
C	-2.48050600	0.29529000	-1.35913300
C	-3.79810900	0.64500900	-1.64913100
H	-4.05054400	1.06171800	-2.62586500
C	-4.78969400	0.44618500	-0.67962600
H	-5.82696400	0.70819400	-0.89595300
C	-4.43683100	-0.08532300	0.56243000
H	-5.18096400	-0.25387900	1.34164700
C	-3.10069300	-0.40349700	0.80612100
H	-2.76017000	-0.81719900	1.75653100
O	-0.06551700	-1.42956200	1.87195900
N	-0.15189000	-2.87672800	1.87517000
O	-0.15575100	-3.33076500	2.95898000

Structure 6: The Cartesian coordinated of **6** were obtained by changing the ONO^- ligand in **4** to a water molecule, and re-optimizing the structure with BP86/TZVP.

Figure S10. Optimized structure of **6** using BP86/TZVP.

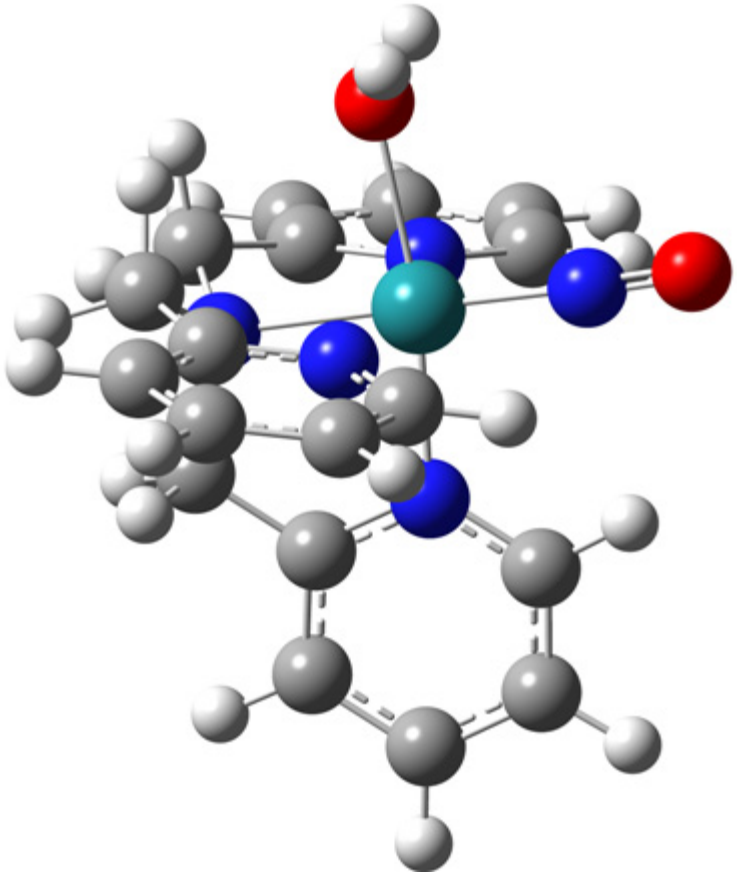


Table S4. Cartesian coordinates of **6** (BP86/TZVP).

Ru	0.08666700	-0.44949500	0.62728300
N	0.10191500	-0.25915500	2.43620100
O	0.14369600	-0.18392100	3.57520000
N	2.18922600	-0.30625000	0.22935100
N	0.12494400	-0.65420500	-1.48575200
N	-0.21454500	1.55592700	0.15243100
N	-2.00259800	-0.72644300	0.26158800
C	3.14524800	0.21594500	1.03957000
H	2.82527200	0.60849800	2.00471600
C	4.48588200	0.24979300	0.66198400
H	5.22394200	0.66499100	1.35069700
C	4.85433400	-0.24278900	-0.59294800
H	5.89780200	-0.22135300	-0.91473100
C	3.86370900	-0.75567000	-1.43989500
H	4.12005400	-1.13624900	-2.43097900

C	2.53914300	-0.78325200	-1.00704800
C	1.41508900	-1.37541600	-1.82086500
H	1.61177300	-1.31153600	-2.90264200
H	1.27644300	-2.43799300	-1.57086600
C	0.12718700	0.72886600	-2.12729900
H	1.15159500	0.92484000	-2.48153400
H	-0.52189500	0.71401100	-3.01539500
C	-0.26692300	1.82913100	-1.18129500
C	-0.57867300	3.11186600	-1.63720000
H	-0.61680600	3.30800700	-2.71106200
C	-0.82751600	4.13199000	-0.71645800
H	-1.06883500	5.14017200	-1.05985500
C	-0.76007800	3.84062800	0.65006200
H	-0.94254400	4.60482200	1.40772600
C	-0.46357000	2.54397500	1.05341700
H	-0.42101300	2.28679800	2.11060300
C	-1.09021200	-1.47219900	-1.87481100
H	-0.83297400	-2.53087200	-1.71286400
H	-1.29919400	-1.34846600	-2.94833800
C	-2.28003300	-1.10959800	-1.02344200
C	-3.59546100	-1.24670700	-1.46463000
H	-3.79492500	-1.55302500	-2.49372900
C	-4.64905600	-0.99903600	-0.57680000
H	-5.68462300	-1.10704700	-0.90651400
C	-4.35555100	-0.61160300	0.73384500
H	-5.14558700	-0.41085300	1.45971500
C	-3.02466500	-0.46927500	1.11832000
H	-2.76485900	-0.15221200	2.12821400
O	0.33133900	-2.66709500	0.78213000
H	1.15176600	-3.03977000	1.16563000
H	-0.40472200	-3.20585600	1.13835700

Structure 6b: The Cartesian coordinated of **6b** (NO trans to py) were obtained by changing the position of NO and H_2O in **6**, and re-optimizing the structure with BP86/TZVP.

Figure S11. Optimized structure of **6b** using BP86/TZVP.

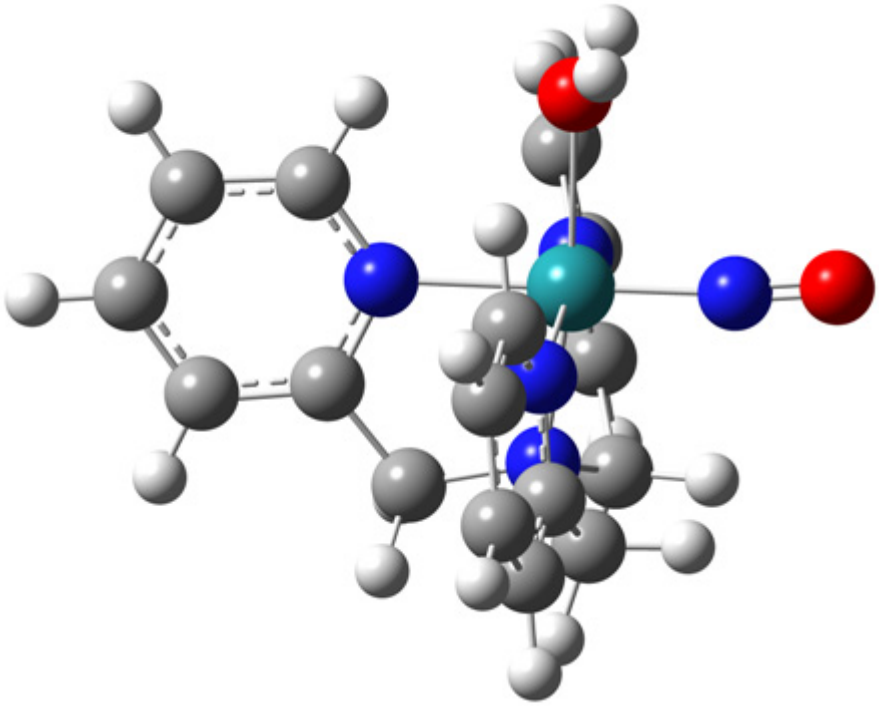


Table S5. Cartesian Coordinates of **6b** (BP86/TZVP).

Ru	-0.04721100	-0.53233100	-0.59748000
N	-0.12674800	-2.33494700	-0.87074400
O	-0.15924600	-3.44034100	-1.15367300
N	-2.15908600	-0.33887800	-0.25385700
N	-0.06458300	-0.54017300	1.48784500
N	0.09428000	1.54648900	-0.31176200
N	2.07093600	-0.54062000	-0.24760200
C	-3.12145900	0.12072000	-1.08576100
H	-2.81151500	0.43721200	-2.08249300
C	-4.45696800	0.19742800	-0.69327900
H	-5.20488000	0.56143000	-1.39979500
C	-4.80613200	-0.19186000	0.60279900
H	-5.84452200	-0.14038500	0.93742500
C	-3.80485900	-0.63901800	1.47497000
H	-4.04967200	-0.93698900	2.49672200
C	-2.48767000	-0.70884400	1.02466400
C	-1.35437500	-1.23906500	1.87519000
H	-1.55188400	-1.10095100	2.94978500

H	-1.21378300	-2.31894900	1.70633400
C	-0.05969600	0.88980600	2.03998200
H	-1.02697400	1.05608800	2.53840400
H	0.71728100	0.95845800	2.81550500
C	0.14012600	1.94722700	0.98794800
C	0.30779100	3.29236700	1.31871400
H	0.34466900	3.59721500	2.36690700
C	0.41995700	4.23953200	0.29652800
H	0.54991400	5.29664900	0.53840500
C	0.36198900	3.81610800	-1.03689700
H	0.44257000	4.52430000	-1.86312200
C	0.20594500	2.46196000	-1.30995400
H	0.16626900	2.08010500	-2.32972700
C	1.18153400	-1.29841200	1.90291900
H	0.97435500	-2.37226900	1.76409000
H	1.38061600	-1.14301600	2.97446000
C	2.35694700	-0.88104600	1.04799900
C	3.67243300	-0.90656600	1.50847800
H	3.88397200	-1.18103700	2.54410200
C	4.71462500	-0.58829700	0.62821400
H	5.75129300	-0.61346600	0.97103300
C	4.41002200	-0.23251300	-0.68857400
H	5.19179300	0.02832700	-1.40394300
C	3.07543600	-0.20782500	-1.09018100
H	2.80164500	0.08567200	-2.10433100
O	-0.03457000	-0.23254200	-2.82814300
H	-0.83107100	-0.44557500	-3.35581600
H	0.72028900	-0.54049700	-3.36996900

Structure 9: The Cartesian coordinated of **9** (NO trans to am) were obtained by changing the position of the ONO^- ligand in **4** to N-bound NO_2^-, and re-optimizing the structure with BP86/TZVP.

Figure S12. Optimized structure of **9** using BP86/TZVP.

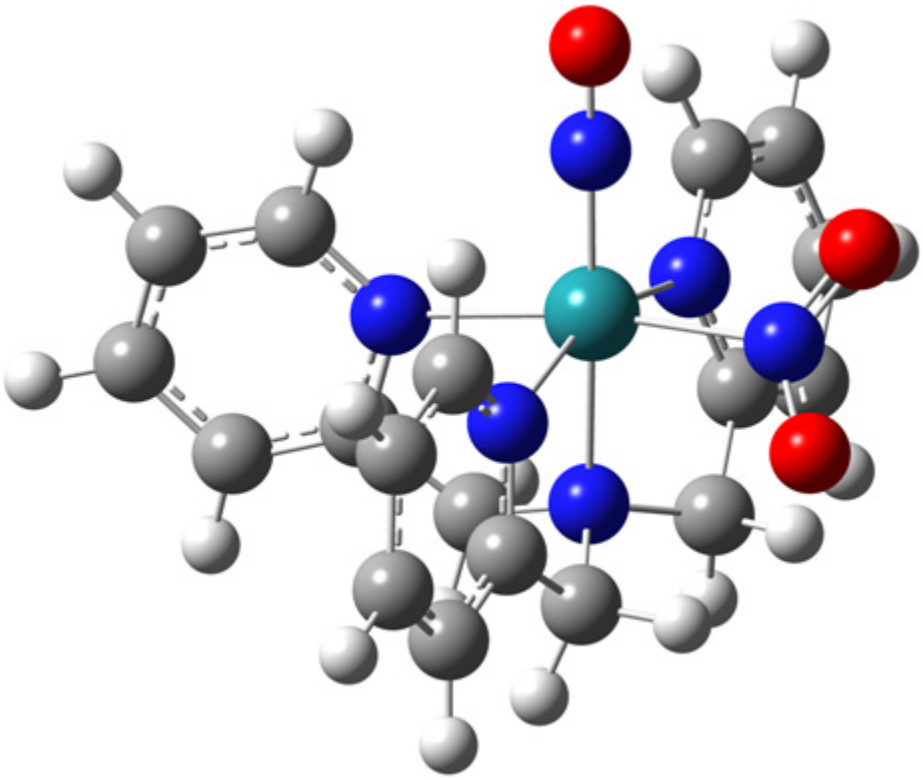


Table S6. Cartesian Coordinates of **9** (BP86/TZVP).

Ru	0.16326600	-0.36935700	0.52151400
N	0.21608700	-0.59665800	2.30981500
O	0.26671500	-0.72595400	3.44865900
N	2.20926100	0.14711000	0.13230900
N	0.14029400	-0.00370300	-1.59883900
N	-0.60770300	1.71340000	0.47673500
N	-1.85329700	-0.91310800	0.10534000
C	3.14063100	0.50958300	1.04464100
H	2.81038900	0.60395200	2.07822100
C	4.46625000	0.74594200	0.68849700
H	5.18529000	1.02443900	1.45964300
C	4.84269500	0.61995500	-0.64980300
H	5.87411300	0.80038400	-0.95736500
C	3.87651000	0.26164500	-1.59551800
H	4.13832300	0.15939000	-2.65015000
C	2.56826000	0.01862100	-1.18085400
C	1.48572700	-0.45265600	-2.12266900
H	1.64364800	-0.07112000	-3.14407700

H	1.47734500	-1.55128300	-2.17110800
C	-0.00372200	1.48344000	-1.85927600
H	1.01596200	1.89627400	-1.92074200
H	-0.47433700	1.63409000	-2.84250400
C	-0.73120200	2.22555700	-0.77190800
C	-1.38560100	3.43635000	-1.00859000
H	-1.47332700	3.82136400	-2.02616000
C	-1.91048600	4.14803300	0.07337200
H	-2.42210000	5.09862000	-0.08705100
C	-1.76631500	3.62482600	1.36129100
H	-2.15452000	4.14902700	2.23534200
C	-1.12190700	2.40085500	1.52316200
H	-1.00727600	1.95728600	2.51279100
C	-0.99991200	-0.80168300	-2.18957800
H	-0.61574300	-1.81221800	-2.39075300
H	-1.31947400	-0.35414300	-3.14256600
C	-2.15066400	-0.94164800	-1.22657400
C	-3.44729600	-1.21329600	-1.66646400
H	-3.66192700	-1.22805700	-2.73642000
C	-4.45028700	-1.48427200	-0.73323500
H	-5.46551200	-1.70952700	-1.06417000
C	-4.13100700	-1.46860600	0.62685900
H	-4.87874300	-1.68237400	1.39136300
C	-2.82865100	-1.16724500	1.01144000
H	-2.54724500	-1.13713000	2.06335800
N	0.80163800	-2.39601300	0.26759800
O	1.62534900	-2.83322800	1.05993500
O	0.31160600	-3.02542100	-0.67781200

Structure 9b: The Cartesian coordinated of **9b** (NO cis to am) were obtained by changing the position of the ONO^- ligand in **4b** to N-bound NO_2^- and re-optimizing the structure with BP86/TZVP.

Figure S13. Optimized structure of **9b** using BP86/TZVP.

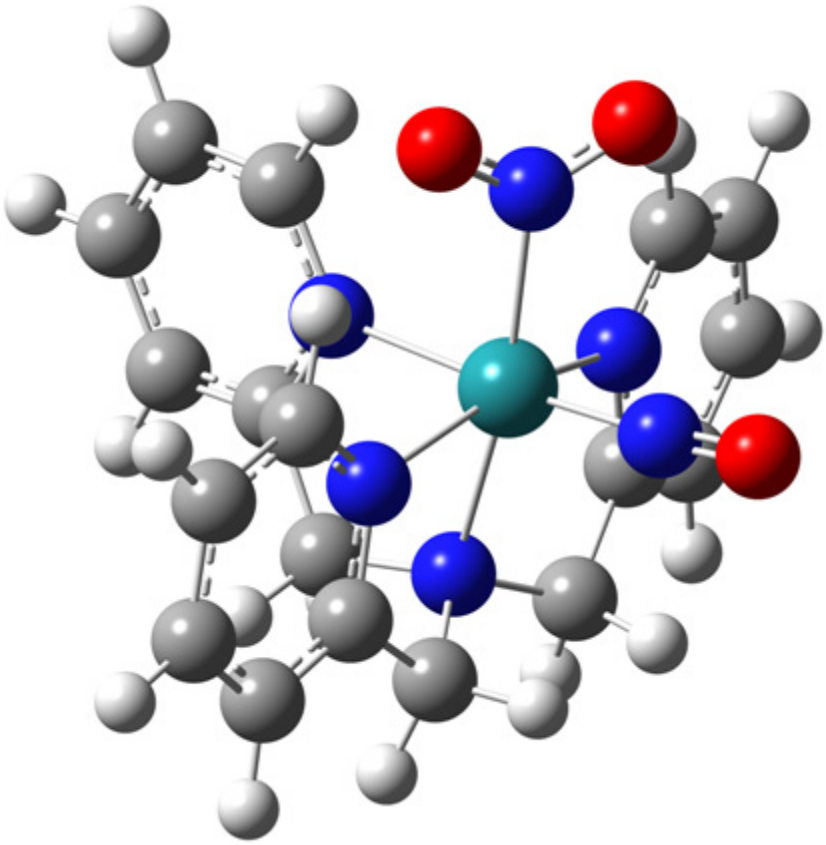


Table S7. Cartesian Coordinates of **9b** (BP86/TZVP).

Ru	-0.07524	-0.63268	0.29232
N	-0.18904	-2.4347	0.23016
O	-0.23921	-3.57949	0.28236
N	2.04104	-0.61062	-0.09082
N	-0.09336	-0.02942	-1.80995
N	0.1284	1.50095	0.49713
N	-2.18398	-0.32867	-0.0182
C	3.04882	-0.6073	0.80768
H	2.75733	-0.70434	1.85398
C	4.38283	-0.52382	0.40842
H	5.16887	-0.53619	1.16426
C	4.67896	-0.42441	-0.95164
H	5.71349	-0.35122	-1.29198
C	3.63055	-0.42575	-1.87976
H	3.83365	-0.35889	-2.9501
C	2.3162	-0.5297	-1.4278
C	1.14315	-0.66219	-2.37968

H	1.38775	-0.23608	-3.3661
H	0.92446	-1.73165	-2.5333
C	-0.07768	1.46956	-1.95156
H	0.64445	1.75678	-2.73136
H	-1.06978	1.78897	-2.30885
C	0.21603	2.20109	-0.66575
C	0.48404	3.57153	-0.67216
H	0.55242	4.10456	-1.62244
C	0.65068	4.24549	0.53849
H	0.86184	5.31628	0.55054
C	0.53396	3.52599	1.73095
H	0.6429	4.00883	2.70266
C	0.27833	2.16054	1.67655
H	0.17023	1.57612	2.58722
C	-1.38351	-0.60069	-2.32744
H	-1.24685	-1.68872	-2.4354
H	-1.62405	-0.20024	-3.3258
C	-2.50705	-0.31931	-1.34769
C	-3.82269	-0.11596	-1.75959
H	-4.0635	-0.10414	-2.8242
C	-4.82501	0.06124	-0.79766
H	-5.86108	0.21245	-1.10611
C	-4.47991	0.04626	0.55422
H	-5.22855	0.18119	1.33573
C	-3.14471	-0.14331	0.91249
H	-2.80872	-0.15629	1.95067
N	-0.01888	-0.85887	2.4223
O	0.94119	-1.45615	2.90268
O	-0.9484	-0.37509	3.07317

Structure 10: The Cartesian coordinated of **10** (NO trans to am) were obtained by changing the ONO^- ligand in **4** to Cl^- and re-optimizing the structure with BP86/TZVP.

Figure S14. Optimized structure of $[Ru(TPA)(Cl)(NO)]^{2+}$ where NO is trans to am, and Cl^- is cis to am (**10**).

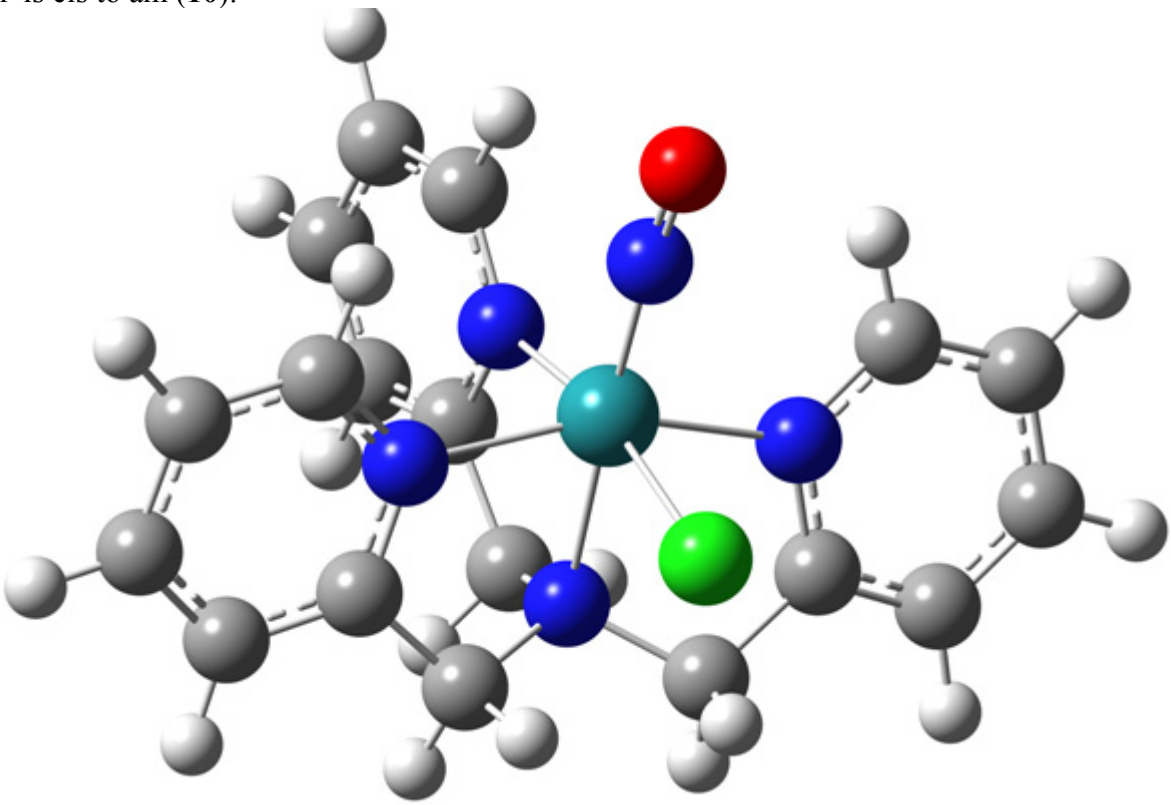


Table S8. Cartesian Coordinates of **10** (BP86/TZVP).

Ru	0.11494600	-0.42827300	0.55353500
Cl	0.45162900	-2.78714700	0.29878300
N	0.15190600	-0.62198100	2.34161400
O	0.21218300	-0.84843100	3.46475300
N	2.19555800	-0.14107500	0.17482700
N	0.13670700	-0.26726600	-1.58164900
N	-0.31458000	1.66653700	0.36499900
N	-1.95449600	-0.73693900	0.16197100
C	3.14098800	0.22064100	1.07254700
H	2.80839900	0.41096300	2.09227900
C	4.48262600	0.33931300	0.71959200
H	5.21296600	0.61851200	1.47977400
C	4.86051200	0.09917000	-0.60308500
H	5.90439900	0.18815900	-0.90855800
C	3.88001600	-0.25532100	-1.53435700
H	4.14176000	-0.44631300	-2.57653600
C	2.55428700	-0.38158800	-1.12124300

C	1.45370300	-0.85553900	-2.03550400
H	1.64674700	-0.59342800	-3.08748000
H	1.37031900	-1.94940400	-1.94709700
C	0.06290200	1.18970600	-1.99732100
H	1.08307500	1.50103500	-2.27252800
H	-0.55415700	1.27776900	-2.90403400
C	-0.42236900	2.11359400	-0.91222600
C	-0.86067500	3.40980500	-1.19382400
H	-0.94349400	3.74189000	-2.23035600
C	-1.17747700	4.27011400	-0.14094200
H	-1.51856200	5.28702900	-0.34222800
C	-1.04751600	3.80797800	1.17229000
H	-1.27806300	4.44559100	2.02652700
C	-0.62548900	2.50070600	1.38857900
H	-0.52873300	2.10107000	2.39763100
C	-1.04063300	-1.07491000	-2.07378100
H	-0.72928000	-2.13094100	-2.04246400
H	-1.28100800	-0.80846000	-3.11425100
C	-2.22979200	-0.92406200	-1.16141300
C	-3.54230100	-1.08541300	-1.60578600
H	-3.73944500	-1.23013200	-2.66935600
C	-4.58778800	-1.08055000	-0.67839300
H	-5.61874700	-1.21747000	-1.00900700
C	-4.29170000	-0.90443500	0.67517500
H	-5.07426700	-0.90248900	1.43467100
C	-2.96619700	-0.72291800	1.06007600
H	-2.69895100	-0.57310300	2.10550100

Structure 10b: The Cartesian coordinated of **10b** (NO cis to am) were obtained by changing the ONO^- ligand in **4b** to Cl^- and re-optimizing the structure with BP86/TZVP.

Figure S15. Optimized structure of $[Ru(TPA)(Cl)(NO)]^{2+}$ where NO is cis to am, and Cl^- is trans to am (**10b**).

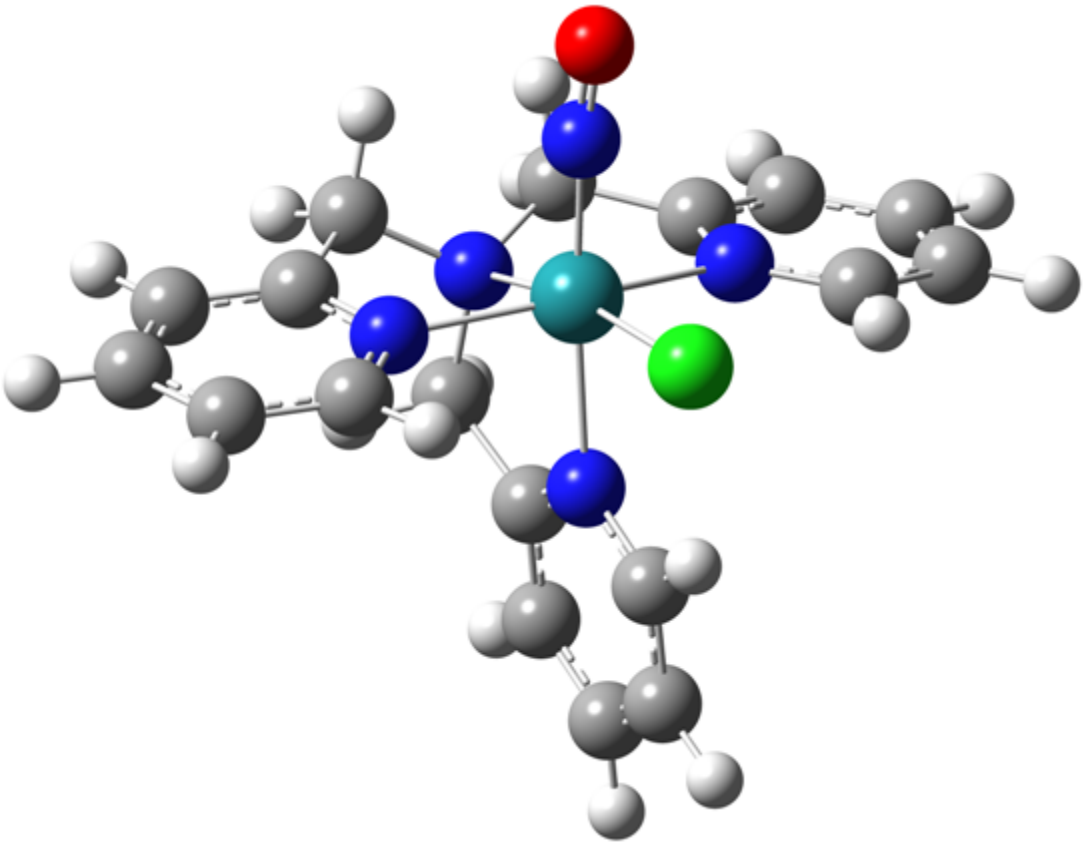


Table S9. Cartesian Coordinates of **10b** (BP86/TZVP).

Ru	0.10110200	-0.60451800	0.40670400
N	0.27422700	-2.39308100	0.51588800
O	0.35248600	-3.51022100	0.75870200
Cl	0.08621400	-0.58088100	2.80157300
N	2.18147200	-0.27477900	0.11856300
N	0.11529100	-0.24139800	-1.70295800
N	-0.20961900	1.52576800	0.39492000
N	-1.99360500	-0.69915500	0.07439600
C	3.10604500	0.04186600	1.04889500
H	2.74377800	0.11738200	2.07582000
C	4.44320200	0.23689300	0.70057200
H	5.16970600	0.48004500	1.47673800
C	4.82005500	0.11573700	-0.63813400
H	5.85860100	0.26805300	-0.93755600
C	3.85201800	-0.20299300	-1.60008200
H	4.12403300	-0.30174000	-2.65253700
C	2.53370400	-0.40368300	-1.19724700

C	1.43044100	-0.83234700	-2.15098000
H	1.66380700	-0.53702800	-3.18661500
H	1.32496900	-1.92889500	-2.13442800
C	0.08250400	1.23803300	-2.01633800
H	1.09219500	1.53055400	-2.34510900
H	-0.59307700	1.41443100	-2.86705200
C	-0.29591500	2.09437500	-0.83754600
C	-0.63166500	3.43940300	-0.99515000
H	-0.69970300	3.86940400	-1.99623500
C	-0.86558500	4.22283300	0.13748100
H	-1.12758900	5.27733200	0.03331100
C	-0.75672400	3.63500000	1.40021800
H	-0.92544900	4.20821900	2.31242800
C	-0.43831000	2.28366500	1.49550700
H	-0.35964000	1.76337800	2.45142200
C	-1.11334500	-0.95764300	-2.20527700
H	-0.86378300	-2.03002700	-2.26030600
H	-1.37059900	-0.62839800	-3.22451900
C	-2.28711600	-0.76981900	-1.25884100
C	-3.61105100	-0.76393000	-1.69367500
H	-3.83665100	-0.81580200	-2.76027700
C	-4.64178000	-0.70484300	-0.74679800
H	-5.68378600	-0.70707000	-1.07185500
C	-4.32288500	-0.64702800	0.61137700
H	-5.09833800	-0.60739000	1.37717400
C	-2.98093600	-0.63458600	0.99224200
H	-2.66278700	-0.58401400	2.03525900

Figure S16. Overlay of the EPR spectra of $[Ru(TPA)Cl_2(NO)]ClO_4$ (**2**, black) and its photoproduct $[Ru(TPA)Cl_2(solv)]^+$ (red). The spectra were obtained in a 1:1 mixture of frozen proptionitrile and butyronitrile at 10K.

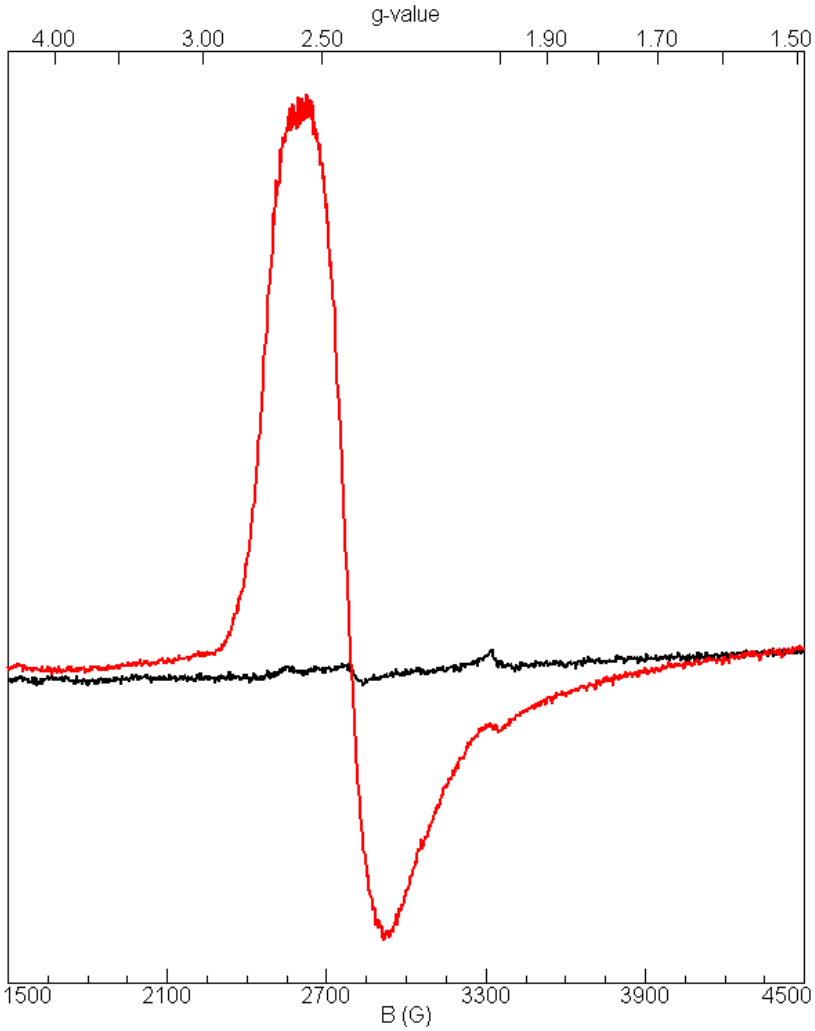


Figure S17. Overlay of the EPR spectra of [Ru(TPA)(ONO)(NO)]$(PF_6)_2$ (**4**, black) and its photoproduct $[Ru(TPA)(ONO)(solv)]^{2+}$ (red). The spectra were obtained in frozen DMF at 10K.

Figure S18. Overlay of the IR spectra of crude **4**, single-crystalline **4**, and **6**.

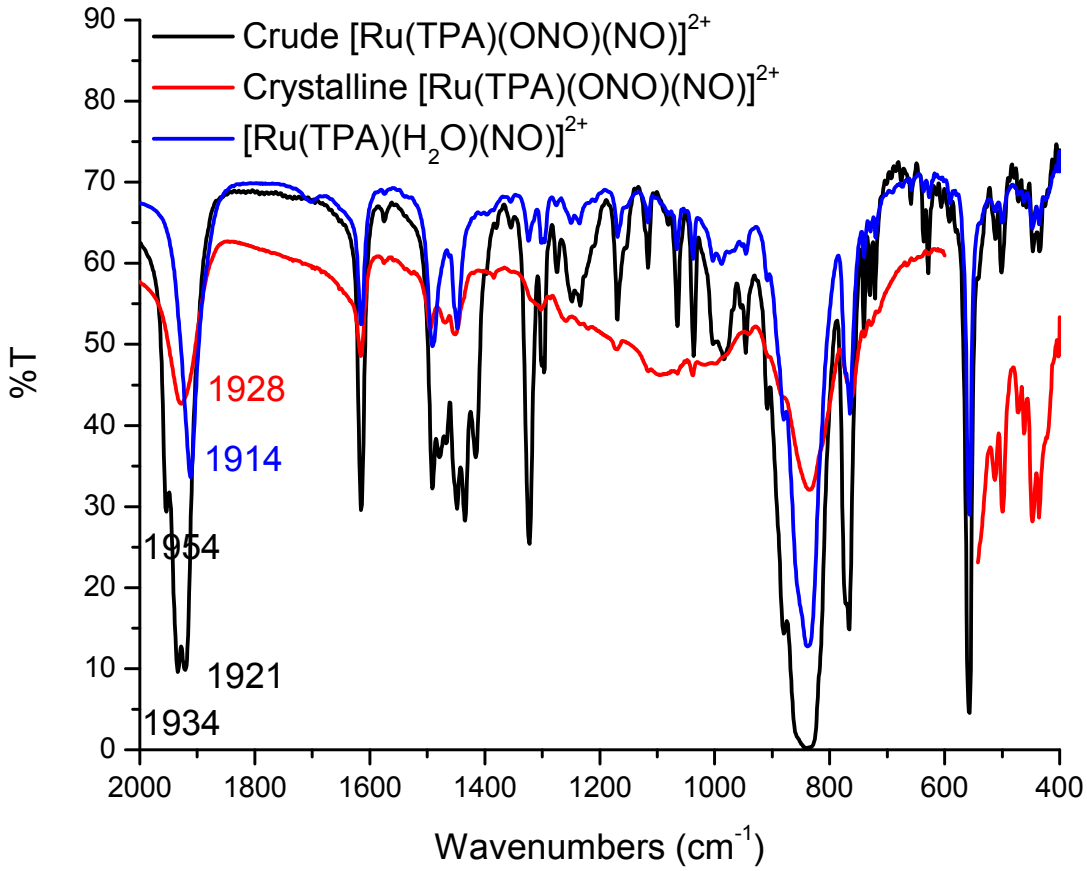


Figure S19. FT-Raman spectra of both the natural abundance (top) and $^{15}N^{18}O$-isotopically labeled (bottom) complex $[Ru(TPA)Cl_2(NO)]PF_6$ (**2**).

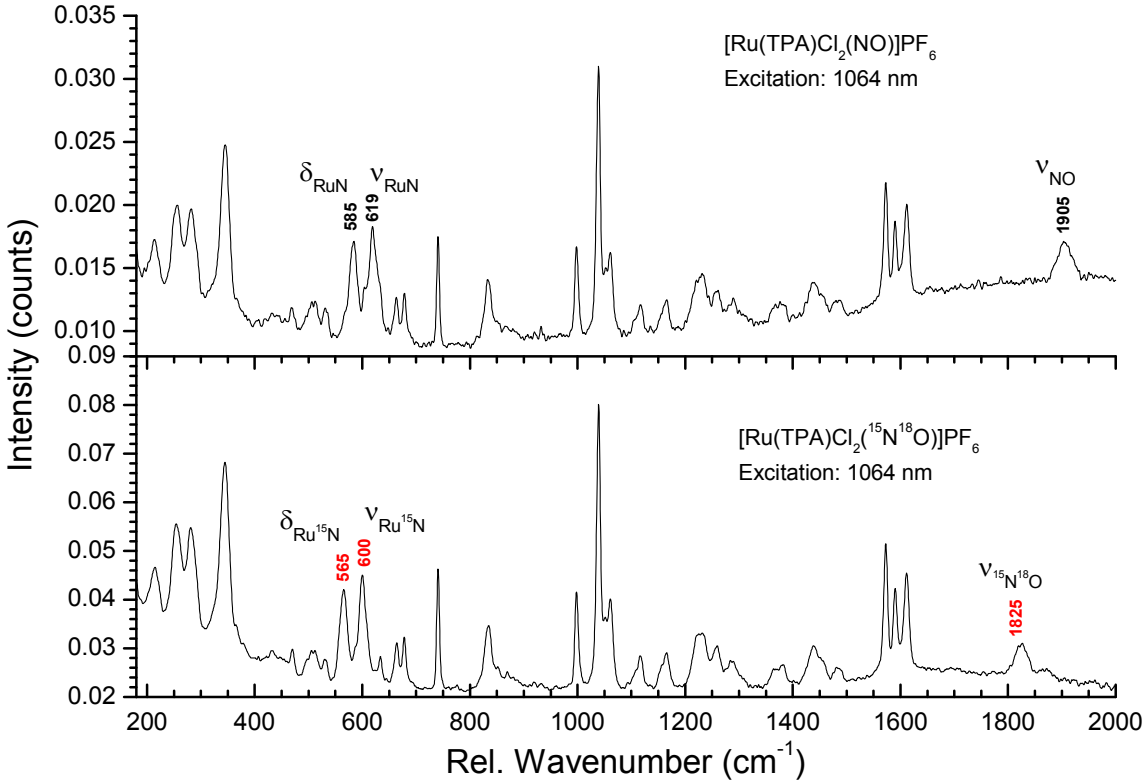


Figure S20. FT-Raman spectra of both the natural abundance (top) and ^{15}NO-isotopically labeled (bottom) complex [Ru(TPA)(Urea)(NO)](PF$_6$)$_3$ (**5**).

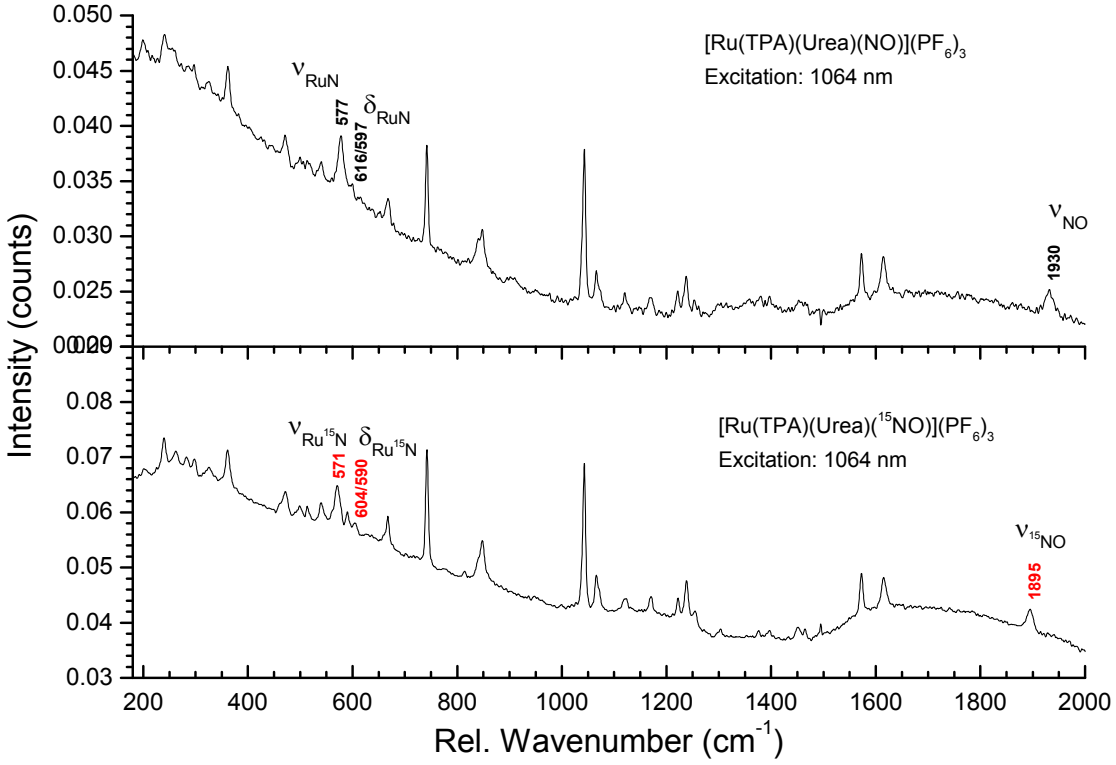


Figure S21. FT-Raman spectra of both the natural abundance (top) and ^{15}NO-isotopically labeled (bottom) complex [Ru(TPA)(H_2O)(NO)](PF_6)$_3$ (**6**).

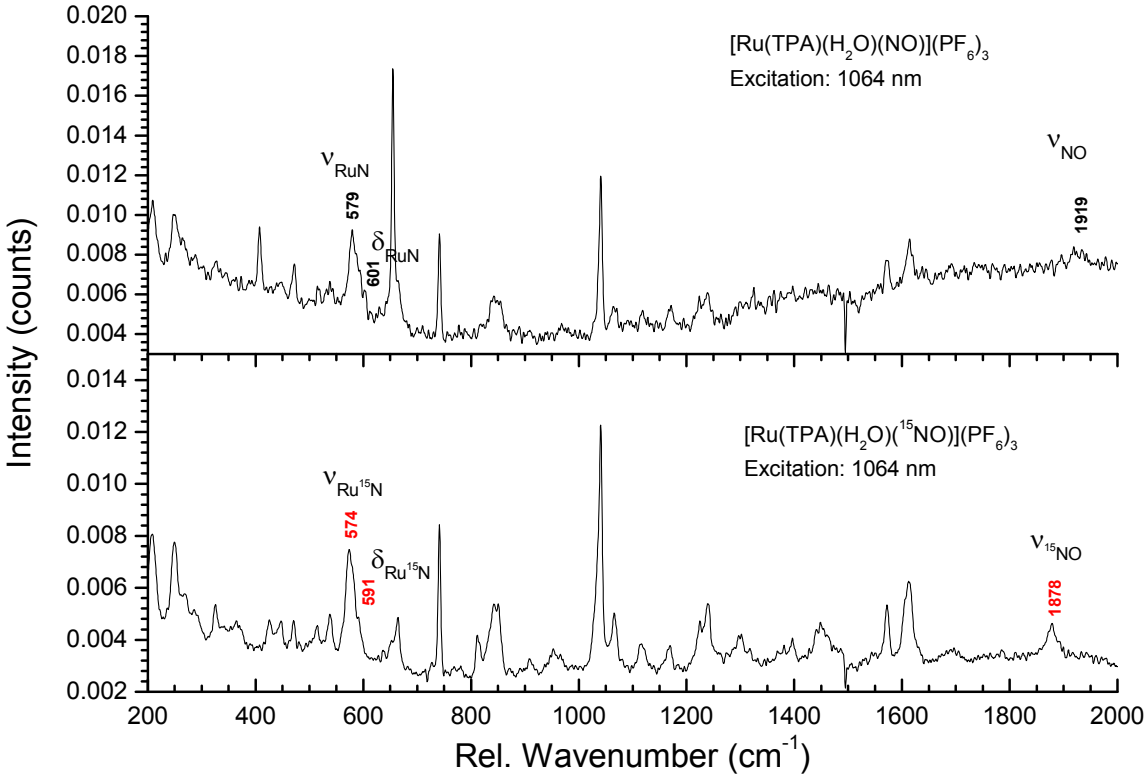


Figure S22. Experimental (black) versus DFT-calculated (blue; BP86/TZVP) absorption spectra of the photoproduct $[Ru(TPA)Cl_2(CH_3CN)]^+$ of **2**. The calculated spectrum overestimates the intensity of the Vis transitions, so we scaled it down by a factor of 2.5 to better match the experimental spectrum. For the calculated spectrum bandwidths at half-height were set to 2500 cm^{-1} for the plot.

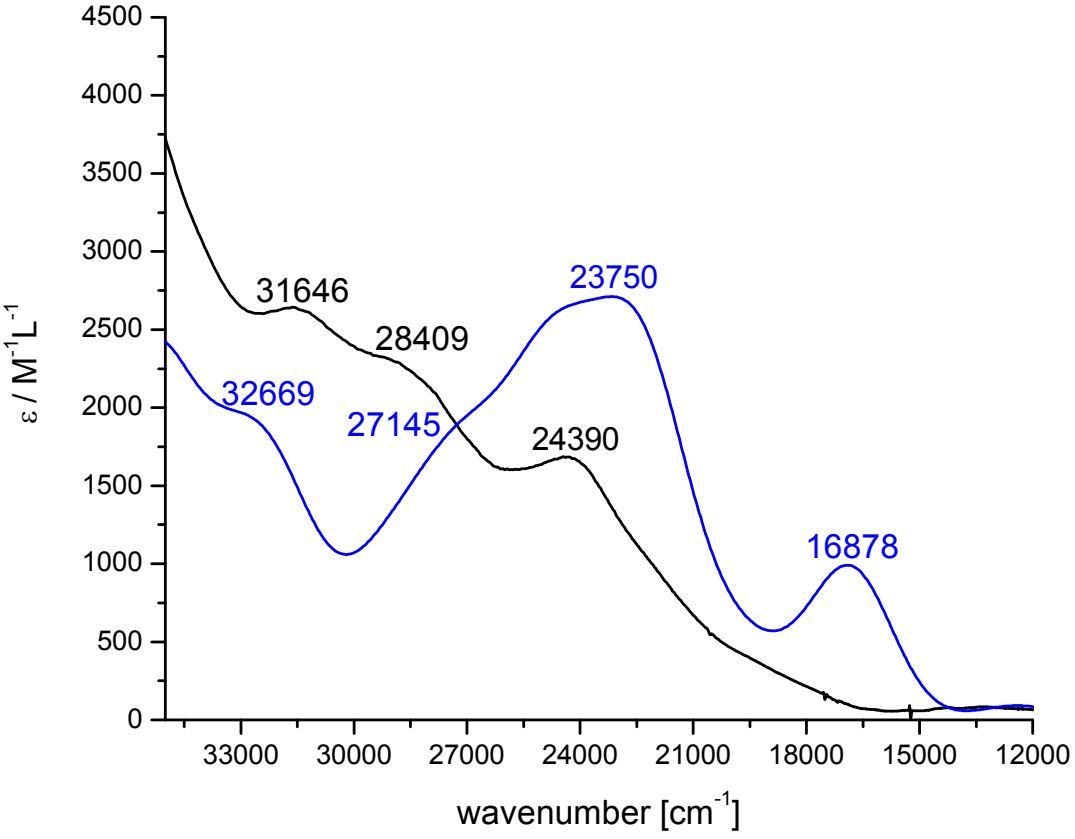


Table S10. Crystal Data and Results of the Structure Refinement for Compounds **1•0.5MeOH•0.5H_2O**, **2•CH_2Cl_2**, **3•2MeOH** , **4**

Complex	**1•0.5MeOH•0.5H_2O**	**2•CH_2Cl_2**	**3•2MeOH**	**4**
Empirical formula	$C_{18.5}H_{21}Cl_3N_4O_5Ru$	$C_{19}H_{20}Cl_5N_5O_5Ru$	$C_{20}H_{26}N_6O_6Ru$	$C_{18}H_{18}F_{12}N_6O_3P_2Ru$
Formula weight (g/mol)	586.81	676.75	547.54	757.39
T(K)	85	85	85	85
Space Group	Monoclinic, P2(1)/c	Monoclinic, P2(1)	Orthorhombic, Pccn	Monoclinic, P2(1)/n
a (Å)	10.4799	9.7546	19.347	16.3726
b (Å)	15.1542	13.7776	14.704	9.9439
c (Å)	14.4573	9.9353	16.562	17.3570
α (deg)	90	90	90	90
β (deg)	108.579	110.935	90	114.313
γ (deg)	90	90	90	90
V ($Å^3$)	2176.4	1247.11	4712	2575.2
Z	4	2	8	4
μ (mm^{-1})	1.129	10.393	0.713	7.272
λ (Å)	0.71073	1.54187	0.71073	1.54178
Collected reflns	75588	16404	63152	39910
Unique reflns	6147	3946	3651	4645
R_{int}	0.0313	0.0343	0.1070	0.0512
GOF	1.073	1.050	1.096	1.159
R1[a] [I > 2σ(I)]	0.0214	0.0175	0.0599	0.0462
wR2 (all data)	0.0578	0.0405	0.1521	0.1137

[a] R1= ∑jj*F*oj - j*F*cjj/∑j*F*oj; wR2) $[\sum[w(Fo^2 - Fc^2)^2]/\sum[w(Fo^2)^2]]^{1/2}$

Table S11. DFT predicted (BP86/TZVP) geometric structures, vibrational frequencies and relative energies of different isomers of complex **4**, and of corresponding species were the nitrite ligand is substituted by H_2O and Cl^-. These are **4** (nitrite trans to py), **4b** (nitrite trans to am), $[Ru(TPA)(NO_2)(NO)]^{2+}$ (N-bound nitrite, trans to py; **9**), $[Ru(TPA)(NO_2)(NO)]^{2+}$ (N-bound nitrite, trans to am; **9b**), **6** (aquo complex, trans to py), **6b** (aquo complex, trans to am), $[Ru(TPA)Cl(NO)]^{2+}$(chloride complex, trans to py; **10**) and $[Ru(TPA)Cl(NO)]^{2+}$ (chloride complex, trans to am; **10b**); see Supporting Information.

	X= ONO^-		X=NO_2^-		X=H_2O		X = Cl^-	
Position of X	Cis am	Trans am	Cis am	Trans am	Cis am	Trans am	Cis am	Trans am
	4	**4b**	**9**	**9b**	**6**	**6b**	**10**	**10b**
Ru-N_{am} [Å]	2.127	2.154	2.150	2.187	2.123	2.085	2.141	2.141
Ru-N_{py} (trans to py) [Å]	2.126, 2.133	2.126, 2.126	2.122, 2.146	2.153, 2.151	2.139, 2.145	2.148, 2.147	2.129, 2.134	2.123, 2.126
Ru-N_{py} (trans to X or NO) [Å]	2.156	2.123	2.226	2.153	2.083	2.103	2.147	2.153
Ru-X [Å]	2.022	2.025	2.140	2.143	2.236	2.251	2.396	2.395
N-O_{NO2} [Å]	1.452, 1.173	1.450, 1.176	1.237, 1.224	1.234, 1.229	-	-	-	-
Ru-NO [Å]	1.818	1.821	1.805	1.807	1.819	1.825	1.799	1.800
N-O [Å]	1.152	1.151	1.146	1.147	1.142	1.141	1.147	1.146
Ru-N-O	175°	177°	179°	175°	177°	174°	174°	171°
ν(N-O) [cm^{-1}]	1878	1885	1908	1911	1930	1933	1911	1919
ν(Ru-NO) [cm^{-1}]	569/519	570/514	564	567	544	529	583[a]	582[a]
δ(Ru-N-O) [cm^{-1}]	580/537	591/537	581/536	595/585/ 529	592/572	596/577	577/552[a]	587/536[a]
Relative ν(N-O)	0	7	30	33	52	55	33	41
Relative Energy (BP86/TZVP)	+1.3	+3.3	+2.2	0	0	+3.5	0	+7.3

[a] These bending and stretching vibrations are strongly mixed.

Table S12. Crystal data and structure refinement for $[Ru(TPA)Cl_2]ClO_4$ (**1**).

Identification code	[Ru(TPA)Cl2]ClO4
Empirical formula	C18.50 H21 Cl3 N4 O5 Ru
Formula weight	586.81
Temperature	85(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 10.4799(8) A alpha = 90 deg. b = 15.1542(12) A beta = 108.579(1)deg. c = 14.4573(11) A gamma = 90 deg.
Volume	2176.4(3) A^3
Z, Calculated density	4, 1.791 Mg/m^3
Absorption coefficient	1.129 mm^-1
F(000)	1180
Crystal size	0.33 x 0.28 x 0.10 mm
Theta range for data collection	2.00 to 29.65 deg.
Limiting indices	-14<=h<=14, -21<=k<=21, -20<=l<=20
Reflections collected / unique	75588 / 6147 [R(int) = 0.0313]
Completeness to theta = 29.65	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8955 and 0.7071
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6147 / 0 / 304
Goodness-of-fit on F^2	1.073
Final R indices [I>2sigma(I)]	R1 = 0.0214, wR2 = 0.0568
R indices (all data)	R1 = 0.0225, wR2 = 0.0578
Largest diff. peak and hole	0.590 and -0.674 e.A^-3

Table S13. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for $[Ru(TPA)Cl_2]ClO_4$ (**1**). U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Ru(1)	2945(1)	1850(1)	6953(1)	11(1)
Cl(1)	5146(1)	1928(1)	6854(1)	16(1)
Cl(2)	2022(1)	2347(1)	5354(1)	18(1)
Cl(3)	7901(1)	995(1)	97(1)	17(1)
N(1)	2952(1)	518(1)	6654(1)	16(1)
N(2)	3591(1)	1369(1)	8366(1)	12(1)
N(3)	1088(1)	1800(1)	7182(1)	13(1)
N(4)	3210(1)	3059(1)	7641(1)	13(1)
O(1)	6831(1)	952(1)	523(1)	27(1)
O(2)	7675(1)	341(1)	-658(1)	31(1)
O(3)	7900(1)	1860(1)	-320(1)	24(1)
O(4)	9174(1)	836(1)	830(1)	32(1)
C(1)	2319(2)	104(1)	5813(1)	22(1)
C(2)	2388(2)	-806(1)	5726(1)	28(1)
C(3)	3100(2)	-1297(1)	6530(1)	26(1)
C(4)	3748(2)	-872(1)	7402(1)	21(1)
C(5)	3674(2)	40(1)	7441(1)	16(1)
C(6)	4413(1)	563(1)	8338(1)	15(1)
C(7)	2413(1)	1087(1)	8675(1)	14(1)
C(8)	1117(1)	1481(1)	8060(1)	13(1)
C(9)	-21(1)	1459(1)	8352(1)	16(1)
C(10)	-1228(2)	1763(1)	7718(1)	18(1)
C(11)	-1257(2)	2094(1)	6815(1)	19(1)
C(12)	-85(1)	2111(1)	6569(1)	17(1)
C(13)	4393(1)	2094(1)	8994(1)	15(1)
C(14)	3848(1)	2990(1)	8612(1)	14(1)
C(15)	4071(2)	3726(1)	9215(1)	18(1)
C(16)	3670(2)	4547(1)	8800(1)	21(1)
C(17)	3033(2)	4613(1)	7804(1)	21(1)
C(18)	2797(2)	3853(1)	7242(1)	17(1)
O(5)	-102(3)	8939(2)	6678(2)	31(1)
C(19)	391(7)	9634(4)	7253(3)	47(1)
O(5A)	-243(6)	9829(3)	6636(6)	60(2)

Table S14. Bond length [Å] and angles [deg] for [Ru(TPA)Cl_2]ClO_4 (**1**).

Ru(1)-N(4)	2.0604(12)
Ru(1)-N(1)	2.0655(12)
Ru(1)-N(2)	2.0700(11)
Ru(1)-N(3)	2.0778(12)
Ru(1)-Cl(2)	2.3287(4)
Ru(1)-Cl(1)	2.3588(4)
Cl(3)-O(4)	1.4357(13)
Cl(3)-O(2)	1.4370(12)
Cl(3)-O(1)	1.4430(12)
Cl(3)-O(3)	1.4431(12)
N(1)-C(1)	1.341(2)
N(1)-C(5)	1.3581(19)
N(2)-C(13)	1.5008(18)
N(2)-C(6)	1.5012(17)
N(2)-C(7)	1.5024(17)
N(3)-C(8)	1.3493(17)
N(3)-C(12)	1.3501(18)
N(4)-C(18)	1.3452(17)
N(4)-C(14)	1.3523(18)
C(1)-C(2)	1.387(2)
C(2)-C(3)	1.382(3)
C(3)-C(4)	1.385(2)
C(4)-C(5)	1.386(2)
C(5)-C(6)	1.506(2)
C(7)-C(8)	1.4909(19)
C(8)-C(9)	1.3864(19)
C(9)-C(10)	1.384(2)
C(10)-C(11)	1.389(2)
C(11)-C(12)	1.383(2)
C(13)-C(14)	1.5082(19)
C(14)-C(15)	1.3886(19)
C(15)-C(16)	1.388(2)
C(16)-C(17)	1.384(2)
C(17)-C(18)	1.386(2)
O(5)-C(19)	1.340(5)
N(4)-Ru(1)-N(1)	163.98(5)
N(4)-Ru(1)-N(2)	83.42(5)
N(1)-Ru(1)-N(2)	80.79(5)
N(4)-Ru(1)-N(3)	86.82(5)
N(1)-Ru(1)-N(3)	93.63(5)
N(2)-Ru(1)-N(3)	81.85(5)
N(4)-Ru(1)-Cl(2)	98.13(3)
N(1)-Ru(1)-Cl(2)	97.84(4)
N(2)-Ru(1)-Cl(2)	174.75(3)
N(3)-Ru(1)-Cl(2)	93.20(3)
N(4)-Ru(1)-Cl(1)	90.05(3)
N(1)-Ru(1)-Cl(1)	88.16(4)
N(2)-Ru(1)-Cl(1)	93.38(3)
N(3)-Ru(1)-Cl(1)	174.56(3)
Cl(2)-Ru(1)-Cl(1)	91.643(13)
O(4)-Cl(3)-O(2)	109.55(8)
O(4)-Cl(3)-O(1)	110.05(8)

O(2)-Cl(3)-O(1)	109.31(8)
O(4)-Cl(3)-O(3)	109.74(8)
O(2)-Cl(3)-O(3)	109.37(8)
O(1)-Cl(3)-O(3)	108.79(7)
C(1)-N(1)-C(5)	119.56(13)
C(1)-N(1)-Ru(1)	127.85(11)
C(5)-N(1)-Ru(1)	112.56(10)
C(13)-N(2)-C(6)	113.38(11)
C(13)-N(2)-C(7)	112.51(11)
C(6)-N(2)-C(7)	108.04(10)
C(13)-N(2)-Ru(1)	106.43(8)
C(6)-N(2)-Ru(1)	105.65(8)
C(7)-N(2)-Ru(1)	110.61(8)
C(8)-N(3)-C(12)	119.05(12)
C(8)-N(3)-Ru(1)	114.91(9)
C(12)-N(3)-Ru(1)	125.86(10)
C(18)-N(4)-C(14)	119.89(12)
C(18)-N(4)-Ru(1)	127.82(10)
C(14)-N(4)-Ru(1)	112.25(9)
N(1)-C(1)-C(2)	121.43(16)
C(3)-C(2)-C(1)	119.26(16)
C(2)-C(3)-C(4)	119.44(15)
C(3)-C(4)-C(5)	118.92(15)
N(1)-C(5)-C(4)	121.36(14)
N(1)-C(5)-C(6)	115.92(12)
C(4)-C(5)-C(6)	122.70(14)
N(2)-C(6)-C(5)	108.04(11)
C(8)-C(7)-N(2)	112.83(11)
N(3)-C(8)-C(9)	122.09(13)
N(3)-C(8)-C(7)	116.61(12)
C(9)-C(8)-C(7)	121.14(12)
C(10)-C(9)-C(8)	118.88(13)
C(9)-C(10)-C(11)	118.98(14)
C(12)-C(11)-C(10)	119.53(14)
N(3)-C(12)-C(11)	121.46(13)
N(2)-C(13)-C(14)	111.36(11)
N(4)-C(14)-C(15)	121.23(13)
N(4)-C(14)-C(13)	117.00(12)
C(15)-C(14)-C(13)	121.62(13)
C(16)-C(15)-C(14)	118.81(14)
C(17)-C(16)-C(15)	119.57(14)
C(16)-C(17)-C(18)	119.11(14)
N(4)-C(18)-C(17)	121.33(14)

Table S15. Anisotropic displacement parameters (A^2 x 10^3) for $[Ru(TPA)Cl_2]ClO_4$ (**1**).The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U11 + ... + 2 h k a^* b^* U12]$

	U11	U22	U33	U23	U13	U12
Ru(1)	15(1)	9(1)	10(1)	0(1)	6(1)	0(1)
Cl(1)	17(1)	15(1)	17(1)	0(1)	9(1)	0(1)
Cl(2)	22(1)	20(1)	12(1)	3(1)	7(1)	2(1)
Cl(3)	18(1)	16(1)	16(1)	-2(1)	6(1)	0(1)
N(1)	22(1)	12(1)	17(1)	-1(1)	11(1)	-1(1)
N(2)	15(1)	10(1)	12(1)	1(1)	6(1)	1(1)
N(3)	15(1)	12(1)	13(1)	0(1)	6(1)	-1(1)
N(4)	17(1)	10(1)	14(1)	1(1)	8(1)	1(1)
O(1)	35(1)	22(1)	34(1)	8(1)	24(1)	5(1)
O(2)	30(1)	32(1)	30(1)	-17(1)	8(1)	-1(1)
O(3)	28(1)	23(1)	23(1)	7(1)	10(1)	-3(1)
O(4)	27(1)	29(1)	30(1)	-1(1)	-5(1)	5(1)
C(1)	34(1)	18(1)	18(1)	-3(1)	11(1)	-3(1)
C(2)	45(1)	19(1)	24(1)	-8(1)	16(1)	-6(1)
C(3)	41(1)	13(1)	31(1)	-5(1)	21(1)	-2(1)
C(4)	29(1)	13(1)	26(1)	1(1)	17(1)	3(1)
C(5)	21(1)	13(1)	19(1)	0(1)	12(1)	1(1)
C(6)	18(1)	11(1)	18(1)	1(1)	8(1)	4(1)
C(7)	16(1)	14(1)	14(1)	3(1)	7(1)	2(1)
C(8)	16(1)	11(1)	13(1)	0(1)	6(1)	0(1)
C(9)	18(1)	17(1)	15(1)	0(1)	8(1)	-1(1)
C(10)	16(1)	20(1)	19(1)	-1(1)	8(1)	-1(1)
C(11)	15(1)	24(1)	18(1)	3(1)	4(1)	1(1)
C(12)	17(1)	19(1)	15(1)	3(1)	4(1)	0(1)
C(13)	19(1)	12(1)	13(1)	0(1)	4(1)	0(1)
C(14)	17(1)	12(1)	14(1)	1(1)	7(1)	0(1)
C(15)	25(1)	16(1)	15(1)	-2(1)	9(1)	-2(1)
C(16)	32(1)	13(1)	22(1)	-3(1)	14(1)	-1(1)
C(17)	32(1)	12(1)	23(1)	1(1)	13(1)	2(1)
C(18)	24(1)	12(1)	16(1)	2(1)	9(1)	2(1)
O(5)	26(1)	28(1)	41(2)	-4(1)	14(1)	-4(1)
C(19)	70(4)	46(3)	23(2)	-7(2)	10(2)	-31(3)
O(5A)	61(3)	29(2)	114(5)	-27(3)	61(4)	-18(2)

Table S16. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for $[Ru(TPA)Cl_2]ClO_4$ (**1**).

	x	y	z	U(eq)
H(1B)	1812	440	5264	27
H(2B)	1951	-1087	5121	34
H(3B)	3145	-1921	6486	31
H(4B)	4234	-1199	7964	25
H(6A)	4536	202	8931	18
H(6B)	5311	738	8313	18
H(7A)	2338	436	8638	17
H(7B)	2578	1262	9363	17
H(9A)	28	1238	8978	19
H(10A)	-2024	1747	7897	22
H(11A)	-2075	2306	6369	23
H(12A)	-106	2347	5956	20
H(13A)	5343	2050	9013	18
H(13B)	4366	2024	9669	18
H(15A)	4490	3668	9899	22
H(16A)	3832	5061	9197	25
H(17A)	2763	5172	7510	25
H(18A)	2333	3894	6562	20
H(5)	-90(50)	8850(30)	5970(40)	34(12)
H(19A)	721	9442	7936	71
H(19B)	-322	10074	7173	71
H(19C)	1133	9895	7072	71

Table S17. Hydrogen bonds for [Ru(TPA)Cl_2)]ClO_4 (**1**) [Å and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(5)-H(5)...Cl(2)#1	1.03(5)	2.94(5)	3.565(3)	120(3)

Symmetry transformations used to generate equivalent atoms:
#1 -x,-y+1,-z+1

Table S18. Crystal data and structure refinement for $[Ru(TPA)Cl_2(NO)](ClO_4)$ (**2**).

Identification code	[Ru(TPA)Cl2(NO)]ClO4
Empirical formula	C19 H20 Cl5 N5 O5 Ru
Formula weight	676.72
Temperature	85(2) K
Wavelength	1.54187 A
Crystal system, space group	Monoclinic, P2(1)
Unit cell dimensions	a = 9.7546(1) A alpha = 90 deg. b = 13.7776(2) A beta = 110.935(8)deg. c = 9.9353(7) A gamma = 90 deg.
Volume	1247.11(11) A^3
Z, Calculated density	2, 1.802 Mg/m^3
Absorption coefficient	10.393 mm^-1
F(000)	676
Crystal size	0.22 x 0.10 x 0.06 mm
Theta range for data collection	4.77 to 67.82 deg.
Limiting indices	-11<=h<=11, -15<=k<=16, -11<=l<=11
Reflections collected / unique	16404 / 3946 [R(int) = 0.0343]
Completeness to theta = 67.82	94.3 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.5744 and 0.2083
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3946 / 1 / 317
Goodness-of-fit on F^2	1.050
Final R indices [I>2sigma(I)]	R1 = 0.0174, wR2 = 0.0405
R indices (all data)	R1 = 0.0175, wR2 = 0.0406
Absolute structure parameter	-0.009(5)
Extinction coefficient	0.00047(8)
Largest diff. peak and hole	0.412 and -0.468 e.A^-3

Table S19. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for [Ru(TPA)Cl_2(NO)]ClO_4 (**2**). U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Ru(1)	9627(1)	-1127(1)	8492(1)	10(1)
Cl(1)	8726(1)	-2138(1)	9931(1)	15(1)
Cl(2)	11397(1)	-2317(1)	8555(1)	17(1)
Cl(3)	2728(1)	8233(1)	4337(1)	27(1)
Cl(4)	4656(1)	7564(1)	7155(1)	31(1)
Cl(5)	2148(1)	4648(1)	6289(1)	13(1)
O(1)	7462(2)	-2078(1)	6075(2)	20(1)
O(2)	2850(2)	4882(1)	5273(2)	20(1)
O(3)	1356(2)	5476(1)	6489(2)	24(1)
O(4)	3264(2)	4385(1)	7647(2)	19(1)
O(5)	1167(2)	3838(2)	5754(2)	23(1)
N(1)	8332(2)	-1648(2)	6966(2)	13(1)
N(2)	10460(2)	-120(2)	7453(2)	13(1)
N(3)	8380(2)	82(2)	8732(2)	10(1)
N(4)	11063(2)	-494(2)	10399(2)	11(1)
N(5)	5610(2)	1489(2)	7381(2)	15(1)
C(1)	11447(3)	-308(2)	6820(2)	14(1)
C(2)	11962(3)	411(2)	6167(2)	16(1)
C(3)	11457(3)	1354(2)	6148(2)	16(1)
C(4)	10446(3)	1546(2)	6800(2)	15(1)
C(5)	9959(3)	798(2)	7439(2)	12(1)
C(6)	8842(3)	978(2)	8122(3)	14(1)
C(7)	8773(3)	202(2)	10332(2)	11(1)
C(8)	10409(3)	131(2)	11034(3)	12(1)
C(9)	11212(3)	656(2)	12251(3)	15(1)
C(10)	12729(3)	542(2)	12812(2)	16(1)
C(11)	13391(3)	-94(2)	12159(3)	17(1)
C(12)	12538(3)	-606(2)	10961(3)	15(1)
C(13)	6747(3)	-94(2)	8016(2)	13(1)
C(14)	5819(3)	715(2)	8257(2)	12(1)
C(15)	5227(3)	648(2)	9342(2)	14(1)
C(16)	4415(3)	1426(2)	9546(3)	18(1)
C(17)	4238(3)	2239(2)	8686(3)	17(1)
C(18)	4843(3)	2239(2)	7619(3)	17(1)
C(19)	3146(3)	7276(2)	5588(3)	28(1)

Table S20. Bond length [Å] and angles [deg] for [Ru(TPA)Cl_2(NO)]ClO_4 (**2**).

Ru(1)-N(1)	1.743(2)
Ru(1)-N(2)	2.062(2)
Ru(1)-N(4)	2.102(2)
Ru(1)-N(3)	2.126(2)
Ru(1)-Cl(2)	2.3647(6)
Ru(1)-Cl(1)	2.3774(6)
Cl(3)-C(19)	1.756(3)
Cl(4)-C(19)	1.764(3)
Cl(5)-O(3)	1.4310(19)
Cl(5)-O(5)	1.443(2)
Cl(5)-O(2)	1.4441(18)
Cl(5)-O(4)	1.4447(17)
O(1)-N(1)	1.148(3)
N(2)-C(1)	1.350(3)
N(2)-C(5)	1.354(3)
N(3)-C(7)	1.505(3)
N(3)-C(6)	1.512(3)
N(3)-C(13)	1.514(3)
N(4)-C(12)	1.353(3)
N(4)-C(8)	1.355(3)
N(5)-C(18)	1.344(3)
N(5)-C(14)	1.346(3)
C(1)-C(2)	1.375(4)
C(2)-C(3)	1.387(4)
C(3)-C(4)	1.385(4)
C(4)-C(5)	1.381(3)
C(5)-C(6)	1.496(3)
C(7)-C(8)	1.499(4)
C(8)-C(9)	1.386(4)
C(9)-C(10)	1.391(4)
C(10)-C(11)	1.381(4)
C(11)-C(12)	1.378(4)
C(13)-C(14)	1.509(4)
C(14)-C(15)	1.396(3)
C(15)-C(16)	1.390(4)
C(16)-C(17)	1.382(4)
C(17)-C(18)	1.386(4)
N(1)-Ru(1)-N(2)	97.72(8)
N(1)-Ru(1)-N(4)	175.68(8)
N(2)-Ru(1)-N(4)	85.21(7)
N(1)-Ru(1)-N(3)	98.88(9)
N(2)-Ru(1)-N(3)	82.66(8)
N(4)-Ru(1)-N(3)	78.30(7)
N(1)-Ru(1)-Cl(2)	91.91(7)
N(2)-Ru(1)-Cl(2)	93.73(6)
N(4)-Ru(1)-Cl(2)	91.06(6)
N(3)-Ru(1)-Cl(2)	168.98(5)
N(1)-Ru(1)-Cl(1)	88.47(7)
N(2)-Ru(1)-Cl(1)	172.59(6)
N(4)-Ru(1)-Cl(1)	88.39(5)
N(3)-Ru(1)-Cl(1)	92.41(5)
Cl(2)-Ru(1)-Cl(1)	90.10(2)

O(3)-Cl(5)-O(5)	110.36(12)
O(3)-Cl(5)-O(2)	109.49(11)
O(5)-Cl(5)-O(2)	109.48(10)
O(3)-Cl(5)-O(4)	109.51(11)
O(5)-Cl(5)-O(4)	109.21(11)
O(2)-Cl(5)-O(4)	108.77(10)
O(1)-N(1)-Ru(1)	171.50(18)
C(1)-N(2)-C(5)	119.3(2)
C(1)-N(2)-Ru(1)	125.33(18)
C(5)-N(2)-Ru(1)	115.36(15)
C(7)-N(3)-C(6)	109.49(19)
C(7)-N(3)-C(13)	110.01(18)
C(6)-N(3)-C(13)	110.86(18)
C(7)-N(3)-Ru(1)	105.35(14)
C(6)-N(3)-Ru(1)	109.30(14)
C(13)-N(3)-Ru(1)	111.67(15)
C(12)-N(4)-C(8)	119.3(2)
C(12)-N(4)-Ru(1)	126.33(17)
C(8)-N(4)-Ru(1)	114.24(15)
C(18)-N(5)-C(14)	117.4(2)
N(2)-C(1)-C(2)	121.6(2)
C(1)-C(2)-C(3)	119.6(2)
C(4)-C(3)-C(2)	118.8(2)
C(5)-C(4)-C(3)	119.5(2)
N(2)-C(5)-C(4)	121.3(2)
N(2)-C(5)-C(6)	118.0(2)
C(4)-C(5)-C(6)	120.7(2)
C(5)-C(6)-N(3)	114.6(2)
C(8)-C(7)-N(3)	108.14(19)
N(4)-C(8)-C(9)	121.6(2)
N(4)-C(8)-C(7)	115.2(2)
C(9)-C(8)-C(7)	123.2(2)
C(8)-C(9)-C(10)	118.6(2)
C(11)-C(10)-C(9)	119.6(2)
C(12)-C(11)-C(10)	119.4(2)
N(4)-C(12)-C(11)	121.5(2)
C(14)-C(13)-N(3)	113.4(2)
N(5)-C(14)-C(15)	122.9(2)
N(5)-C(14)-C(13)	116.4(2)
C(15)-C(14)-C(13)	120.8(2)
C(16)-C(15)-C(14)	118.5(2)
C(17)-C(16)-C(15)	119.1(2)
C(16)-C(17)-C(18)	118.6(2)
N(5)-C(18)-C(17)	123.5(2)
Cl(3)-C(19)-Cl(4)	111.46(16)

Table S21. Anisotropic displacement parameters (A^2 x 10^3) for [Ru(TPA)Cl_2(NO)]ClO_4 (**2**). The anisotropic displacement factor exponent takes the form: $-2\,pi^2\,[\,h^2\,a^{*2}\,U11 + ... + 2\,h\,k\,a^*\,b^*\,U12\,]$

	U11	U22	U33	U23	U13	U12
Ru(1)	12(1)	9(1)	11(1)	1(1)	5(1)	0(1)
Cl(1)	16(1)	13(1)	17(1)	4(1)	9(1)	1(1)
Cl(2)	19(1)	13(1)	24(1)	2(1)	12(1)	4(1)
Cl(3)	39(1)	20(1)	23(1)	5(1)	12(1)	3(1)
Cl(4)	26(1)	40(1)	22(1)	-2(1)	2(1)	-3(1)
Cl(5)	13(1)	14(1)	11(1)	1(1)	3(1)	1(1)
O(1)	26(1)	18(1)	16(1)	-4(1)	7(1)	-5(1)
O(2)	26(1)	21(1)	17(1)	-2(1)	12(1)	-3(1)
O(3)	25(1)	21(1)	28(1)	2(1)	12(1)	11(1)
O(4)	15(1)	24(1)	14(1)	3(1)	-1(1)	3(1)
O(5)	22(1)	24(1)	22(1)	-3(1)	7(1)	-12(1)
N(1)	18(1)	10(1)	13(1)	2(1)	9(1)	2(1)
N(2)	12(1)	15(1)	10(1)	-2(1)	4(1)	-3(1)
N(3)	11(1)	12(1)	8(1)	1(1)	3(1)	0(1)
N(4)	11(1)	11(1)	12(1)	5(1)	5(1)	1(1)
N(5)	12(1)	12(1)	18(1)	2(1)	3(1)	1(1)
C(1)	12(1)	19(2)	12(1)	-2(1)	5(1)	0(1)
C(2)	14(1)	25(2)	8(1)	-2(1)	4(1)	-4(1)
C(3)	17(1)	20(2)	10(1)	2(1)	2(1)	-7(1)
C(4)	16(1)	13(2)	12(1)	0(1)	-1(1)	-4(1)
C(5)	12(1)	14(2)	6(1)	0(1)	0(1)	-2(1)
C(6)	14(1)	8(1)	19(1)	3(1)	5(1)	2(1)
C(7)	13(1)	12(2)	9(1)	-1(1)	4(1)	1(1)
C(8)	16(1)	8(1)	13(1)	2(1)	7(1)	1(1)
C(9)	17(1)	14(2)	15(1)	1(1)	7(1)	-2(1)
C(10)	16(1)	17(2)	10(1)	2(1)	1(1)	-5(1)
C(11)	12(1)	21(2)	18(1)	8(1)	5(1)	2(1)
C(12)	13(1)	17(2)	16(1)	6(1)	7(1)	2(1)
C(13)	10(1)	16(1)	11(1)	-1(1)	2(1)	-1(1)
C(14)	7(1)	14(2)	11(1)	-1(1)	-2(1)	-2(1)
C(15)	14(1)	16(2)	12(1)	2(1)	3(1)	0(1)
C(16)	14(1)	26(2)	15(1)	-1(1)	5(1)	0(1)
C(17)	13(1)	16(2)	19(1)	-4(1)	2(1)	0(1)
C(18)	14(1)	13(2)	19(1)	2(1)	2(1)	-1(1)
C(19)	35(2)	20(2)	21(1)	4(1)	2(1)	-5(1)

Table S22. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for [Ru(TPA)Cl_2(NO)]ClO_4 (**2**).

	x	y	z	U(eq)
H(1A)	11793	-953	6826	17
H(2B)	12660	264	5731	19
H(3B)	11798	1859	5697	19
H(4B)	10090	2187	6808	18
H(6A)	7960	1270	7394	17
H(6B)	9245	1457	8908	17
H(7A)	8431	841	10543	14
H(7B)	8296	-311	10708	14
H(9A)	10736	1086	12691	18
H(10A)	13304	898	13639	19
H(11A)	14426	-178	12532	21
H(12A)	12996	-1048	10519	18
H(13A)	6511	-176	6967	15
H(13B)	6492	-707	8391	15
H(15A)	5375	85	9927	17
H(16A)	3988	1399	10267	22
H(17A)	3712	2788	8823	20
H(18A)	4710	2797	7024	20
H(19A)	3373	6686	5139	33
H(19B)	2281	7136	5854	33

Table S23. Crystal data and structure refinement for [Ru(TPA)(NO_2)$_2$] (**3**).

Identification code	[Ru(TPA)(NO2)2]
Empirical formula	C20 H26 N6 O6 Ru
Formula weight	547.54
Temperature	85(2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, Pccn
Unit cell dimensions	a = 19.347(7) A alpha = 90 deg. b = 14.704(5) A beta = 90 deg. c = 16.562(6) A gamma = 90 deg.
Volume	4712(3) A^3
Z, Calculated density	8, 1.544 Mg/m^3
Absorption coefficient	0.713 mm^-1
F(000)	2240
Crystal size	0.20 x 0.06 x 0.06 mm
Theta range for data collection	1.74 to 23.99 deg.
Limiting indices	-21<=h<=21, -16<=k<=16, -18<=l<=18
Reflections collected / unique	63152 / 3651 [R(int) = 0.1070]
Completeness to theta = 23.99	98.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9585 and 0.8705
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3650 / 0 / 302
Goodness-of-fit on F^2	1.096
Final R indices [I>2sigma(I)]	R1 = 0.0599, wR2 = 0.1521
R indices (all data)	R1 = 0.0844, wR2 = 0.1684
Largest diff. peak and hole	1.485 and -0.820 e.A^-3

Table S24. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for [Ru(TPA)$(NO_2)_2$ (**3**). U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Ru(1)	5620(1)	2234(1)	3046(1)	39(1)
N(1)	6062(3)	3515(4)	2823(3)	42(1)
N(2)	5158(3)	3002(4)	3972(3)	46(1)
N(3)	6338(3)	1979(4)	3944(3)	45(1)
N(4)	5038(3)	1209(4)	3562(3)	48(1)
N(5)	6110(3)	1470(4)	2197(3)	45(1)
N(6)	4876(3)	2444(4)	2202(3)	50(1)
C(1)	6643(3)	3731(5)	2440(4)	45(2)
C(2)	6889(4)	4596(6)	2387(4)	58(2)
C(3)	6511(4)	5299(5)	2729(5)	62(2)
C(4)	5921(4)	5092(5)	3146(4)	54(2)
C(5)	5699(4)	4208(5)	3183(4)	47(2)
C(6)	5061(4)	3927(5)	3626(4)	53(2)
C(7)	5626(4)	3045(5)	4690(4)	52(2)
C(8)	6188(4)	2345(4)	4678(4)	44(2)
C(9)	6560(4)	2117(5)	5347(4)	52(2)
C(10)	7117(4)	1537(5)	5291(4)	54(2)
C(11)	7283(4)	1188(5)	4554(4)	52(2)
C(12)	6888(4)	1420(5)	3895(4)	49(2)
C(13)	4509(4)	2540(6)	4180(5)	62(2)
C(14)	4574(4)	1545(5)	4118(4)	53(2)
C(15)	4183(4)	940(6)	4579(5)	67(2)
C(16)	4237(5)	27(6)	4468(5)	73(3)
C(17)	4700(5)	-309(6)	3917(5)	65(2)
C(18)	5097(4)	304(5)	3479(4)	52(2)
C(20)	3045(8)	3547(14)	1504(11)	209(10)
O(1)	5815(3)	822(4)	1857(3)	66(2)
O(2)	6724(3)	1627(4)	2003(3)	53(1)
O(3)	4245(3)	2430(5)	2376(4)	82(2)
O(4)	5012(3)	2566(4)	1492(3)	71(2)
O(6)	3415(5)	2853(9)	1055(5)	155(4)
C(19)	6847(7)	-628(9)	597(8)	127(5)
O(5)	6358(4)	101(5)	429(4)	95(2)

Table S25. Bond length [Å] and angles [deg] for [Ru(TPA)(NO_2)$_2$] (**3**).

Ru(1)-N(6)	2.031(6)
Ru(1)-N(5)	2.033(6)
Ru(1)-N(4)	2.067(5)
Ru(1)-N(3)	2.068(6)
Ru(1)-N(1)	2.101(6)
Ru(1)-N(2)	2.105(5)
N(1)-C(1)	1.329(8)
N(1)-C(5)	1.375(9)
N(2)-C(13)	1.468(9)
N(2)-C(6)	1.488(9)
N(2)-C(7)	1.496(9)
N(3)-C(12)	1.347(9)
N(3)-C(8)	1.361(8)
N(4)-C(18)	1.343(9)
N(4)-C(14)	1.377(9)
N(5)-O(1)	1.245(7)
N(5)-O(2)	1.252(7)
N(6)-O(4)	1.218(7)
N(6)-O(3)	1.255(8)
C(1)-C(2)	1.361(10)
C(2)-C(3)	1.387(11)
C(3)-C(4)	1.368(11)
C(4)-C(5)	1.371(10)
C(5)-C(6)	1.494(10)
C(7)-C(8)	1.498(10)
C(8)-C(9)	1.364(10)
C(9)-C(10)	1.376(10)
C(10)-C(11)	1.361(10)
C(11)-C(12)	1.376(10)
C(13)-C(14)	1.471(11)
C(14)-C(15)	1.396(11)
C(15)-C(16)	1.359(12)
C(16)-C(17)	1.371(12)
C(17)-C(18)	1.389(10)
C(20)-O(6)	1.450(18)
C(19)-O(5)	1.456(14)
N(6)-Ru(1)-N(5)	86.4(2)
N(6)-Ru(1)-N(4)	90.5(2)
N(5)-Ru(1)-N(4)	97.9(2)
N(6)-Ru(1)-N(3)	176.8(2)
N(5)-Ru(1)-N(3)	94.8(2)
N(4)-Ru(1)-N(3)	86.4(2)
N(6)-Ru(1)-N(1)	91.8(2)
N(5)-Ru(1)-N(1)	100.6(2)
N(4)-Ru(1)-N(1)	161.5(2)
N(3)-Ru(1)-N(1)	90.9(2)
N(6)-Ru(1)-N(2)	96.8(2)
N(5)-Ru(1)-N(2)	176.8(2)
N(4)-Ru(1)-N(2)	81.9(2)
N(3)-Ru(1)-N(2)	81.9(2)
N(1)-Ru(1)-N(2)	79.6(2)
C(1)-N(1)-C(5)	117.5(6)

C(1)-N(1)-Ru(1)	130.0(5)
C(5)-N(1)-Ru(1)	112.3(4)
C(13)-N(2)-C(6)	114.0(6)
C(13)-N(2)-C(7)	110.5(6)
C(6)-N(2)-C(7)	110.1(6)
C(13)-N(2)-Ru(1)	106.6(4)
C(6)-N(2)-Ru(1)	105.3(4)
C(7)-N(2)-Ru(1)	110.1(4)
C(12)-N(3)-C(8)	117.6(6)
C(12)-N(3)-Ru(1)	126.7(4)
C(8)-N(3)-Ru(1)	115.3(5)
C(18)-N(4)-C(14)	118.7(6)
C(18)-N(4)-Ru(1)	129.3(5)
C(14)-N(4)-Ru(1)	111.7(5)
O(1)-N(5)-O(2)	117.3(6)
O(1)-N(5)-Ru(1)	121.5(5)
O(2)-N(5)-Ru(1)	121.2(5)
O(4)-N(6)-O(3)	115.7(6)
O(4)-N(6)-Ru(1)	122.2(5)
O(3)-N(6)-Ru(1)	122.0(5)
N(1)-C(1)-C(2)	123.4(7)
C(1)-C(2)-C(3)	119.1(7)
C(4)-C(3)-C(2)	118.7(7)
C(3)-C(4)-C(5)	119.7(7)
C(4)-C(5)-N(1)	121.5(7)
C(4)-C(5)-C(6)	122.9(7)
N(1)-C(5)-C(6)	115.5(6)
N(2)-C(6)-C(5)	109.7(6)
N(2)-C(7)-C(8)	113.6(5)
N(3)-C(8)-C(9)	121.1(7)
N(3)-C(8)-C(7)	116.0(6)
C(9)-C(8)-C(7)	122.8(6)
C(8)-C(9)-C(10)	120.7(6)
C(11)-C(10)-C(9)	118.6(6)
C(10)-C(11)-C(12)	119.2(7)
N(3)-C(12)-C(11)	122.8(6)
N(2)-C(13)-C(14)	111.8(6)
N(4)-C(14)-C(15)	119.3(7)
N(4)-C(14)-C(13)	117.3(6)
C(15)-C(14)-C(13)	123.3(7)
C(16)-C(15)-C(14)	120.9(8)
C(15)-C(16)-C(17)	119.8(8)
C(16)-C(17)-C(18)	118.4(8)
N(4)-C(18)-C(17)	122.8(7)

Table S26. Anisotropic displacement parameters (A^2 x 10^3) for [Ru(TPA) $(NO)_2$] (**3**). The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U11 + ... + 2 h k a^* b^* U12]$

	U11	U22	U33	U23	U13	U12
Ru(1)	44(1)	47(1)	27(1)	0(1)	3(1)	-1(1)
N(1)	54(4)	46(3)	26(3)	4(2)	-5(2)	2(3)
N(2)	50(3)	50(3)	39(3)	-2(3)	9(3)	4(3)
N(3)	58(4)	51(3)	25(3)	1(2)	5(3)	-1(3)
N(4)	55(4)	57(4)	32(3)	10(3)	-1(3)	-9(3)
N(5)	53(4)	55(4)	28(3)	0(3)	-1(3)	0(3)
N(6)	50(4)	61(4)	40(3)	2(3)	-2(3)	-5(3)
C(1)	47(4)	56(4)	30(3)	0(3)	-3(3)	-10(3)
C(2)	52(5)	74(5)	49(4)	8(4)	-3(4)	-1(4)
C(3)	73(6)	50(5)	64(5)	13(4)	-14(4)	-5(4)
C(4)	63(5)	57(5)	41(4)	0(4)	-7(4)	2(4)
C(5)	56(4)	51(4)	34(4)	-1(3)	-1(3)	4(4)
C(6)	64(5)	51(4)	44(4)	-2(3)	4(3)	14(4)
C(7)	71(5)	55(4)	31(4)	-3(3)	5(3)	2(4)
C(8)	59(4)	45(4)	28(3)	-1(3)	7(3)	-12(3)
C(9)	76(5)	61(5)	20(3)	-2(3)	-3(3)	-10(4)
C(10)	63(5)	69(5)	29(4)	10(3)	-11(3)	-11(4)
C(11)	49(4)	63(5)	44(4)	6(4)	-5(3)	-8(4)
C(12)	48(4)	60(4)	38(4)	0(3)	2(3)	4(4)
C(13)	59(5)	79(5)	47(4)	1(4)	17(4)	8(4)
C(14)	49(4)	68(5)	42(4)	6(4)	3(3)	-5(4)
C(15)	63(5)	90(7)	48(5)	2(5)	5(4)	-14(5)
C(16)	82(6)	78(6)	59(5)	9(5)	1(4)	-40(5)
C(17)	91(6)	59(5)	45(4)	3(4)	-10(4)	-25(4)
C(18)	67(5)	53(5)	38(4)	-1(3)	-10(3)	-10(4)
C(20)	148(14)	330(30)	152(15)	25(17)	21(12)	127(17)
O(1)	79(4)	68(4)	52(3)	-23(3)	12(3)	-17(3)
O(2)	51(3)	72(3)	34(3)	2(2)	7(2)	3(3)
O(3)	50(4)	125(5)	71(4)	20(4)	-7(3)	3(3)
O(4)	66(4)	112(5)	34(3)	10(3)	-6(3)	-5(3)
O(6)	111(7)	264(13)	89(6)	33(7)	-17(5)	35(8)
C(19)	154(12)	122(10)	106(9)	1(8)	28(9)	-40(10)
O(5)	130(6)	99(5)	56(4)	0(4)	33(4)	15(5)

Table S27. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for [Ru(TPA)$(NO)_2$] (**3**).

	x	y	z	U(eq)
H(1A)	6900	3258	2190	53
H(2A)	7313	4717	2119	70
H(3A)	6659	5912	2674	75
H(4A)	5668	5559	3410	65
H(6A)	4964	4366	4065	64
H(6B)	4662	3926	3252	64
H(7A)	5347	2962	5185	63
H(7B)	5839	3657	4715	63
H(9A)	6434	2361	5857	63
H(10A)	7379	1382	5756	64
H(11A)	7667	790	4497	62
H(12A)	7009	1176	3383	58
H(13A)	4139	2750	3812	74
H(13B)	4375	2704	4738	74
H(15A)	3875	1169	4977	81
H(16A)	3955	-377	4771	87
H(17A)	4749	-946	3838	78
H(18A)	5425	73	3105	63
H(20A)	3354	4063	1606	314
H(20B)	2888	3294	2019	314
H(20C)	2645	3752	1190	314
H(6)	3797	2752	1278	232
H(19A)	6745	-893	1127	191
H(19B)	7318	-384	597	191
H(19C)	6806	-1099	181	191
H(5)	6213	318	866	143

Figure S28. Hydrogen bonds for [Ru(TPA)(NO_2)$_2$] (**3**) [Å and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(5)-H(5)...O(1)	0.84	1.96	2.797(8)	176.5

Table S29. Crystal data and structure refinement for [Ru(TPA)(ONO)(NO)]$(PF_6)_2$ (**4**).

Identification code	[Ru(TPA)(ONO)(NO)](PF6)2
Empirical formula	C18 H18 F12 N6 O3 P2 Ru
Formula weight	757.39
Temperature	85(2) K
Wavelength	1.54178 A
Crystal system, space group	Monoclinic, P 2(1)/n
Unit cell dimensions	a = 16.3726(3) A alpha = 90 deg. b = 9.9439(2) A beta = 114.313(8)deg. c = 17.3570(12) A gamma = 90 deg.
Volume	2575.2(2) A^3
Z, Calculated density	4, 1.954 Mg/m^3
Absorption coefficient	7.272 mm^-1
F(000)	1496
Crystal size	0.17 x 0.13 x 0.08 mm
Theta range for data collection	3.12 to 68.22 deg.
Limiting indices	-19<=h<=19, -11<=k<=11, -20<=l<=20
Reflections collected / unique	39910 / 4645 [R(int) = 0.0512]
Completeness to theta = 68.22	99.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.559 and 0.301
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4645 / 0 / 379
Goodness-of-fit on F^2	1.159
Final R indices [I>2sigma(I)]	R1 = 0.0462, wR2 = 0.1137
R indices (all data)	R1 = 0.0473, wR2 = 0.1143
Largest diff. peak and hole	0.679 and -0.914 e.A^-3

Table S30. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for [Ru(TPA)(ONO)(NO)]$(PF_6)_2$ (**4**). U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Ru(1)	2924(1)	3584(1)	1063(1)	22(1)
P(1)	6451(1)	2035(1)	581(1)	24(1)
P(2)	4996(1)	8895(1)	3525(1)	24(1)
F(1)	5599(2)	1369(3)	-153(2)	38(1)
F(2)	7011(1)	677(2)	645(2)	32(1)
F(3)	6785(2)	2614(3)	-103(1)	36(1)
F(4)	7311(2)	2672(3)	1323(1)	33(1)
F(5)	5891(2)	3368(3)	517(2)	40(1)
F(6)	6139(2)	1434(3)	1279(2)	35(1)
F(7)	4548(2)	7489(3)	3540(2)	38(1)
F(8)	4636(2)	8820(3)	2519(2)	39(1)
F(9)	5902(2)	8152(3)	3622(2)	43(1)
F(10)	5464(2)	10319(3)	3522(2)	36(1)
F(11)	5382(2)	8998(3)	4538(2)	39(1)
F(12)	4114(2)	9663(3)	3445(2)	46(1)
N(1)	2365(2)	5138(3)	989(2)	28(1)
N(2)	2998(3)	3791(5)	2812(3)	50(1)
N(3)	1851(2)	2288(3)	449(2)	26(1)
N(4)	3686(3)	1788(4)	1168(3)	34(1)
N(5)	4227(2)	4277(3)	1713(2)	24(1)
N(6)	2965(2)	3658(3)	-124(2)	24(1)
O(1)	2056(2)	6168(3)	943(2)	37(1)
O(2)	2941(2)	2974(3)	2186(2)	37(1)
O(3)	3008(2)	4953(4)	2672(2)	54(1)
C(1)	1010(3)	2639(5)	-33(2)	29(1)
C(2)	395(3)	1707(5)	-500(3)	32(1)
C(3)	632(3)	380(4)	-497(3)	30(1)
C(4)	1511(3)	3(4)	16(3)	33(1)
C(5)	2122(3)	989(4)	491(2)	26(1)
C(6)	3058(3)	671(4)	1107(3)	29(1)
C(7)	4510(3)	5570(4)	1789(3)	28(1)
C(8)	5400(3)	5905(5)	2268(3)	31(1)
C(9)	6001(3)	4895(5)	2669(3)	33(1)
C(10)	5712(3)	3581(5)	2583(3)	32(1)
C(11)	4830(3)	3300(4)	2107(2)	26(1)
C(12)	4460(3)	1889(4)	1989(3)	29(1)
C(13)	2473(3)	4486(4)	-756(3)	28(1)
C(14)	2394(3)	4280(5)	-1572(3)	34(1)
C(15)	2833(3)	3183(5)	-1747(3)	34(1)
C(16)	3342(3)	2357(5)	-1088(3)	29(1)
C(17)	3406(2)	2617(4)	-273(2)	21(1)
C(18)	3998(2)	1821(4)	469(2)	25(1)

Table S31. Bond length [Å] and angles [deg] for [Ru(TPA)(ONO)(NO)]$(PF_6)_2$ (**4**).

Ru(1)-N(1)	1.772(3)
Ru(1)-O(2)	2.030(3)
Ru(1)-N(5)	2.078(3)
Ru(1)-N(3)	2.083(3)
Ru(1)-N(6)	2.091(4)
Ru(1)-N(4)	2.143(4)
P(1)-F(5)	1.589(3)
P(1)-F(1)	1.596(2)
P(1)-F(4)	1.597(2)
P(1)-F(3)	1.604(3)
P(1)-F(2)	1.610(3)
P(1)-F(6)	1.613(3)
P(2)-F(7)	1.583(3)
P(2)-F(12)	1.587(3)
P(2)-F(8)	1.599(3)
P(2)-F(9)	1.604(3)
P(2)-F(11)	1.607(3)
P(2)-F(10)	1.612(3)
N(1)-O(1)	1.131(4)
N(2)-O(3)	1.182(6)
N(2)-O(2)	1.329(5)
N(3)-C(1)	1.332(5)
N(3)-C(5)	1.357(5)
N(4)-C(12)	1.470(5)
N(4)-C(6)	1.486(6)
N(4)-C(18)	1.498(6)
N(5)-C(11)	1.353(5)
N(5)-C(7)	1.355(5)
N(6)-C(13)	1.342(5)
N(6)-C(17)	1.346(5)
C(1)-C(2)	1.362(6)
C(2)-C(3)	1.375(6)
C(3)-C(4)	1.396(6)
C(4)-C(5)	1.401(6)
C(5)-C(6)	1.497(5)
C(7)-C(8)	1.389(5)
C(8)-C(9)	1.377(6)
C(9)-C(10)	1.377(7)
C(10)-C(11)	1.366(6)
C(11)-C(12)	1.507(6)
C(13)-C(14)	1.384(6)
C(14)-C(15)	1.407(7)
C(15)-C(16)	1.376(6)
C(16)-C(17)	1.399(6)
C(17)-C(18)	1.482(5)
N(1)-Ru(1)-O(2)	97.67(15)
N(1)-Ru(1)-N(5)	97.73(14)
O(2)-Ru(1)-N(5)	88.45(12)
N(1)-Ru(1)-N(3)	101.62(14)
O(2)-Ru(1)-N(3)	88.95(13)
N(5)-Ru(1)-N(3)	160.66(13)
N(1)-Ru(1)-N(6)	97.03(15)
O(2)-Ru(1)-N(6)	164.43(13)
N(5)-Ru(1)-N(6)	94.62(12)

O(2)-Ru(1)-N(6)	164.43(13)
N(5)-Ru(1)-N(6)	94.62(12)
N(3)-Ru(1)-N(6)	83.09(12)
N(1)-Ru(1)-N(4)	175.82(16)
O(2)-Ru(1)-N(4)	83.82(16)
N(5)-Ru(1)-N(4)	78.38(14)
N(3)-Ru(1)-N(4)	82.29(14)
N(6)-Ru(1)-N(4)	81.87(15)
F(5)-P(1)-F(1)	90.04(14)
F(5)-P(1)-F(4)	90.97(14)
F(1)-P(1)-F(4)	178.83(15)
F(5)-P(1)-F(3)	90.68(15)
F(1)-P(1)-F(3)	90.63(14)
F(4)-P(1)-F(3)	89.95(13)
F(5)-P(1)-F(2)	179.50(15)
F(1)-P(1)-F(2)	89.61(13)
F(4)-P(1)-F(2)	89.38(13)
F(3)-P(1)-F(2)	89.68(14)
F(5)-P(1)-F(6)	90.52(15)
F(1)-P(1)-F(6)	90.11(14)
F(4)-P(1)-F(6)	89.29(13)
F(3)-P(1)-F(6)	178.58(14)
F(2)-P(1)-F(6)	89.12(14)
F(7)-P(2)-F(12)	90.93(15)
F(7)-P(2)-F(8)	90.66(14)
F(12)-P(2)-F(8)	90.81(16)
F(7)-P(2)-F(9)	90.33(15)
F(12)-P(2)-F(9)	178.44(16)
F(8)-P(2)-F(9)	90.09(15)
F(7)-P(2)-F(11)	90.89(14)
F(12)-P(2)-F(11)	90.03(16)
F(8)-P(2)-F(11)	178.23(16)
F(9)-P(2)-F(11)	89.04(15)
F(7)-P(2)-F(10)	179.17(15)
F(12)-P(2)-F(10)	89.65(15)
F(8)-P(2)-F(10)	89.92(14)
F(9)-P(2)-F(10)	89.08(15)
F(11)-P(2)-F(10)	88.52(14)
O(1)-N(1)-Ru(1)	175.7(3)
O(3)-N(2)-O(2)	115.6(4)
C(1)-N(3)-C(5)	120.9(3)
C(1)-N(3)-Ru(1)	126.5(3)
C(5)-N(3)-Ru(1)	111.9(2)
C(12)-N(4)-C(6)	114.5(4)
C(12)-N(4)-C(18)	109.7(4)
C(6)-N(4)-C(18)	114.5(4)
C(12)-N(4)-Ru(1)	105.3(3)
C(6)-N(4)-Ru(1)	104.8(3)
C(18)-N(4)-Ru(1)	107.1(3)
C(11)-N(5)-C(7)	118.9(3)
C(11)-N(5)-Ru(1)	114.1(3)
C(7)-N(5)-Ru(1)	126.9(3)
C(13)-N(6)-C(17)	120.3(4)
C(13)-N(6)-Ru(1)	125.0(3)
C(17)-N(6)-Ru(1)	113.5(3)
N(2)-O(2)-Ru(1)	124.8(3)
N(3)-C(1)-C(2)	121.0(4)

C(1)-C(2)-C(3)	120.8(4)
C(2)-C(3)-C(4)	118.4(4)
C(3)-C(4)-C(5)	119.1(4)
N(3)-C(5)-C(4)	119.7(3)
N(3)-C(5)-C(6)	117.1(3)
C(4)-C(5)-C(6)	123.0(4)
N(4)-C(6)-C(5)	111.5(3)
N(5)-C(7)-C(8)	121.3(4)
C(9)-C(8)-C(7)	118.8(4)
C(10)-C(9)-C(8)	119.7(4)
C(11)-C(10)-C(9)	119.4(4)
N(5)-C(11)-C(10)	121.9(4)
N(5)-C(11)-C(12)	115.5(3)
C(10)-C(11)-C(12)	122.6(4)
N(4)-C(12)-C(11)	109.5(3)
N(6)-C(13)-C(14)	121.1(4)
C(13)-C(14)-C(15)	119.7(4)
C(16)-C(15)-C(14)	118.1(4)
C(15)-C(16)-C(17)	119.9(4)
N(6)-C(17)-C(16)	120.9(3)
N(6)-C(17)-C(18)	117.1(3)
C(16)-C(17)-C(18)	122.0(4)
C(17)-C(18)-N(4)	113.3(3)

Table S32. Anisotropic displacement parameters (A^2 x 10^3) for [Ru(TPA)(ONO)(NO)]$(PF_6)_2$ (**4**). The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a^{*2} U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Ru(1)	26(1)	19(1)	27(1)	0(1)	16(1)	1(1)
P(1)	23(1)	22(1)	27(1)	0(1)	11(1)	0(1)
P(2)	25(1)	23(1)	25(1)	2(1)	12(1)	0(1)
F(1)	29(1)	33(1)	41(1)	-9(1)	3(1)	2(1)
F(2)	27(1)	30(1)	38(1)	3(1)	13(1)	8(1)
F(3)	40(1)	46(2)	24(1)	9(1)	16(1)	2(1)
F(4)	35(1)	35(1)	28(1)	-1(1)	12(1)	-11(1)
F(5)	43(1)	24(1)	58(2)	-3(1)	24(1)	5(1)
F(6)	35(1)	39(1)	40(1)	4(1)	24(1)	-5(1)
F(7)	50(1)	26(1)	39(1)	4(1)	18(1)	-9(1)
F(8)	51(1)	35(1)	24(1)	1(1)	8(1)	-2(1)
F(9)	30(1)	47(2)	51(2)	-10(1)	16(1)	8(1)
F(10)	40(1)	31(1)	34(1)	3(1)	14(1)	-10(1)
F(11)	50(1)	38(1)	27(1)	-1(1)	14(1)	-4(1)
F(12)	25(1)	45(2)	66(2)	-12(1)	16(1)	6(1)
N(1)	32(2)	20(2)	39(2)	-1(1)	22(1)	1(1)
N(2)	52(2)	52(3)	54(2)	-8(2)	29(2)	4(2)
N(3)	35(2)	21(2)	36(2)	1(1)	27(1)	-3(1)
N(4)	38(2)	26(2)	41(2)	5(2)	20(2)	8(2)
N(5)	25(1)	28(2)	20(1)	1(1)	11(1)	-3(1)
N(6)	18(1)	23(2)	32(2)	-1(1)	10(1)	-4(1)
O(1)	37(1)	27(2)	50(2)	-2(1)	21(1)	3(1)
O(2)	46(2)	40(2)	34(1)	-5(1)	25(1)	-1(1)
O(3)	65(2)	60(2)	48(2)	-8(2)	34(2)	-1(2)
C(1)	31(2)	32(2)	34(2)	1(2)	24(2)	-1(2)
C(2)	35(2)	35(2)	34(2)	-2(2)	23(2)	-5(2)
C(3)	33(2)	33(2)	33(2)	-6(2)	23(2)	-13(2)
C(4)	46(2)	24(2)	41(2)	1(2)	32(2)	-2(2)
C(5)	31(2)	27(2)	27(2)	0(2)	19(1)	1(2)
C(6)	36(2)	18(2)	40(2)	3(2)	23(2)	-1(2)
C(7)	29(2)	28(2)	31(2)	1(2)	15(2)	3(2)
C(8)	33(2)	28(2)	34(2)	-7(2)	17(2)	-5(2)
C(9)	28(2)	41(3)	28(2)	-4(2)	12(2)	-3(2)
C(10)	31(2)	37(2)	26(2)	1(2)	10(2)	7(2)
C(11)	31(2)	28(2)	23(2)	-1(2)	14(2)	3(2)
C(12)	31(2)	27(2)	29(2)	5(2)	12(2)	5(2)
C(13)	27(2)	26(2)	29(2)	3(2)	10(2)	-4(2)
C(14)	37(2)	39(2)	26(2)	4(2)	12(2)	-7(2)
C(15)	39(2)	41(3)	25(2)	-1(2)	15(2)	-13(2)
C(16)	28(2)	33(2)	30(2)	-6(2)	15(2)	-7(2)
C(17)	20(2)	20(2)	25(2)	-1(1)	12(1)	-5(1)
C(18)	27(2)	23(2)	30(2)	-3(2)	17(2)	-1(2)

Table S33. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for [Ru(TPA)(ONO)(NO)]$(PF_6)_2$ (**4**).

	x	y	z	U(eq)
H(1A)	835	3554	-53	35
H(2A)	-205	1978	-831	38
H(3A)	209	-264	-836	36
H(4A)	1692	-910	43	39
H(6A)	3063	504	1671	35
H(6B)	3263	-159	926	35
H(7A)	4092	6260	1509	34
H(8A)	5591	6816	2319	37
H(9A)	6612	5104	3003	39
H(10A)	6123	2876	2852	39
H(12A)	4929	1242	2011	35
H(12B)	4275	1666	2449	35
H(13A)	2174	5227	-640	34
H(14A)	2045	4877	-2012	41
H(15A)	2780	3017	-2305	41
H(16A)	3649	1611	-1186	35
H(18A)	4610	2207	689	30
H(18B)	4033	888	285	30