Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

$\{RuNO\}^6$ vs. Co-Ligand Oxidation: Two Non-Innocent Groups in One Ruthenium Nitrosyl Complex

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Computational Procedures

The structure of $[Ru(L)(PPh_3)(NO)(Cl)]^{2+}$ was fully optimized for the singlet ($S = 0$) ground state of this complex, and the structures of $[Ru(L)(PPh_3)(NO)(Cl)]^{+/3+}$ were fully optimized for their doublet ($S = 1/2$) ground states using the BP86 functional[1] and the TZVP basis set.[2] The crystal structure of $[Ru(L)(PPh_3)(NO)(Cl)]^{2+}$ was used as a starting point for the geometry optimization of $[Ru(L)(PPh_3)(NO)(Cl)]^{2+}$. Vibrational frequencies calculated for all structures show no imaginary frequencies. All of these calculations were performed using the program package Gaussian 09.[3] For comparison, the structure of $[Ru(L)(PPh_3)(NO)(Cl)]^{2+}$ was also fully optimized for the singlet ground state using the BP86 functional and the def2-TZVPP basis set[4] in conjunction with the ZORA approximation[5], using the program ORCA.[6] Molecular orbital, TD-DFT, and g-tensor calculations were performed with BP86/TZVP (on the optimized structures) using the program ORCA. In all Gaussian calculations, convergence was reached when the relative change in the density matrix between subsequent iterations was less than 1×10^{-8}. Molecular orbitals were plotted using the program orca_plot included in the ORCA package and visualized using GaussView 3.0.

Table S1. Coordinates (Å) of the optimized structure for the S = 0 singlet ground state of $[Ru(L)(PPh_3)(NO)(Cl)]^{2+}$, calculated with BP86/TZVP (L = 1-phenyl-1-(pyridin-2-yl)-2-(pyridin-2-ylmethylene)hydrazine).

Atom	X	Y	Z
Ru	0.09666300	-0.24961900	-1.40588200
Cl	-1.39075000	-0.94635500	-3.19673900
P	1.48324200	0.42630400	0.61280400
O	2.32177200	0.45510500	-3.21216500
N	1.45398600	0.18001500	-2.50784400
N	-1.04904600	1.53827800	-1.41833400
N	-1.52902700	-0.72458900	-0.22544000
N	0.38545200	-2.33977900	-1.04292600
N	-2.45220000	0.25660500	-0.02473900
C	-0.81658900	2.63872500	-2.17603700
H	0.11789400	2.65384800	-2.73341100
C	-1.71591100	3.69324000	-2.24524900
H	-1.48881400	4.55244500	-2.87582000
C	-2.89776700	3.61965000	-1.49743000
H	-3.62344500	4.43408500	-1.52377400
C	-3.15584800	2.49040300	-0.72690300
H	-4.07315400	2.38997000	-0.14830100
C	-2.22004400	1.44630400	-0.72710600
C	-3.73455600	-0.06190700	0.57424200
C	-3.92208000	0.15779700	1.94420000
H	-3.11346800	0.57179200	2.54968300
C	-5.16276200	-0.15505900	2.51016500
H	-5.33189800	0.01916100	3.57403700
C	-6.18565300	-0.68323200	1.71311700
H	-7.15218300	-0.92264200	2.16016700
C	-5.97971600	-0.90210000	0.34453500
H	-6.78218200	-1.30872400	-0.27319500
C	-4.74725000	-0.59303400	-0.23824400
H	-4.57088500	-0.75360500	-1.30438900
C	-1.66623200	-1.97074200	0.14805200
H	-2.54841100	-2.31035900	0.69360500
C	-0.63262000	-2.88309300	-0.28927900
C	-0.67958100	-4.25788600	-0.02410100
H	-1.49668000	-4.66042400	0.57646000
C	0.30395400	-5.09468000	-0.55528200
H	0.27464300	-6.16903700	-0.36759400
C	1.31126800	-4.53530700	-1.34189800
H	2.08947300	-5.15050500	-1.79413300
C	1.31949200	-3.15478400	-1.56257700
H	2.08845200	-2.69345500	-2.17935400
C	3.71113300	-1.12177500	-0.20374600
H	3.46569700	-0.82068700	-1.22248400
C	4.85739100	-1.89305400	0.00638300
H	5.46942000	-2.19767600	-0.84480700
C	5.22377700	-2.26464100	1.30527800
H	6.11834800	-2.86807000	1.46943500
C	4.44822700	-1.84901100	2.39177600
H	4.73739200	-2.12192100	3.40835100
C	3.30471800	-1.06902400	2.18898500
H	2.72605900	-0.73659300	3.05065800

C	2.92180600	-0.70364500	0.88484500
C	0.57403700	0.44159400	2.21956600
C	0.08136100	-0.77684500	2.73065500
H	0.22832900	-1.70684100	2.17858400
C	-0.53977700	-0.81528200	3.98131800
H	-0.89478600	-1.76704800	4.38144500
C	-0.68519100	0.35969800	4.73025100
H	-1.15862600	0.32641800	5.71333700
C	-0.19760700	1.57019100	4.22808400
H	-0.28678300	2.48443400	4.81785900
C	0.43180800	1.61653300	2.97865100
H	0.83994600	2.56154700	2.62011600
C	3.60183000	2.27813000	0.30158900
H	4.27150500	1.42420500	0.40551600
C	4.14185300	3.55618300	0.12267000
H	5.22552700	3.67880900	0.07791500
C	3.30367800	4.66946100	0.01330900
H	3.73073200	5.66497300	-0.1203950
C	1.91500500	4.50586600	0.08547800
H	1.25721500	5.37432600	0.01565500
C	1.36477600	3.23238200	0.25260600
H	0.28120400	3.12558600	0.31937700
C	2.20674600	2.10696600	0.36860900

Table S2. Coordinates (Å) of the optimized structure for the $S = 1/2$ doublet ground state of $[Ru(L)(PPh_3)(NO)(Cl)]^{3+}$, calculated with BP86/TZVP (L = 1-phenyl-1-(pyridin-2-yl)-2-(pyridin-2-ylmethylene)hydrazine).

Atom	X	Y	Z
Ru	-0.03345700	-0.21000200	-1.30485800
Cl	-1.55681300	-0.97786300	-3.02305100
P	1.66488400	0.39302100	0.59865900
O	1.76766700	0.34477200	-3.56627000
N	1.17324600	0.14769600	-2.60875800
N	-1.12343100	1.60296100	-1.24073900
N	-1.63962400	-0.65874500	-0.09909000
N	0.27796500	-2.29308300	-0.88956800
N	-2.60095400	0.29480400	0.04817100
C	-0.85144000	2.73684200	-1.93335100
H	0.10499900	2.77412500	-2.45203800
C	-1.74366600	3.80201700	-1.99474700
H	-1.48334300	4.68541100	-2.57900300
C	-2.96514700	3.70977200	-1.30955900
H	-3.68577800	4.52887400	-1.34535100
C	-3.26193300	2.55540800	-0.59565900
H	-4.20756200	2.43667700	-0.06729100
C	-2.32711700	1.50574600	-0.58924500
C	-3.90279400	-0.04379900	0.59725800
C	-4.22787300	0.36445100	1.89809000
H	-3.50767400	0.91644700	2.50495500
C	-5.49534200	0.04563600	2.39676500
H	-5.76953800	0.34871000	3.40875100
C	-6.40946000	-0.66215100	1.60236700
H	-7.39893200	-0.89975200	1.99739500
C	-6.06489500	-1.06149400	0.30300000
H	-6.78609000	-1.59823300	-0.31602200
C	-4.80328400	-0.75804800	-0.21363200
H	-4.53034300	-1.03871000	-1.23390300
C	-1.78454200	-1.91421000	0.27567400
H	-2.67210100	-2.24309400	0.82137900
C	-0.75398200	-2.82920900	-0.13984400
C	-0.81480900	-4.20343700	0.13757400
H	-1.63985600	-4.59665600	0.73447200
C	0.16926900	-5.05218500	-0.37768500
H	0.12919900	-6.12619000	-0.18721400
C	1.19161600	-4.50091900	-1.14995600
H	1.97234100	-5.12428300	-1.58846600
C	1.21651300	-3.11660000	-1.38122900
H	2.00886800	-2.66733600	-1.97795100
C	3.83099000	-0.91735600	-0.64980500
H	3.52470100	-0.41912500	-1.57149600
C	4.99215200	-1.69204100	-0.66243400
H	5.55920900	-1.80744100	-1.58822300
C	5.43565000	-2.31134000	0.51683200
H	6.34438100	-2.91632600	0.50547600
C	4.72043200	-2.14259500	1.70828700
H	5.07362100	-2.60908200	2.62988100

C	3.56058100	-1.36240500	1.73307600
H	3.03053800	-1.22035200	2.67497100
C	3.11108000	-0.73651100	0.55156300
C	0.96680100	0.34099400	2.29588400
C	0.36204800	-0.84655600	2.75719000
H	0.27404800	-1.71559000	2.10290500
C	-0.06865600	-0.94368100	4.08152000
H	-0.51171900	-1.87327200	4.44404800
C	0.08691400	0.14488000	4.95594300
H	-0.24669500	0.06330400	5.99223900
C	0.68902100	1.32375400	4.50429900
H	0.83516000	2.16225000	5.18787200
C	1.13088500	1.42935700	3.18229800
H	1.63590400	2.33982300	2.86006000
C	3.61372000	2.35471000	-0.02170300
H	4.32871800	1.53731000	-0.11224800
C	4.05936100	3.67227300	-0.15874100
H	5.11267800	3.86439000	-0.37219100
C	3.16916900	4.74735400	0.00491200
H	3.52900300	5.77258400	-0.10213600
C	1.82593800	4.50354200	0.32105800
H	1.13870200	5.33847700	0.46901100
C	1.36603600	3.19187200	0.44701600
H	0.32183500	3.01281000	0.70820800
C	2.26487300	2.10410800	0.29660000

Table S3. Coordinates (Å) of the optimized structure for the $S = 1/2$ doublet ground state of $[Ru(L)(PPh_3)(NO)(Cl)]^+$, calculated with BP86/TZVP (L = 1-phenyl-1-(pyridin-2-yl)-2-(pyridin-2-ylmethylene)hydrazine).

Atom	X	Y	Z
Ru	-0.06044600	-0.25662500	-1.22414200
Cl	-1.65912000	-0.84871200	-2.97561600
P	1.62559800	0.36711500	0.48051900
O	1.32200800	0.17299700	-3.77342300
N	1.19180700	0.06815600	-2.60658000
N	-1.08895400	1.59474500	-1.16287500
N	-1.63772900	-0.65782100	0.03425000
N	0.16654300	-2.34623300	-0.86083400
N	-2.54686300	0.35175700	0.21660800
C	-0.79694200	2.71746500	-1.85972200
H	0.13153700	2.69324600	-2.42811100
C	-1.62627400	3.83161800	-1.86782000
H	-1.35147200	4.70399900	-2.45969300
C	-2.79770000	3.79832600	-1.10261600
H	-3.46891200	4.65812600	-1.07393200
C	-3.11352200	2.65291200	-0.37892200
H	-4.02166600	2.58927400	0.21855900
C	-2.24844000	1.54959000	-0.44684000
C	-3.89250400	0.04724500	0.65559300
C	-4.22364800	0.18833300	2.00790300
H	-3.47064600	0.53297700	2.71929800
C	-5.52690100	-0.11066900	2.42088100
H	-5.80178500	0.00235900	3.47107800
C	-6.47449800	-0.54977900	1.48896600
H	-7.49048500	-0.77974400	1.81552600
C	-6.12678700	-0.69591900	0.13976900
H	-6.86811400	-1.03953800	-0.58391600
C	-4.82938700	-0.39883700	-0.28729000
H	-4.53234200	-0.50937200	-1.33319500
C	-1.89040800	-1.92083700	0.30216500
H	-2.82581800	-2.24642600	0.75893400
C	-0.88242800	-2.86162500	-0.12417800
C	-0.95627900	-4.23600600	0.15693100
H	-1.79514200	-4.61477000	0.74288400
C	0.02955400	-5.09311900	-0.32600100
H	-0.02235500	-6.16379400	-0.12274900
C	1.08069700	-4.55935100	-1.07872500
H	1.86860400	-5.19232700	-1.48680900
C	1.11424600	-3.18550600	-1.31872600
H	1.91716500	-2.73271600	-1.89922400
C	3.81533000	-0.84200000	-0.85278900
H	3.40776000	-0.38145400	-1.75443000
C	4.99104300	-1.59421800	-0.93807300
H	5.48559000	-1.71438800	-1.90429300
C	5.53145100	-2.18738600	0.20856200
H	6.44821600	-2.77638500	0.14096300
C	4.89470000	-2.01736200	1.44147900
H	5.31291000	-2.47187100	2.34196800

C	3.72368200	-1.25708600	1.53471800
H	3.24592700	-1.12566700	2.50609800
C	3.17140100	-0.66225800	0.38725800
C	1.12413200	0.23283500	2.26288000
C	0.47623400	-0.93938000	2.69434400
H	0.25786000	-1.73748600	1.98424400
C	0.13205600	-1.10603800	4.03889900
H	-0.36124900	-2.02531600	4.36161900
C	0.42245700	-0.10108700	4.96851100
H	0.15208100	-0.23014100	6.01842200
C	1.07291800	1.06344600	4.54895900
H	1.31656200	1.84606000	5.27037200
C	1.42789700	1.23051200	3.20563400
H	1.95093200	2.13650400	2.89836900
C	3.52082100	2.42925500	-0.11160400
H	4.23987300	1.63391200	-0.31005800
C	3.91606300	3.76444500	-0.25412300
H	4.93433200	3.99178400	-0.57592300
C	3.02005200	4.80033800	0.02489100
H	3.33425700	5.84058400	-0.08005600
C	1.72083000	4.49794500	0.44902500
H	1.01792100	5.30093600	0.68013600
C	1.31664600	3.16660600	0.57917800
H	0.30392500	2.94501400	0.92174800
C	2.21609800	2.11780700	0.30513400

Table S4. Coordinates (Å) of the optimized structure for the S = 0 singlet ground state of $[Ru(L)(PPh_3)(NO)(Cl)]^{2+}$, calculated with BP86/TZVP in conjunction with the ZORA approximation (L = 1-phenyl-1-(pyridin-2-yl)-2-(pyridin-2-ylmethylene)hydrazine).

Atom	X	Y	Z
Ru	0.09350000	-0.32860000	-1.35300000
Cl	-1.39650000	-1.05430000	-3.12630000
P	1.49010000	0.39250000	0.60820000
O	2.09460000	0.18900000	-3.42400000
N	1.37830000	-0.01170000	-2.54450000
N	-0.97630000	1.48210000	-1.44410000
N	-1.55290000	-0.71440000	-0.19440000
N	0.34160000	-2.38360000	-0.89720000
N	-2.45190000	0.29790000	-0.04430000
C	-0.67840000	2.55920000	-2.21200000
H	0.27260000	2.53040000	-2.73870000
C	-1.53390000	3.64410000	-2.32860000
H	-1.25510000	4.48020000	-2.96800000
C	-2.73660000	3.63280000	-1.61380000
H	-3.42850000	4.47300000	-1.67770000
C	-3.05740000	2.53360000	-0.82470000
H	-3.99020000	2.48410000	-0.26610000
C	-2.16480000	1.45540000	-0.77730000
C	-3.76100000	0.03210000	0.51910000
C	-3.97800000	0.26730000	1.88100000
H	-3.17150000	0.65200000	2.50700000
C	-5.24540000	0.00970000	2.41220000
H	-5.43710000	0.19610000	3.46930000
C	-6.26580000	-0.47850000	1.58870000
H	-7.25340000	-0.67400000	2.00840000
C	-6.03020000	-0.71410000	0.22870000
H	-6.83040000	-1.09030000	-0.40960000
C	-4.77040000	-0.46110000	-0.31910000
H	-4.57000000	-0.63520000	-1.37810000
C	-1.73600000	-1.94400000	0.21140000
H	-2.63920000	-2.24220000	0.74450000
C	-0.71380000	-2.89090000	-0.17000000
C	-0.79240000	-4.25500000	0.13240000
H	-1.63940000	-4.62770000	0.70890000
C	0.20160000	-5.11920000	-0.32830000
H	0.14820000	-6.18640000	-0.11180000
C	1.25460000	-4.59600000	-1.07760000
H	2.04750000	-5.23300000	-1.46790000
C	1.29220000	-3.22480000	-1.34090000
H	2.10140000	-2.78960000	-1.92280000
C	3.77270000	-1.00690000	-0.31300000
H	3.48210000	-0.68940000	-1.31420000
C	4.96430000	-1.71870000	-0.15780000
H	5.56700000	-1.96370000	-1.03350000
C	5.38650000	-2.10660000	1.11810000
H	6.31650000	-2.66340000	1.24010000
C	4.62080000	-1.76690000	2.23620000
H	4.95260000	-2.05340000	3.23500000
C	3.43160000	-1.04670000	2.08830000
H	2.85940000	-0.77350000	2.97400000

C	2.99340000	-0.66550000	0.80770000
C	0.62700000	0.31220000	2.23920000
C	0.19890000	-0.94320000	2.71510000
H	0.37740000	-1.84600000	2.12960000
C	-0.39470000	-1.05350000	3.97380000
H	-0.70040000	-2.03290000	4.34470000
C	-0.57660000	0.08520000	4.76720000
H	-1.03040000	-0.00410000	5.75510000
C	-0.14850000	1.33130000	4.30250000
H	-0.26310000	2.21820000	4.92720000
C	0.45260000	1.44970000	3.04490000
H	0.81360000	2.42340000	2.71630000
C	3.49920000	2.35980000	0.29070000
H	4.21290000	1.53760000	0.32630000
C	3.96970000	3.66930000	0.15620000
H	5.04280000	3.84760000	0.07680000
C	3.07620000	4.74280000	0.13640000
H	3.44910000	5.76310000	0.03930000
C	1.70210000	4.50660000	0.25210000
H	1.00140000	5.34270000	0.25190000
C	1.22130000	3.20140000	0.37470000
H	0.14820000	3.03880000	0.47740000
C	2.11890000	2.11570000	0.40250000

Table S5. Coordinates (Å) of the optimized structure for the *S* = 0 singlet ground state of $[Ru(L)(PPh_3)(NO)(Cl)]^{2+}$, calculated with BP86/def2-TZVPP(L = 1-phenyl-1-(pyridin-2-yl)-2-(pyridin-2-ylmethylene)hydrazine).

Atom	X	Y	Z
Ru	0.10350000	-0.31690000	-1.34420000
Cl	-1.37220000	-1.03470000	-3.11870000
P	1.51190000	0.40140000	0.63010000
O	2.12430000	0.25160000	-3.37930000
N	1.39910000	0.02360000	-2.51740000
N	-0.97830000	1.49810000	-1.42960000
N	-1.55400000	-0.70700000	-0.19230000
N	0.34620000	-2.38550000	-0.89210000
N	-2.45760000	0.29720000	-0.05060000
C	-0.68260000	2.58010000	-2.18750000
H	0.26980000	2.55940000	-2.71060000
C	-1.54070000	3.66270000	-2.30120000
H	-1.26280000	4.50320000	-2.93370000
C	-2.74660000	3.64050000	-1.59360000
H	-3.44180000	4.47710000	-1.65480000
C	-3.06550000	2.53460000	-0.81460000
H	-4.00050000	2.47740000	-0.26220000
C	-2.16760000	1.46100000	-0.76870000
C	-3.76560000	0.02750000	0.50990000
C	-3.98710000	0.25650000	1.87140000
H	-3.18420000	0.64130000	2.50040000
C	-5.25380000	-0.00720000	2.39940000
H	-5.44740000	0.17450000	3.45600000
C	-6.27050000	-0.49630000	1.57310000
H	-7.25710000	-0.69710000	1.98990000
C	-6.03130000	-0.72580000	0.21370000
H	-6.82760000	-1.10280000	-0.42730000
C	-4.77170000	-0.46630000	-0.33030000
H	-4.56930000	-0.63640000	-1.38850000
C	-1.73490000	-1.93760000	0.20860000
H	-2.63930000	-2.24080000	0.73530000
C	-0.71130000	-2.88450000	-0.16770000
C	-0.80030000	-4.24820000	0.13180000
H	-1.65070000	-4.61470000	0.70550000
C	0.18730000	-5.11880000	-0.32790000
H	0.12600000	-6.18490000	-0.11270000
C	1.24330000	-4.60270000	-1.07650000
H	2.03060000	-5.24410000	-1.46850000
C	1.28910000	-3.23160000	-1.33680000
H	2.09900000	-2.80240000	-1.92100000
C	3.75560000	-1.03400000	-0.29650000
H	3.44870000	-0.74430000	-1.30020000
C	4.94220000	-1.75240000	-0.14180000
H	5.52690000	-2.02720000	-1.01960000
C	5.38260000	-2.10890000	1.13620000
H	6.30790000	-2.67180000	1.25750000
C	4.63860000	-1.73250000	2.25650000
H	4.98330000	-1.99510000	3.25650000
C	3.45480000	-1.00580000	2.10800000
H	2.90050000	-0.70530000	2.99500000

C	2.99650000	-0.65290000	0.82540000
C	0.64630000	0.31880000	2.23920000
C	0.22530000	-0.94160000	2.70960000
H	0.41900000	-1.83970000	2.12320000
C	-0.38270000	-1.06190000	3.95910000
H	-0.68180000	-2.04480000	4.32330000
C	-0.58460000	0.07190000	4.75380000
H	-1.04990000	-0.02470000	5.73460000
C	-0.16450000	1.32300000	4.29750000
H	-0.29490000	2.20620000	4.92270000
C	0.45070000	1.45060000	3.04870000
H	0.80410000	2.42850000	2.72770000
C	3.50650000	2.35290000	0.26090000
H	4.22060000	1.53200000	0.28770000
C	3.97380000	3.65940000	0.09990000
H	5.04380000	3.83600000	-0.00700000
C	3.08070000	4.73240000	0.09030000
H	3.45050000	5.75080000	-0.02700000
C	1.71040000	4.49760000	0.24100000
H	1.01040000	5.33300000	0.24850000
C	1.23310000	3.19510000	0.38930000
H	0.16310000	3.03370000	0.51470000
C	2.12910000	2.10710000	0.40830000

Table S6. Coordinates (Å) of the optimized structure for the S = 0 singlet ground state of $[Ru(L)(PPh_3)(NO)(Cl)]^{2+}$, calculated with BP86/def2-TZVPP in conjunction with the ZORA approximation (L = 1-phenyl-1-(pyridin-2-yl)-2-(pyridin-2-ylmethylene)hydrazine).

Atom	X	Y	Z
Ru	0.09920000	-0.31480000	-1.33760000
Cl	-1.36750000	-1.02880000	-3.10650000
P	1.49430000	0.39620000	0.61910000
O	2.13860000	0.26380000	-3.32900000
N	1.39100000	0.02900000	-2.48520000
N	-0.97280000	1.48510000	-1.42870000
N	-1.54580000	-0.70970000	-0.18980000
N	0.34940000	-2.36610000	-0.90710000
N	-2.44670000	0.29590000	-0.03700000
C	-0.67910000	2.56260000	-2.19480000
H	0.26970000	2.53570000	-2.72410000
C	-1.53450000	3.64680000	-2.30870000
H	-1.25750000	4.48260000	-2.94760000
C	-2.73600000	3.63300000	-1.59390000
H	-3.42850000	4.47160000	-1.65540000
C	-3.05390000	2.53200000	-0.80740000
H	-3.98600000	2.47980000	-0.24970000
C	-2.15960000	1.45650000	-0.76160000
C	-3.75280000	0.02650000	0.52790000
C	-3.96890000	0.25530000	1.89000000
H	-3.16350000	0.63970000	2.51600000
C	-5.23360000	-0.00790000	2.42260000
H	-5.42320000	0.17370000	3.48000000
C	-6.25350000	-0.49620000	1.60020000
H	-7.23870000	-0.69650000	2.02070000
C	-6.01970000	-0.72530000	0.24000000
H	-6.81870000	-1.10150000	-0.39810000
C	-4.76230000	-0.46620000	-0.30870000
H	-4.56440000	-0.63560000	-1.36780000
C	-1.72340000	-1.94070000	0.21110000
H	-2.62320000	-2.24620000	0.74390000
C	-0.69820000	-2.88020000	-0.17700000
C	-0.77470000	-4.24580000	0.11340000
H	-1.61760000	-4.62210000	0.69180000
C	0.21500000	-5.10600000	-0.36130000
H	0.16360000	-6.17400000	-0.15330000
C	1.25940000	-4.57630000	-1.11620000
H	2.04740000	-5.20880000	-1.52080000
C	1.29350000	-3.20350000	-1.36710000
H	2.09400000	-2.76510000	-1.95710000
C	3.74390000	-1.04210000	-0.29080000
H	3.44710000	-0.75140000	-1.29700000
C	4.92850000	-1.76170000	-0.12760000
H	5.51870000	-2.03710000	-1.00160000
C	5.36050000	-2.11790000	1.15310000
H	6.28450000	-2.68140000	1.28070000
C	4.61010000	-1.73890000	2.26800000
H	4.94810000	-2.00030000	3.27050000
C	3.42820000	-1.01110000	2.11110000

H	2.86960000	-0.70860000	2.99470000
C	2.97780000	-0.65990000	0.82570000
C	0.62560000	0.32110000	2.22870000
C	0.20780000	-0.93670000	2.70780000
H	0.40540000	-1.83890000	2.12910000
C	-0.40050000	-1.04990000	3.95770000
H	-0.69690000	-2.03110000	4.32850000
C	-0.60510000	0.08850000	4.74470000
H	-1.06990000	-0.00260000	5.72630000
C	-0.18740000	1.33710000	4.28020000
H	-0.31920000	2.22430000	4.89930000
C	0.42800000	1.45740000	3.03070000
H	0.77990000	2.43390000	2.70380000
C	3.49940000	2.34020000	0.26120000
H	4.21020000	1.51670000	0.29380000
C	3.97320000	3.64450000	0.10160000
H	5.04460000	3.81610000	0.00140000
C	3.08490000	4.72110000	0.08440000
H	3.45970000	5.73770000	-0.03180000
C	1.71300000	4.49200000	0.22640000
H	1.01630000	5.33030000	0.22860000
C	1.22930000	3.19180000	0.37330000
H	0.15800000	3.03570000	0.49330000
C	2.12040000	2.10030000	0.39900000

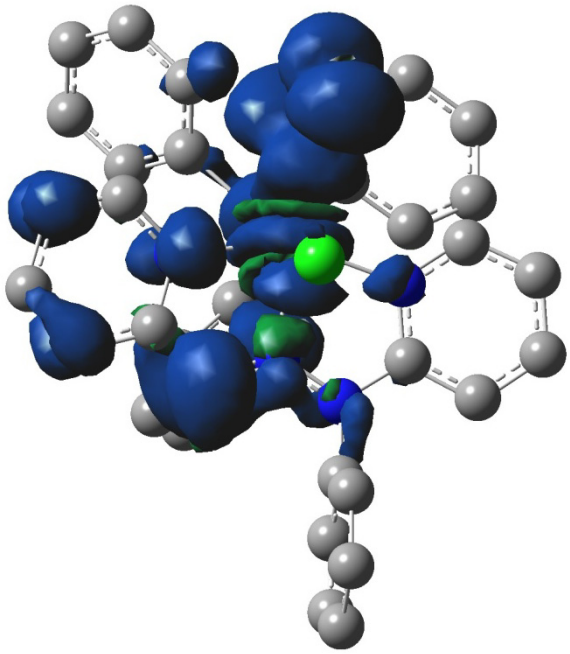

Figure S1. Spin density plot for the S = 1/2 doublet ground state of $[Ru(L)(PPh_3)(NO)(Cl)]^+$ calculated with BP86/TZVP. Hydrogen atoms are omitted for clarity.

Table S7. Comparison of geometric parameters and N–O stretching frequencies of $[Ru(L)(PPh_3)(NO)(Cl)]^{2+}$ and $[Ru(L)(PPh_3)(NO)(Cl)]^{3+}$ (calculated structures obtained with BP86/TZVP).

	Geometric Parameters (Å)					
Complex	**Ru–N(N–O)**	**N–O**	**Ru–Cl**	**Ru–P**	**<Ru–N–O**	**ν(N–O) (cm^{-1})**
$[Ru(L)(PPh_3)(NO)(Cl)]^{2+}$, cryst. struc.	1.731	1.142	2.386	2.401	174	1890
$[Ru(L)(PPh_3)(NO)(Cl)]^{3+}$, exp.	-	-	-	-	-	1910
			DFT-optimized			
$[Ru(L)(PPh_3)(NO)(Cl)]^{2+}$, $S = 0$	1.800	1.151	2.430	2.541	180	1889
$[Ru(L)(PPh_3)(NO)(Cl)]^{3+}$, $S = 1/2$	1.812	1.144	2.421	2.621	169	1911
$[Ru(L)(PPh_3)(NO)(Cl)]^{+}$, $S = 1/2$	1.890	1.180	2.440	2.480	144	1705

Table S8. Comparison of geometric parameters and N–O stretching frequencies of $[Ru(L)(PPh_3)(NO)(Cl)]^{2+}$ obtained with BP86/TZVP, TPSSh/TZVP, and BP86/6-31G*.

	Geometric Parameters (Å)					
Complex	**Ru-N**	**N-O**	**Ru-Cl**	**Ru-P**	**<Ru-N-O**	**ν(N–O) (cm^{-1})**
$[Ru(L)(PPh_3)(NO)(Cl)]^{2+}$, cryst. struc.	1.731	1.142	2.386	2.406	174	1890
BP86/TZVP opt. $[Ru(L)(PPh_3)(NO)(Cl)]^{2+}$, $S = 0$	1.800	1.151	2.430	2.541	180	1889
TPSSh/TZVP opt. $[Ru(L)(PPh_3)(NO)(Cl)]^{2+}$, $S = 0$	1.796	1.136	2.422	2.519	171	1970
BP86/6-31G opt.* $[Ru(L)(PPh_3)(NO(Cl))]^{2+}$, $S = 0$	1.794	1.163	2.434	2.521	173	1904

Table S9. Comparison of geometric parameters and N–O stretching frequencies of $[Ru(L)(PPh_3)(NO)(Cl)]^{2+}$ obtained with BP86/TZVP, BP86/TZVP with the ZORA approximation, BP86/def2-TZVPP, and BP86/def2-TZVPP with the ZORA approximation.

	Geometric Parameters (Å)					
Complex	**Ru-N**	**N-O**	**Ru-Cl**	**Ru-P**	**<Ru-N-O**	**ν(N-O) (cm^{-1})**
$[Ru(L)(PPh_3)(NO)(Cl)]^{2+}$, cryst. struc.	1.731	1.142	2.386	2.406	174	1890
BP86/TZVP opt. $[Ru(L)(PPh_3)(NO)(Cl)]^{2+}$, $S = 0$	1.800	1.151	2.430	2.541	180	1889
BP86/TZVP with ZORA opt. $[Ru(L)(PPh_3)(NO)(Cl)]^{2+}$, $S = 0$	1.781	1.152	2.427	2.513	172	1892
BP86/def2-TZVPP opt. $[Ru(L)(NO)(Cl)]^{2+}$, $S = 0$	1.781	1.149	2.417	2.529	172	1889
BP86/def2-TZVPP with ZORA opt. $[Ru(L)(NO)(Cl)]^{2+}$, $S = 0$	1.762	1.152	2.407	2.507	173	1886

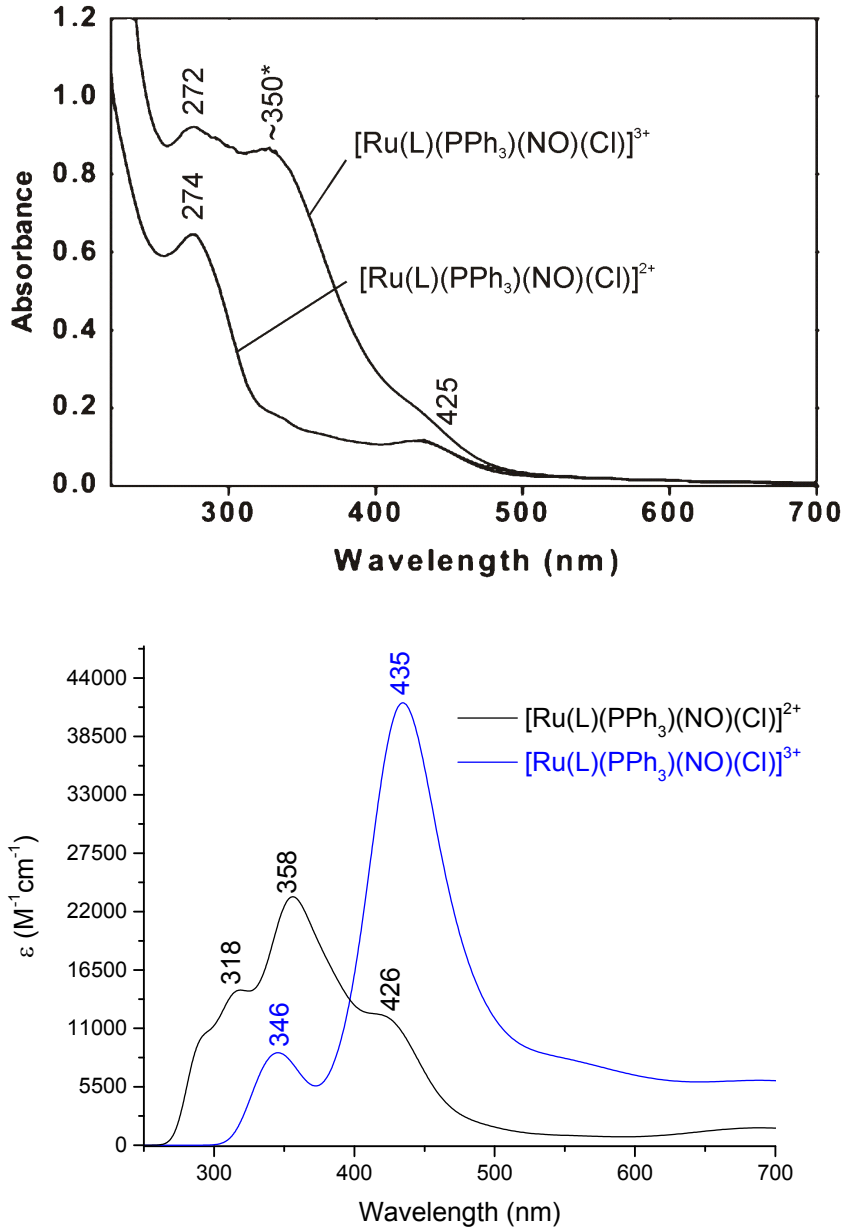

Figure S2. Comparison of the experimental UV-vis spectra of $[Ru(L)(PPh_3)(NO)(Cl)]^{2+/3+}$ (top) and the calculated UV-vis spectra of $[Ru(L)(PPh_3)(NO)(Cl)]^{2+}$ (black) and $[Ru(L)(PPh_3)(NO)(Cl)]^{3+}$ (blue; BP86/TZVP optimized structures; bottom). The * in the experimental UV-vis spectrum indicates that the wavelength of this band is not given in reference 7. For the calculated spectra band widths at half-height were set to 2500 cm^{-1}. The experimental UV-vis spectra are adapted from reference 7 with permission from The Royal Society of Chemistry. The calculations indicate that the new absorption feature at ~350 nm (calculated at 435 nm) that appears in the spectrum upon oxidation of the complex is mainly due to $\pi \rightarrow \pi*$ transitions of the generated co-ligand radical.

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