Electronic Supplementary Information (ESI)

Mixed valence di-ruthenium(II, III) complexes of redox non-innocent *N*-aryl-*o*-phenylenediamine derivatives

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Table S1 Crystallographic data of L_3H_2, **1**.$CHCl_3$, **2** and **3**.MeOH

Complex	L_3H_2	**1**.$CHCl_3$	**2**	**3**.MeOH
CCDC No	2050932	2050935	2050933	2050934
formula	$C_{11}H_{10}N_4O_2$	$C_{48}H_{39}Cl_5N_4O_2P_2Ru$	$C_{60}H_{46}Cl_4N_8O_8P_2Ru_2$	$C_{48}H_{41}Cl_5N_4O_3P_2Ru_2$
f_w	230.23	1044.09	1412.93	1163.18
crystal colour	red	violet	black	black
crystal system	monoclinic	triclinic	triclinic	triclinic
space group	*P* 21/n	*P*-1	*P*-1	*P*-1
a/Å	4.43110(10)	10.5528(3)	9.9317(4)	9.4309(8)
b/Å	24.7331(9)	13.5142(4)	10.6409(4)	13.1135(11)
c/Å	9.2143(3)	18.0956(6)	14.8740(6)	19.2559(17)
$\alpha/^0$	90	79.7780(10)	71.9080(10)	87.976(3)
$\beta/^0$	91.2650(10)	73.1470(10)	87.1700(10)	88.366(3)
$\gamma/^0$	90	69.4680(10)	89.0720(10)	84.158(3)
V/Å^3	1009.59(5)	2304.65(12)	1492.38(10)	2366.8(4)
Z	4	2	1	2
T/K	105(2)	294(2)	293(2)	293(2)
ρ calcd (g cm^{-3})	1.515	1.505	1.574	1.632
refl. Collected ($2\theta_{max}$)	57.02	56.63	51.00	49.99
unique refl.	2535	11398	5475	7992
ref (I>2 σ)	2321	9717	4992	6882
λ(Å)	0.71073	0.71073	0.71073	0.71073
μ(mm^{-1})	0.109	0.744	0.801	1.035
F(000)	480	1060	712	1168
$R_1{}^a$ [$I>2\sigma(I)$]	0.0489	0.0444	0.0331	0.0764
GOF^b	1.082	1.084	1.221	1.171
$R_1{}^a$ (all data)	0.0530	0.0549	0.0387	0.0901
$wR_2{}^c$ [$I>2\sigma(I)$]	0.1225	0.1076	0.0735	0.1695
no. of Parameter / restr.	569/13	564/0	379/0	579/0
residual density (eÅ^{-3})	0.418/-0.257	1.043/-1.115	0.500/-0.510	1.910/-1.821

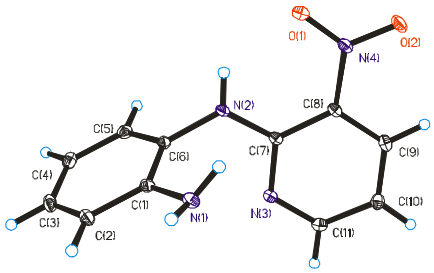
Observation criterion: $I > 2\sigma(I)$. $^aR_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$ ^{b}GOF = $\{\Sigma[w(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2}$
$^c wR_2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (aP)^2+bP]$, $P = (F_o^2+2F_c^2)/$

Table S2 Selected experimental bond lengths [Å] of **1**.$CHCl_3$ and **2** and the corresponding calculated bond lengths of **1** with singlet and triplet spin states, $\mathbf{1}^+$ with doublet spin state and **2** with singlet spin state obtained from the DFT calculations at the PBE0 level using Def2-TZVP basis set for ruthenium and Def2-SVP for other elements

	Exp.		Calc.		Exp.	Calc.
	1.$CHCl_3$	1	1	1^+	2	2
		(s_t = 0)	(s_t = 1)	(s_t = ½)		(s_t = 0)
Ru(1)-N(1)	1.923(2)	1.890	1.973	1.946	1.939(3)	1.915
Ru(1)-N(2)	2.074(2)	2.085	2.092	2.061	2.034(2)	2.040
Ru(1)-P(1)	2.435(7)	2.413	2.435	2.465	2.312(8)	2.334
Ru(1)-Cl(1)	2.424(7)	2.408	2.355	2.328	2.418(7)	2.420
Ru(1)-Cl(2)	2.444(7)	2.449	2.388	2.356	2.424(7)	2.477
Ru(1)-Cl(2A)					2.487(7)	2.441
Ru(1)-P(2)	2.425(7)	2.425	2.445	2.472		
C(1)-N(1)	1.318(4)	1.329	1.338	1.315	1.316(4)	1.322
C(6)-N(2)	1.348(3)	1.352	1.375	1.339	1.340(4)	1.333
C(1)-C(2)	1.418(4)	1.423	1.415	1.427	1.431(5)	1.426
C(2)-C(3)	1.340(6)	1.369	1.379	1.364	1.345(6)	1.367
C(3)-C(4)	1.426(7)	1.423	1.410	1.432	1.422(6)	1.429
C(4)-C(5)	1.362(5)	1.373	1.386	1.368	1.356(5)	1.369
C(5)-C(6)	1.422(4)	1.425	1.410	1.427	1.428(5)	1.425
C(6)-C(1)	1.439(4)	1.439	1.430	1.446	1.454(4)	1.446
C(7)-N(2)	1.419(3)	1.400	1.392	1.420	1.427(3)	1.506

Table S3 Selected experimental bond lengths [Å] of **3**.MeOH and the corresponding calculated bond lengths of **3** with doublet spin state in gas phase and CH_2Cl_2, $\mathbf{3}^-$ with singlet spin state and $\mathbf{3}^{2-}$ with doublet spin state obtained from the DFT calculations at the PBE0 level using Def2-TZVP basis set for ruthenium and Def2-SVP for other elements

	Exp.	Calc (PBE0)			
	3.MeOH	**3** (gas phase) (s_t = ½)	**3** (DCM) (s_t = ½)	$\mathbf{3}^-$ (s_t = 0)	$\mathbf{3}^{2-}$ (s_t = ½)
Ru(1)-N(1)	1.930(7)	1.902	1.905	1.908	1.932
Ru(1)-N(2)	2.030(7)	2.036	2.035	2.030	2.086
Ru(1)-Cl(1)	2.365(2)	2.384	2.395	2.414	2.442
Ru(1)-Cl(2)	2.498(2)	2.490	2.507	2.472	2.478
Ru(1)-Cl(3)	2.220(5)	2.445	2.457	2.435	2.460
Ru(1)-P(1)	2.318(2)	2.318	2.318	2.320	2.276
Ru(2)-N(3)	2.284(6)	2.240	2.241	2.197	2.206
Ru(2)-Cl(2)	2.427(2)	2.448	2.440	2.493	2.511
Ru(2)-Cl(3)	2.153(5)	2.427	2.417	2.408	2.418
Ru(2)-Cl(4)	2.343(2)	2.319	2.328	2.413	2.425
Ru(2)-Cl(5)	2.318(2)	2.322	2.331	2.417	2.427
Ru(2)-P(2)	2.314(2)	2.333	2.343	2.295	2.252
C(1)-N(1)	1.310(12)	1.327	1.325	1.329	1.346
C(6)-N(2)	1.350(11)	1.344	1.343	1.346	1.376
C(1)-C(2)	1.426(13)	1.422	1.424	1.422	1.409
C(2)-C(3)	1.341(18)	1.370	1.368	1.372	1.388
C(3)-C(4)	1.430(19)	1.424	1.427	1.424	1.402
C(4)-C(5)	1.347(15)	1.373	1.373	1.375	1.392
C(5)-C(6)	1.411(13)	1.421	1.423	1.422	1.406
C(6)-C(1)	1.460(13)	1.443	1.446	1.443	1.431
C(7)-N(2)	1.408(11)	1.385	1.389	1.387	1.352
C(7)-N(3)	1.327(10)	1.343	1.343	1.343	1.363



C(1)-N(1) 1.392(18)
C(6)-N(2) 1.433(17)
C(1)-C(2) 1.402(19)
C(2)-C(3) 1.389(2)
C(3)-C(4) 1.391(2)
C(4)-C(5) 1.393(2)
C(5)-C(6) 1.390(19)
C(6)-C(1) 1.406(2)
C(7)-N(2) 1.348(18)
C(7)-N(3) 1.359(17)

Fig. S1 Molecular geometry of L_3H_2 in crystals (50% thermal ellipsoids) and selected experimental bond lengths [Å].

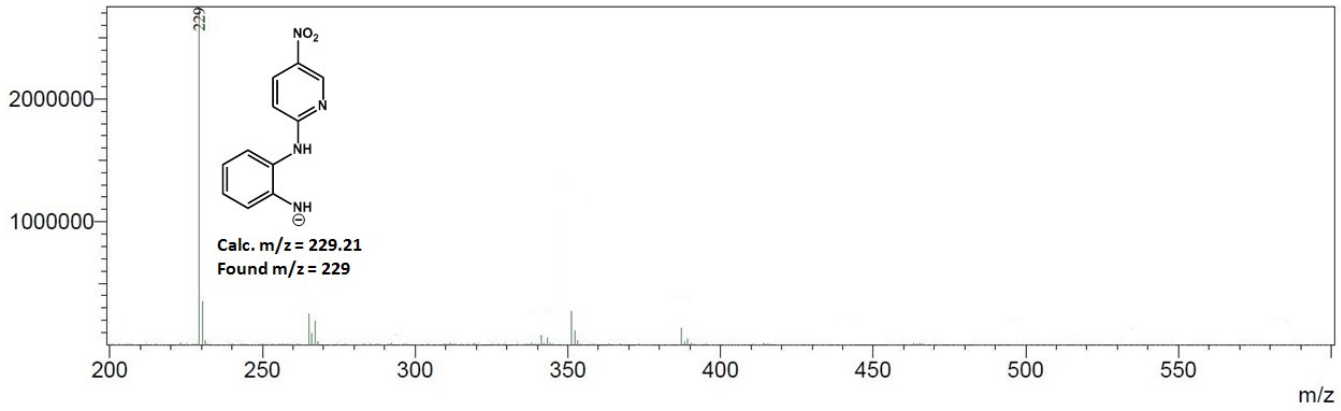


Fig. S2 ESI mass spectrum of L_1H_2.

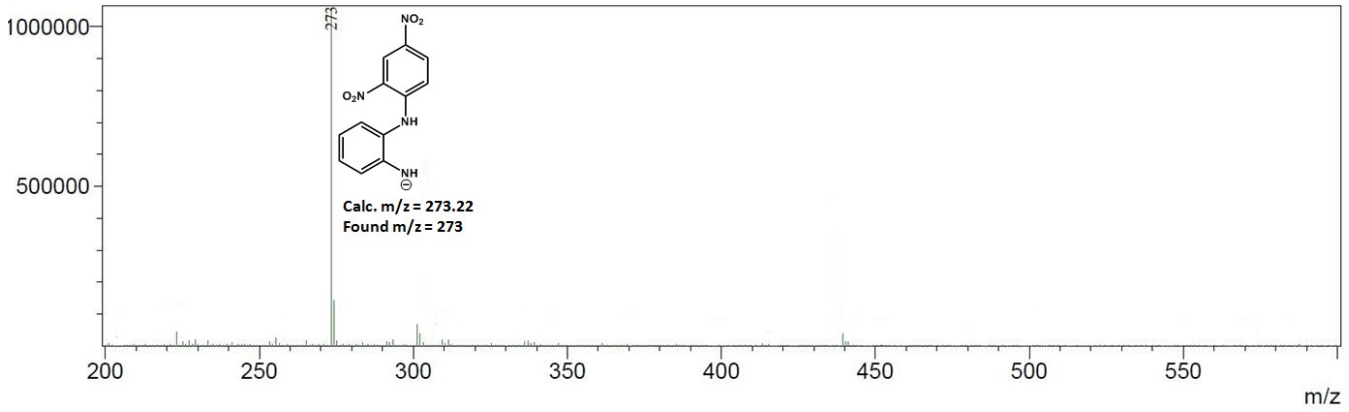


Fig. S3 ESI mass spectrum of L_2H_2.

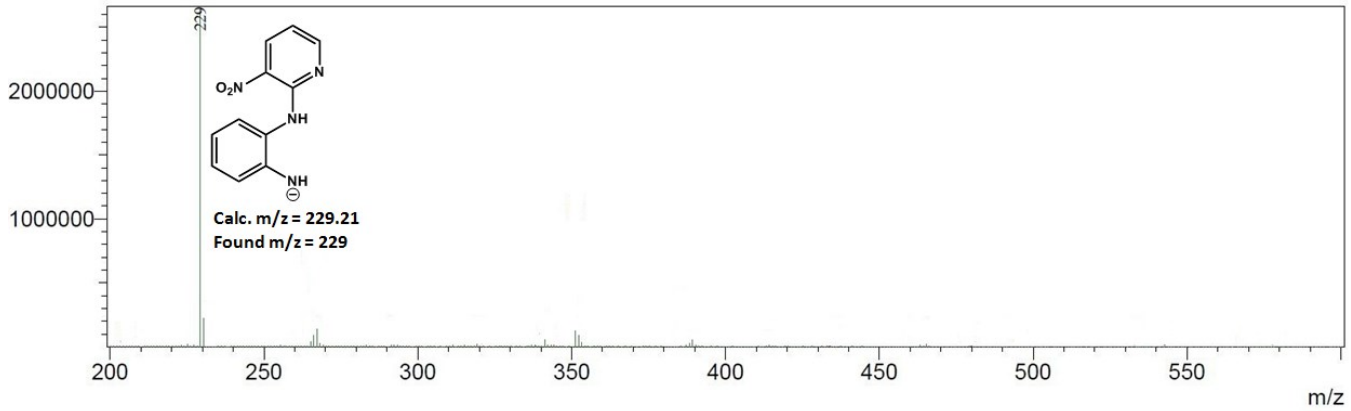


Fig. S4 ESI mass spectrum of L_3H_2.

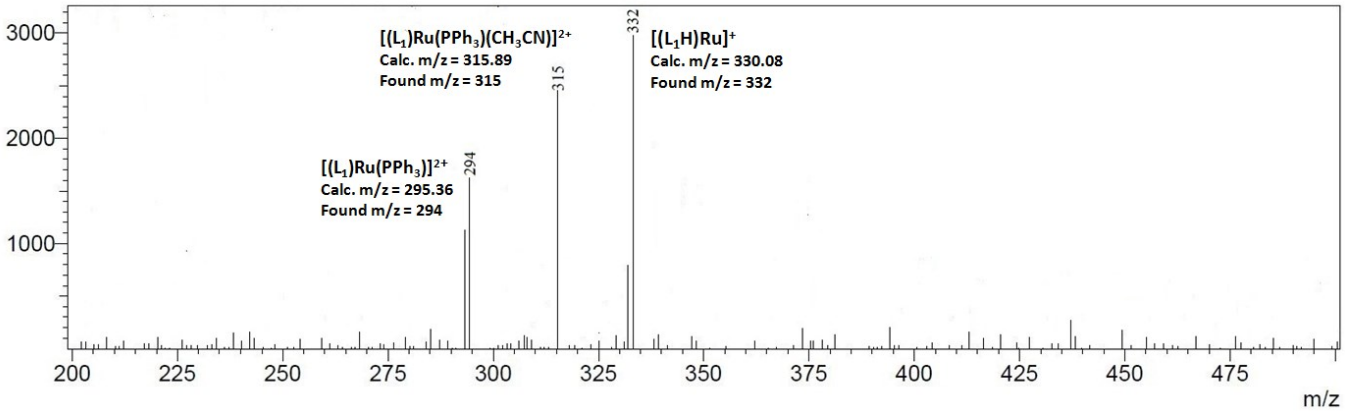


Fig. S5 ESI mass spectrum of **1**.

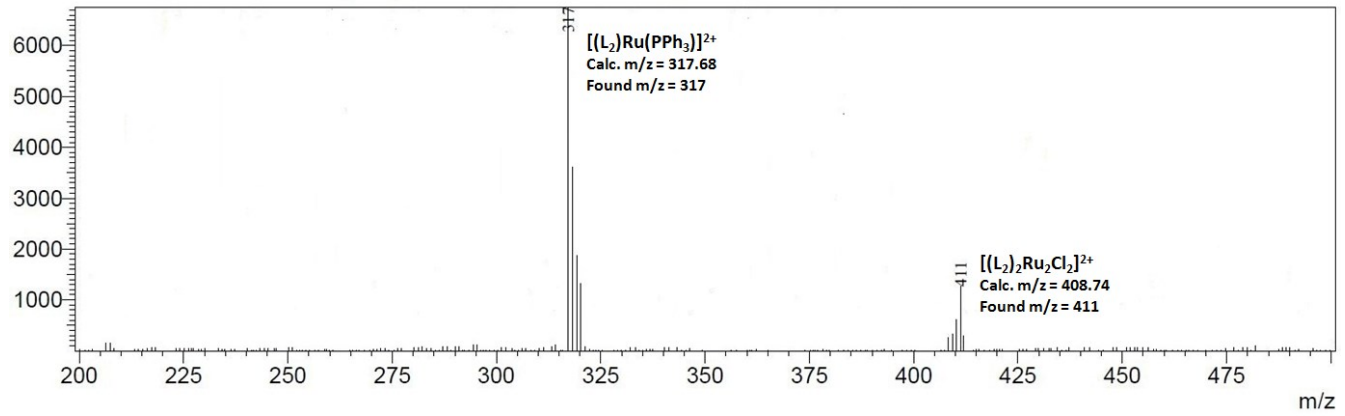


Fig. S6 ESI mass spectrum of **2**.

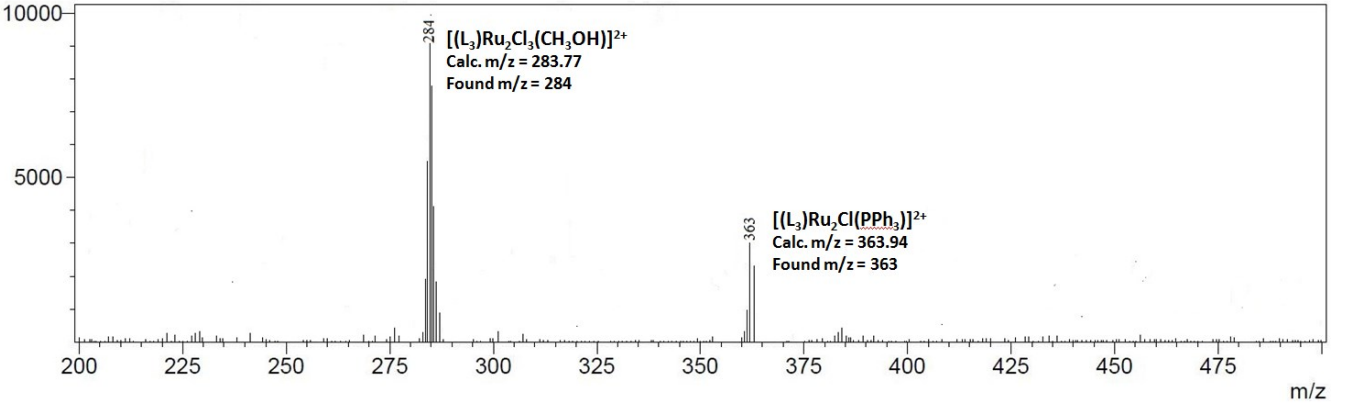


Fig. S7 ESI mass spectrum of **3**.

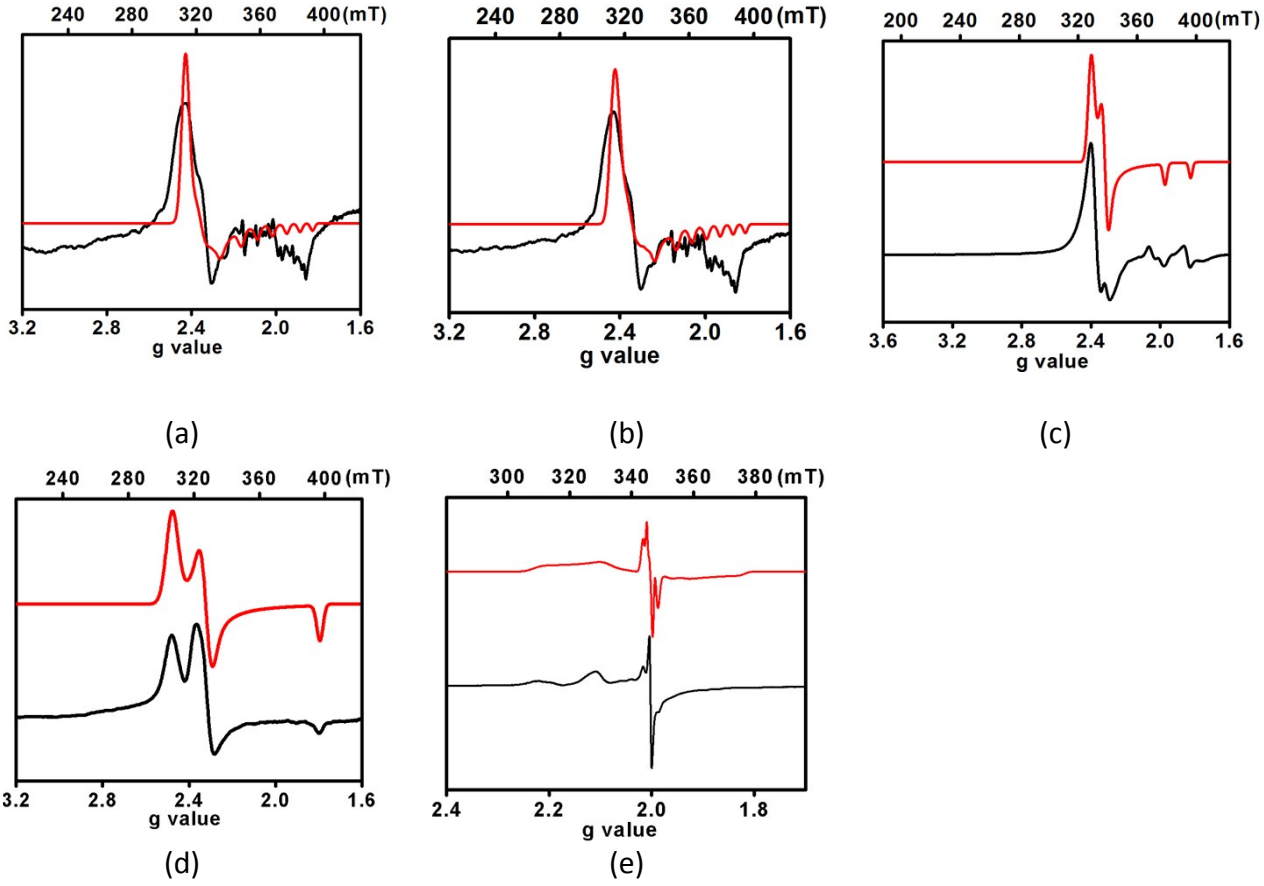
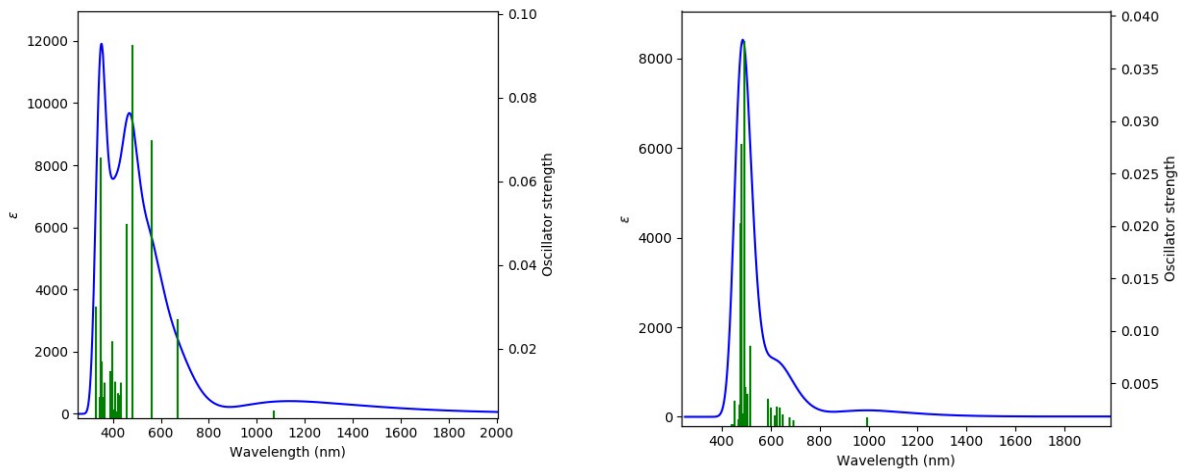


Fig. S8 X-band EPR spectra of (a) $\mathbf{1}^{+}$ ion, frozen glass at 103 K (frequency, 9.46860 MHz) (experimental, black and simulated, red), (b) $\mathbf{2}^{+}$ ion, frozen glass at 103 K (frequency, 9.46924 MHz), (experimental, black and simulated, red), (c) simulation of the powder spectrum of **3** at 103 K (frequency, 9.46504 MHz) (experimental, black and simulated, red), (d) simulation of the frozen glass spectrum of **3** at 103 K (frequency, 9.46734 MHz) (experimental, black and simulated, red) and (e) simulation of frozen glass spectrum of 3^{2-} at 103 K (experimental, black and simulated, red).



(a) (b)

Fig. S9 Calculated UV-vis-NIR absorption spectra of (a) **1** and (b) **3** obtained from TD DFT calculations in CH_2Cl_2 using B3LYP functional.

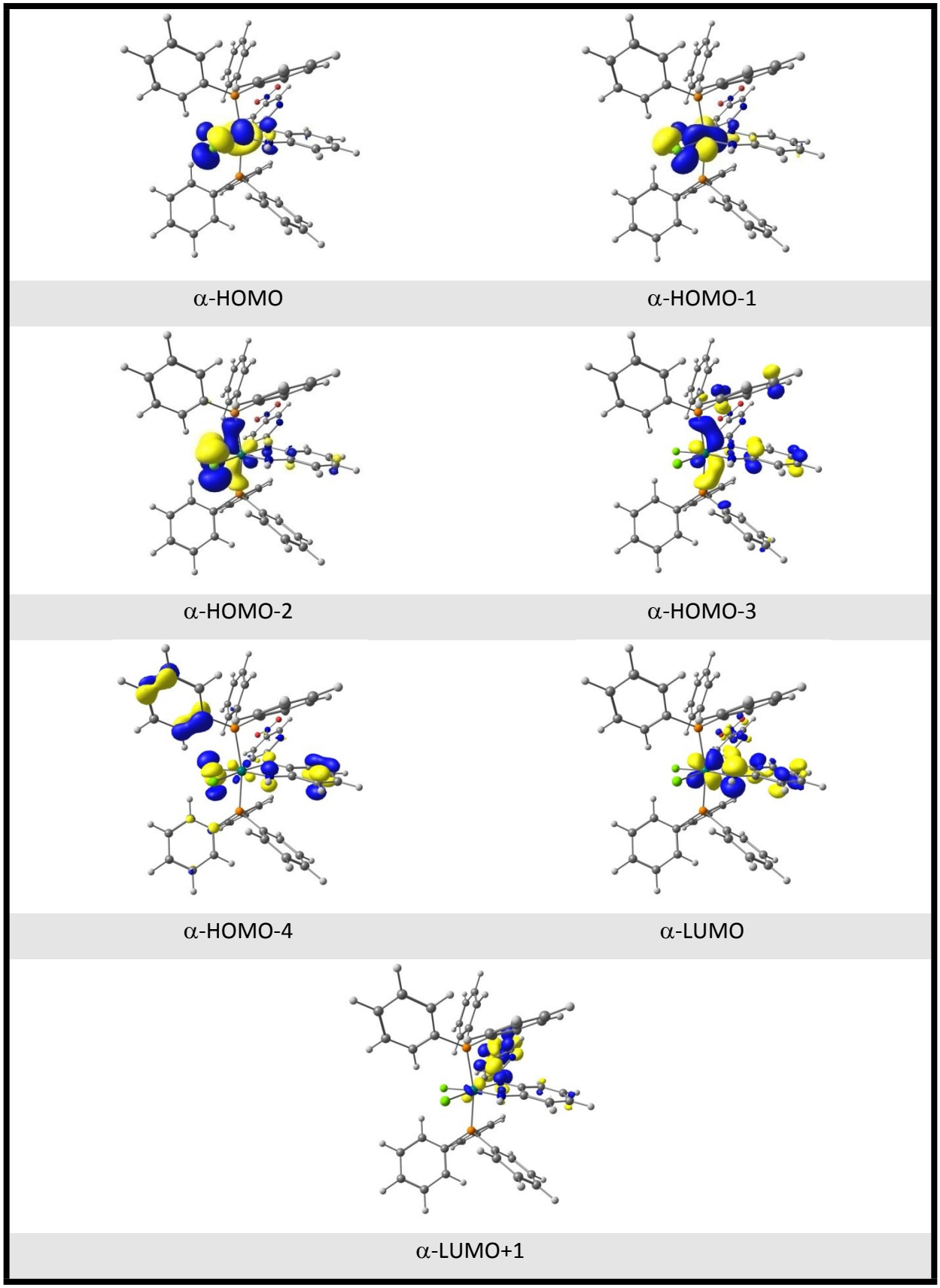


Fig. S10 Frontier molecular orbitals of **1**.

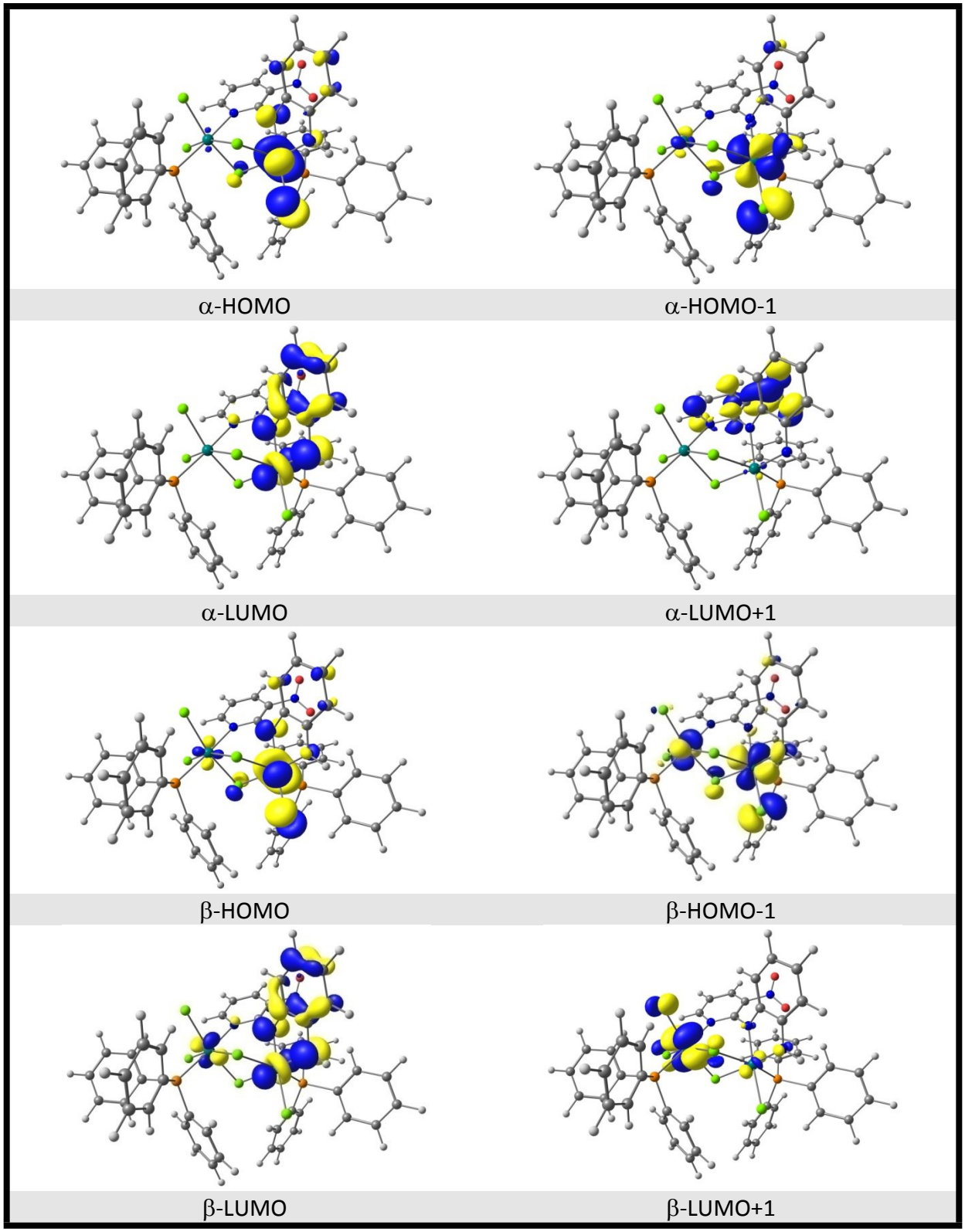


Fig. S11 Frontier molecular orbitals of **3**.

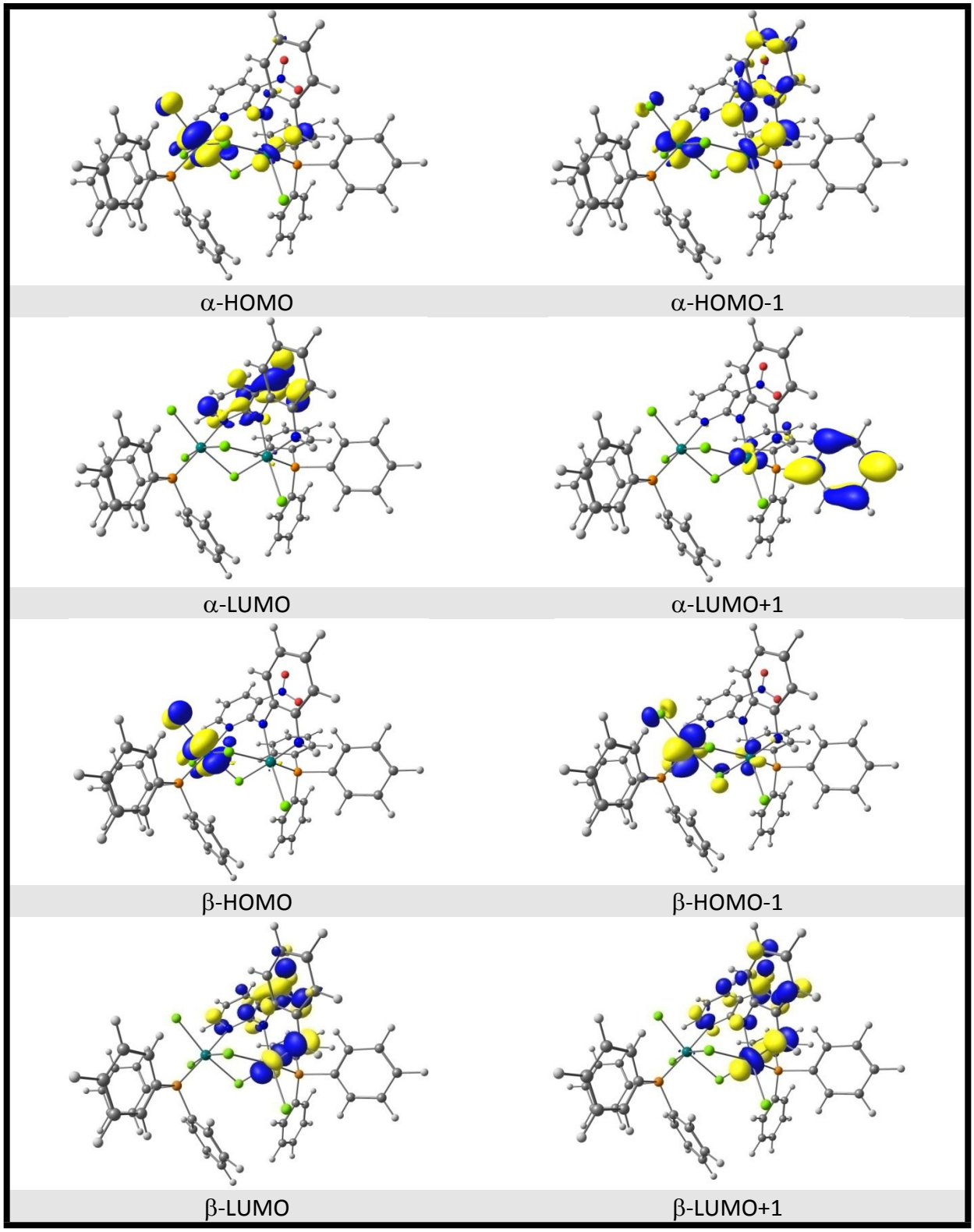


Fig. S12 Frontier molecular orbitals of $\mathbf{3}^{2-}$.

Table S4 Calculated excitation energies (λ/nm), experimental wavelength, oscillator strengths (f) and transition types obtained from TD DFT calculation on **1** and **3**

λ_{cal}(nm)	f	λ_{exp}(nm)	Significant Transitions (>10%)	Transitions Types
			1	
1068.7	0.005	1030	α-HOMO-1 → α-LUMO (64%)	$d_{Ru} \rightarrow \pi^*_{o\text{-diiminobenzoquinone}}$ (MLCT)
688.3	0.027		α-HOMO → α-LUMO+1 (82%)	$d_{Ru} \rightarrow \pi^*_{o\text{-diiminobenzoquinone}}$ (MLCT)
562.8	0.07		α-HOMO-3 → α-LUMO (20%)	$d_{Ru} \rightarrow \pi^*_{nitropyridyl}$ (MLCT)
			α-HOMO-1 → α-LUMO+1 (51%)	
483.7	0.09	495	α-HOMO-4 → α-LUMO (24%)	$d_{Ru} \rightarrow \pi^*_{nitropyridyl}$ (MLCT)
			α-HOMO-3 → α-LUMO (17%)	
			α-HOMO-2 → α-LUMO (17%)	
			α-HOMO-1 → α-LUMO+1 (29%)	
456.9	0.05		α-HOMO-4 → α-LUMO (54%)	$d_{Ru} \rightarrow \pi^*_{nitropyridyl}$ (MLCT)
			3	
995.7	0.001	1000	α-HOMO-2 → α-LUMO (41%)	$d_{Ru} \rightarrow \pi^*_{o\text{-diiminobenzoquinone}}$ (MLCT)
			β-HOMO-1 → β-LUMO+1 (24%)	
493.1	0.037	510	β-HOMO-2 → β-LUMO+2 (29%)	$d_{Ru} \rightarrow \pi^*_{nitropyridyl}$ (MLCT)
			β-HOMO-8 → β-LUMO (14.5%)	
479.3	0.027		β-HOMO-8 → β-LUMO (30%)	$d_{Ru} \rightarrow \pi^*_{nitropyridyl}$ (MLCT)
477.3	0.020		β-HOMO-2 → β-LUMO+2 (21%)	$d_{Ru} \rightarrow \pi^*_{nitropyridyl}$ (MLCT)

Table S5 Gas phase optimized coordinates of **1** with singlet spin state (S_t = 0)

C	6.19475575487938	3.56145181222037	2.89280190598125
Cl	9.37043447481139	6.11765190534438	1.69273312168263
N	7.12972232469102	4.42869781850265	2.51547316175887
O	9.81970942415104	0.88914625750552	10.03584147542120
P	9.73560839301024	2.83101889617723	1.84363584951662
Ru	8.81585512192711	4.47857427306615	3.36739813795330
C	4.95239381615167	3.34063692009432	2.23842033256101
H	4.71466196441345	3.92113891398031	1.34428873387022
Cl	11.07384522367005	4.35961158677950	4.31023661813438
N	7.75669802489365	3.16597580412413	4.59293326678061
O	7.76304721968090	1.33960934555716	10.49063750981879
P	8.33750930527134	6.37622337606116	4.77974632092321
C	4.09874378936239	2.38976288415192	2.73077729758598
H	3.14868754823211	2.18889208366792	2.23169678996685
N	7.08291459087449	2.81581361125401	6.80428965353430
C	4.45388356062837	1.63849704553723	3.88593041241409
H	3.76818100919907	0.86768634492355	4.24668063500210
N	8.72477661475682	1.32355115448461	9.75199074793639
C	5.63129107613584	1.85295405942428	4.55985527480407
H	5.86830384851088	1.26313093981899	5.44232763081131
C	6.54676692147129	2.83753050430890	4.08674491628798
C	8.06443857575311	2.75317589065066	5.89481002316786
C	9.35770053457845	2.29726337984447	6.21274132972173
H	10.14536760930411	2.33168405789975	5.46095918019574
C	9.59502958791932	1.82447450453440	7.49271287857536
H	10.56355511049322	1.42347947716008	7.79475103383322
C	8.54531210469411	1.85442325447404	8.40695478871652
C	7.31233457403837	2.38438052514332	8.03263563707225
H	6.50122830900429	2.44381444076646	8.76413930921944
C	8.45786834637735	2.20731198455619	0.66696739755301
C	7.93539051454272	3.13398485983078	-0.25153196058065
H	8.30772053868585	4.16420573238677	-0.24586628191040
C	6.96213372458726	2.74554742303123	-1.16808097587348
H	6.57114090380949	3.47533161558823	-1.88119139522627
C	6.48709101718674	1.43141236814755	-1.17762066570890
H	5.71997374809291	1.12703337929026	-1.89423157447740
C	6.99874059401289	0.51076647116172	-0.26854657538901
H	6.63253303429622	-0.51880938663492	-0.26975968673223
C	7.98268747073332	0.89268637329977	0.64827061227457
H	8.38507412687202	0.14925753032140	1.33860575385032
C	11.08014435513029	3.34136027834498	0.69734136671076
C	11.22890989450483	2.68163166325719	-0.53159447065181
H	10.51290055102741	1.91292563691865	-0.83182988693292
C	12.28494404170951	3.00529483263607	-1.38202615269852
H	12.38764206965748	2.48596053620241	-2.33760176808445
C	13.20306726189276	3.98842511743820	-1.01331045293279
H	14.02629344585478	4.24745333713637	-1.68392572253437
C	13.06082594836409	4.64364755478992	0.20879032519040
H	13.77295640491408	5.41776177734307	0.50484676913423
C	12.00660304207512	4.32495110226127	1.06309827141341
H	11.89834523231956	4.83572147306358	2.01972317934847
C	10.42301349647736	1.32052781267848	2.63403234958160
C	9.62628013321582	0.55272894867298	3.49617135898874

H	8.59523602962745	0.85153909201165	3.69538330469760
C	10.14204772842908	-0.58466412639581	4.11420097197135
H	9.50870734942264	-1.17007780941912	4.78548060319400
C	11.46131537856351	-0.97218948388562	3.88121049380411
H	11.86765745344186	-1.86139915086378	4.36917070940013
C	12.25881414583060	-0.21598562279939	3.02489176595147
H	13.28966329721448	-0.51798977348795	2.82454012442721
C	11.74668955243467	0.92461050517170	2.40795309143903
H	12.38370693837547	1.51116816609701	1.74359228890330
C	8.45068918963682	6.23900719585658	6.61522875130205
C	9.52525615096073	5.53116934914356	7.17026752575078
H	10.20922526699805	4.98864681991347	6.51193131865140
C	9.74628508197361	5.55544012452924	8.54775207561894
H	10.59066215262864	5.00471179806091	8.97094235942709
C	8.90932507402213	6.29661711302404	9.37974431671473
H	9.10270200238213	6.33863361837263	10.45505905971454
C	7.83455594519411	6.99854227337341	8.83353472523922
H	7.17395527232428	7.58092775821353	9.48033803172365
C	7.60539638390925	6.97331981185812	7.45949879229895
H	6.76871616364949	7.54058499097602	7.04515489622287
C	9.27234402639990	7.94097532663509	4.54976406511140
C	10.61846675333156	7.90597305923530	4.17306794954629
H	11.08642630753763	6.95020044930356	3.92995642098496
C	11.35167196971394	9.08997673730414	4.11313824041436
H	12.39915315685954	9.05570645050824	3.80514885424267
C	10.75536132712171	10.31138511334749	4.42068334442882
H	11.33461489465515	11.23599867111990	4.35791017471839
C	9.41705954825995	10.34838477199883	4.80944584964889
H	8.93976438670248	11.29656278273168	5.06935339633649
C	8.68181449551731	9.16822293958483	4.88141468545395
H	7.63943738773257	9.21118410147537	5.20344894731647
C	6.58784137750916	6.80606137377277	4.44596423355242
C	5.55980795278268	6.12265980220709	5.11163914752264
H	5.79931267724513	5.38510412646890	5.88375743924784
C	4.22658935381799	6.37920298202862	4.79042786707415
H	3.43623187559106	5.84895674231737	5.32637440668766
C	3.90604893751146	7.30338359927397	3.79570761502830
H	2.86192169327066	7.51474212973962	3.54982485554094
C	4.92659079807498	7.95510284919235	3.10403385705039
H	4.68288899297146	8.66995671035403	2.31393960908114
C	6.26099289242393	7.70433042103828	3.42013017092561
H	7.05377826252859	8.20893957403621	2.86438533291613
H	6.92582506657482	5.04475114739653	1.72336654315811

Table S6 Gas phase optimized coordinates of **1** with triplet spin state (S_t = 1)

C	6.24790579825214	3.52702642261873	2.89891820235075
Cl	9.42895226242187	6.13405633872363	1.74092193879993
N	7.16899585660202	4.39340015392844	2.45985087991393
O	9.77171892128652	1.23933781418570	10.20257384202709
P	9.70739019186086	2.80826491375863	1.72443901367165
Ru	8.93771249214971	4.46802086751870	3.33141055419527
C	5.01003326349796	3.24970773696899	2.27230591103710
H	4.73711372133442	3.80116254549566	1.36951471795856
Cl	11.11908821635767	4.26668088262018	4.28124747143339
N	7.85924025286301	3.19117860115083	4.58912615982140
O	7.88246337075068	2.15077192097128	10.68941376035571
P	8.33051352109367	6.31633953966105	4.81252393250931
C	4.18426332744218	2.27754804692240	2.79849623606419
H	3.23639335550153	2.04149638048140	2.30996515047514
N	7.17439622587433	3.09969980945470	6.82354141843051
C	4.56648362424641	1.57212876150866	3.95750048927068
H	3.91079419136801	0.79389869946732	4.35523852892550
N	8.75714147583724	1.83629949804672	9.90926729532764
C	5.76194933995177	1.84696490187033	4.60227724080190
H	6.03457080333993	1.29363865624557	5.50004593722384
C	6.62629633483396	2.83755438608778	4.09321138802692
C	8.14109430799221	2.88222049989109	5.91633796924267
C	9.38713451524280	2.32759729741381	6.27720072297377
H	10.15393495162349	2.18079185593062	5.51920703915209
C	9.60080326558835	1.96421229168873	7.59356715593416
H	10.52854960700254	1.49694784253891	7.92664773475777
C	8.58055448720260	2.19987865790004	8.51348775234495
C	7.38800320814856	2.78311156237225	8.08865329558901
H	6.59733206147699	2.98981323242119	8.81573826861530
C	8.44698344671484	2.27352373141848	0.49438110976093
C	7.96965212011248	3.25164470417851	-0.39450764415195
H	8.36120727776458	4.27255257091471	-0.33637153182304
C	7.02000234550021	2.92378332524450	-1.35883752941706
H	6.65965309964452	3.69367094567655	-2.04532945821331
C	6.53436772942192	1.61753692617436	-1.45279255927957
H	5.78937344909952	1.35891245733100	-2.20947598924887
C	7.00760933449961	0.64364970918831	-0.57819203725088
H	6.63485752364993	-0.38091276176631	-0.65154133985804
C	7.95881185074541	0.96716735410941	0.39332377707961
H	8.32476955029281	0.18861882060685	1.06534960705582
C	11.11026840924830	3.28760876164310	0.63522190994700
C	11.29808681915236	2.61917678687938	-0.58422612341364
H	10.58093807071473	1.86158294769383	-0.90933353276671
C	12.39417330869724	2.91933884179617	-1.39089962075917
H	12.52940630227553	2.39167451636418	-2.33778906845881
C	13.31148860104647	3.89172465932402	-0.99186611670584
H	14.16594363669874	4.13314203055283	-1.62898294400185
C	13.12937619318445	4.55847079089458	0.21813760189806
H	13.84112871617410	5.32320823381030	0.53871288932543
C	12.03694015378428	4.25927171663507	1.03053469526715
H	11.90536413717760	4.77651942236574	1.98047912545721
C	10.30148802143680	1.26940056243370	2.52763623659574
C	9.44622909567795	0.55062357465748	3.37625057896385

H	8.41955555182451	0.88828246103574	3.53219115572199
C	9.90397873047023	-0.58546843670787	4.04052009211856
H	9.22787762713231	-1.13294983814016	4.70162161663256
C	11.21950845014888	-1.01680740932265	3.87050929186930
H	11.58004349651023	-1.90339199723650	4.39784140069392
C	12.07220249443425	-0.30970382430953	3.02569144624074
H	13.10099015421638	-0.64626149149880	2.87608570548440
C	11.62014564971521	0.82911096287214	2.36117449955423
H	12.30094697137434	1.38110273613181	1.71090139912483
C	8.49299467860658	6.18735118969191	6.64297764061858
C	9.63025580460442	5.56361261249176	7.17263705758615
H	10.33694481113426	5.06568988773037	6.50339158366426
C	9.87334945805371	5.59645108550070	8.54589027316770
H	10.76056438227336	5.10220468385192	8.95063971372027
C	8.99783969811664	6.26629275584658	9.39840507196116
H	9.20314703308329	6.30796673507481	10.47132911032738
C	7.86728255091235	6.89386861191113	8.87493293992307
H	7.17721140787943	7.42286781348396	9.53662255754990
C	7.61396460040569	6.85731913778221	7.50538736425037
H	6.73053926688062	7.36291067163021	7.10898321649116
C	9.20361694648355	7.92130138650962	4.59659095842825
C	10.57268226593558	7.92720001705642	4.30798590057675
H	11.08958360567935	6.98581232080515	4.10915645171327
C	11.27315442110449	9.13161751521235	4.28024330618229
H	12.33997059899204	9.12710706033491	4.04484905744167
C	10.61994054181926	10.33720584127235	4.53044303769709
H	11.17360904665420	11.27882106275653	4.49570785290874
C	9.25904440420760	10.33480448392347	4.83162101603179
H	8.73753311676584	11.27038323431566	5.04838404318977
C	8.55696552036764	9.13293649721741	4.87451259628967
H	7.49724168863174	9.14474587561489	5.13765540296963
C	6.56485111221122	6.66859632628717	4.49779001251704
C	5.57808742726090	5.93879384026748	5.17577267242862
H	5.86117507972598	5.20190810657477	5.93462839173839
C	4.23163324704819	6.13754864428344	4.86921620754367
H	3.47151242223753	5.56994546684574	5.41035065441134
C	3.85897211277441	7.04655110773238	3.87897484468376
H	2.80348524736777	7.20888402099384	3.64420380879722
C	4.84004061531075	7.74224756097093	3.17371014325769
H	4.55539009192308	8.44309052021475	2.38474405037951
C	6.18718838664058	7.54999896750026	3.47462034747968
H	6.94925386455456	8.08917226742628	2.90798675602602
H	6.97637027466916	4.90698278209444	1.60423930737547

Table S7 Gas phase optimized coordinates of **1**$^{+}$ with doublet spin state (S_t = ½)

C	6.112760	3.376150	2.929205
Cl	9.181700	6.031693	1.777050
N	7.048816	4.166458	2.450390
O	9.804462	1.574534	10.294377
P	9.703461	2.797016	1.674707
Ru	8.769797	4.356344	3.339778
C	4.858132	3.079105	2.316647
H	4.607379	3.536880	1.357708
Cl	10.912023	4.084104	4.282614
N	7.694383	3.155486	4.624324
O	7.897775	2.468161	10.758143
P	8.316113	6.268079	4.839636
C	4.012614	2.218771	2.953937
H	3.051510	1.960699	2.504618
N	7.126696	3.247154	6.883437
C	4.373057	1.623448	4.205865
H	3.677333	0.919923	4.669239
N	8.762843	2.108263	9.993508
C	5.557530	1.901768	4.832168
H	5.808339	1.432271	5.781095
C	6.476800	2.793315	4.201315
C	8.024112	2.863446	5.974683
C	9.215025	2.203101	6.294468
H	9.917738	1.918491	5.513998
C	9.466492	1.926547	7.631727
H	10.366233	1.405285	7.963229
C	8.529556	2.346330	8.566307
C	7.371866	3.007226	8.162226
H	6.645954	3.343658	8.906356
C	8.482249	2.257004	0.413633
C	8.005581	3.228297	-0.484967
H	8.387267	4.253250	-0.435246
C	7.072690	2.884687	-1.460367
H	6.717745	3.645524	-2.159358
C	6.607111	1.570812	-1.557607
H	5.881186	1.299537	-2.327906
C	7.084661	0.603799	-0.677625
H	6.734922	-0.427869	-0.761619
C	8.018309	0.941092	0.306861
H	8.394497	0.165016	0.976104
C	11.099542	3.415639	0.664048
C	11.371202	2.762912	-0.549653
H	10.723785	1.955384	-0.900604
C	12.473067	3.138446	-1.314764
H	12.681547	2.620985	-2.253646
C	13.303458	4.173984	-0.886546
H	14.160891	4.474849	-1.493015
C	13.034116	4.827100	0.314310
H	13.680318	5.638938	0.655649
C	11.940418	4.450304	1.090292
H	11.746954	4.958264	2.033480
C	10.341422	1.275127	2.463692
C	9.509067	0.507261	3.291898

H	8.471958	0.807842	3.459726
C	9.998804	-0.639091	3.913877
H	9.341847	-1.232563	4.554352
C	11.323442	-1.032229	3.717237
H	11.708101	-1.930277	4.206055
C	12.152976	-0.275306	2.893231
H	13.186942	-0.583911	2.722507
C	11.669940	0.876207	2.273277
H	12.333565	1.465653	1.638332
C	8.491109	6.126719	6.661522
C	9.631709	5.502006	7.185710
H	10.332895	4.994945	6.519444
C	9.888562	5.547311	8.555517
H	10.780315	5.057602	8.956033
C	9.025659	6.233001	9.409340
H	9.245365	6.291538	10.478341
C	7.893288	6.860886	8.890581
H	7.216925	7.405550	9.553187
C	7.622775	6.810662	7.524276
H	6.740182	7.321718	7.133931
C	9.289214	7.794266	4.567865
C	10.653792	7.719461	4.268228
H	11.119997	6.751826	4.073996
C	11.418968	8.882381	4.224027
H	12.482352	8.817441	3.983035
C	10.834492	10.123835	4.470779
H	11.438700	11.032690	4.425251
C	9.478163	10.200762	4.781539
H	9.011349	11.165387	4.994135
C	8.709201	9.041326	4.840424
H	7.654632	9.118210	5.112932
C	6.573343	6.671937	4.489729
C	5.551956	5.981416	5.160527
H	5.799283	5.258192	5.944073
C	4.217552	6.223912	4.831456
H	3.428655	5.698266	5.373762
C	3.892951	7.135492	3.826558
H	2.847974	7.337127	3.577475
C	4.908609	7.793524	3.133041
H	4.659611	8.502934	2.340152
C	6.243948	7.560842	3.455735
H	7.030323	8.077577	2.902383
H	6.875658	4.616628	1.550257

Table S8 Gas phase optimized coordinates of **2** with singlet spin state ($S_t = 0$)

Ru	4.70681784383439	5.59062682697660	1.75657611642564
Cl	4.52149020146035	6.86588725908091	-0.31713115005719
Cl	2.54251176177625	4.55790100090957	1.42900656079347
P	3.76531167904365	7.39456545653202	2.89945507082115
N	5.35846172570451	4.53277795468964	3.37506035039004
O	5.59409130353300	5.57542688262527	5.93016638809975
N	6.52529691976597	6.17869218009257	1.88160983133057
H	6.94223968514090	6.83718281876729	1.21538433775376
C	4.09073658811383	2.49879218104683	3.44420148511942
H	4.34474544744497	2.39952852710289	2.38796489251583
C	5.10253501963752	8.61586429338609	3.20257366636322
C	6.67767613918817	4.59260951050147	3.55705395544390
N	4.66822457605594	4.89797629141735	6.32290771703466
C	2.43004653300940	8.35355176797603	2.07042807184523
C	3.33112936749147	1.53448718221517	4.08564672339229
H	2.97234646441826	0.64701447554419	3.56384678874207
O	1.96456541688450	-0.31943651080280	5.52000805835130
C	2.94282906739044	7.08691042704683	4.51642745152041
C	4.23219744348685	3.77096143053968	5.48532981901068
C	4.58375692061450	3.62893091342599	4.12282188054521
C	7.45949617132214	3.82625145457593	4.46966378533759
H	6.97922119040158	3.06946187184927	5.09110122731401
C	7.34529501010065	5.55569370827733	2.71047567814171
C	3.01642356539515	1.71219747244788	5.43100035111212
C	1.69819090110386	7.82436078658813	1.00369030450586
H	1.95648409536764	6.84284304950996	0.60543732118471
C	2.01062589122691	6.03984117220550	4.57356253928647
H	1.88098195535505	5.38155392427987	3.70761937352774
C	3.43776320989250	2.82726122452848	6.13095315763283
H	3.16050388779050	2.96863890642478	7.17428426147905
N	2.23432335817449	0.68710320257134	6.13563316858372
C	3.08703106638410	7.94017222983513	5.61844019793376
H	3.80324974063584	8.76447713848357	5.58945866528057
O	4.09356429863476	5.06554539769902	7.37302646823440
C	6.03672920842666	8.39828673079863	4.22845935335999
H	5.90094549827661	7.57623077539902	4.93650142058064
C	5.32309377618686	9.65456349893208	2.28743018180075
H	4.61439273513547	9.82624334085785	1.47384124796704
C	8.80485581916963	4.06331678869870	4.56193840806545
H	9.40379424413218	3.48252287272710	5.26744609557114
C	1.23594145797876	5.85523215501248	5.71809503563420
H	0.50999953913079	5.03842165601559	5.75205977239291
C	8.74884663951378	5.77337589899763	2.83512428882038
H	9.22890937748717	6.51114327481284	2.18907250393799
C	0.61839867022098	8.53363916654957	0.47609060238969
H	0.05460467667754	8.10475187234730	-0.35591265003519
C	2.05551191111274	9.59265529371253	2.61353228432270
H	2.60380443837432	10.01031121960615	3.46243404365410
C	9.45439023075786	5.04910011904407	3.75584176883061
H	10.52626412920799	5.21744439278415	3.88302469561378
C	2.31833585919114	7.73964484606545	6.76425799406516
H	2.45569198220081	8.39824528403332	7.62542904419926
C	1.38936948671067	6.70090770164883	6.81524628007742

H	0.79365461487126	6.53944811641511	7.71690617316047
C	0.25598662252942	9.76611599774704	1.01127169032198
H	-0.59177015737271	10.31739735498782	0.59681679192040
C	0.97479035573715	10.29337875920442	2.08578157095601
H	0.68340516943401	11.25101664068516	2.52374006658369
C	7.15719837349247	9.22049926121461	4.34401988156298
H	7.87397111452539	9.03746260040286	5.14876279901462
C	6.45008466815643	10.46915285752071	2.40500971490403
H	6.61177355200875	11.27560959263397	1.68532254122962
O	1.92262402473909	0.91042433294241	7.28330128092829
C	7.36968130936328	10.25476048772989	3.43127195123592
H	8.25286741062274	10.89242428301177	3.51943215874292
Ru	5.39708658842736	5.04971510798920	-1.75658123853167
Cl	5.58262068397481	3.77467863143329	0.31709974309512
Cl	7.56109931067211	6.08316262512423	-1.42950709403085
P	6.33863695710965	3.24538671685581	-2.89896887569538
N	4.74502719364262	6.10693635574447	-3.37535823198152
O	4.51007946234094	5.06232272970543	-5.92999672625170
N	3.57868521938625	4.46128800664852	-1.88134040872932
H	3.16190804100276	3.80297428227518	-1.21483673370846
C	6.01272563815189	8.14076081344740	-3.44538282424387
H	5.75902962209892	8.24018389625914	-2.38908426958682
C	5.00195984510797	2.02309658725537	-3.20072465111235
C	3.42582663993573	6.04672249551244	-3.55731359039098
N	5.43469888420447	5.74094867978666	-6.32363226442137
C	7.67499954767276	2.28739055567953	-2.07041743444826
C	6.77210157287252	9.10496832957866	-4.08722149654514
H	7.13103568691598	9.99253757519816	-3.56568453854190
O	8.13723617514393	10.95912529764858	-5.52258318728677
C	7.16034198636398	3.55274512616183	-4.51638268977446
C	5.87068920902216	6.86817897267052	-5.48628111286901
C	5.51950059887793	7.01049389317719	-4.12366242918613
C	2.64382210892762	6.81249217217346	-4.47026329226961
H	3.12390973475414	7.56917134948805	-5.09198006475590
C	2.75848794875628	5.08376675373096	-2.71038918786243
C	7.08641657667286	8.92701631184324	-5.43262763660630
C	8.40660508379700	2.81680463736433	-1.00362651561442
H	8.14760176435858	3.79794576084303	-0.60492907932713
C	8.09085447095153	4.60125852370621	-4.57455868509705
H	8.21941745679489	5.26065103971806	-3.70928931624423
C	6.66490962372806	7.81182598681848	-6.13227267644719
H	6.94193120281032	7.67024564581823	-7.17564282624972
N	7.86821559597890	9.95205006650046	-6.13766976743138
C	7.01744877841386	2.69819326240521	-5.61755707108760
H	6.30260142295392	1.87273512999772	-5.58771484390348
O	6.00814297748475	5.57440641099583	-7.37458705713116
C	4.06727456342261	2.23891707866582	-4.22650063874721
H	4.20203757229399	3.06061317430813	-4.93518470633013
C	4.78265701397327	0.98488930777795	-2.28467423886969
H	5.49166495140506	0.81452262061344	-1.47107742888566
C	1.29853927025237	6.57497047018721	-4.56250914994666
H	0.69945362350805	7.15525729228102	-5.26830792740506
C	8.86521684089434	4.78598898241506	-5.71929779364079
H	9.58985617555968	5.60392020551712	-5.75409104704101
C	1.35499147772264	4.86568466357098	-2.83492179462286
H	0.87510385328592	4.12811676094525	-2.18851030617519

C	9.48716319548138	2.10826995124249	-0.47655888987518
H	10.05077353388648	2.53733337114621	0.35547285011952
C	8.05074031026461	1.04897927785818	-2.61427817994400
H	7.50280257174565	0.63128270327798	-3.46338930992707
C	0.64928235058879	5.58934903576341	-3.75599707453898
H	-0.42254519046201	5.42067275750388	-3.88311205367036
C	7.78583733677655	2.89879388846805	-6.76357376972878
H	7.64954653357432	2.23912212598251	-7.62409207230980
C	8.71315440584541	3.93895564455059	-6.81559002263727
H	9.30859865925176	4.10047225349201	-7.71741708506057
C	9.85063414192611	0.87638194606210	-1.01236173881786
H	10.69900069775765	0.32571727065799	-0.59833636025569
C	9.13216429748969	0.34898001356106	-2.08702924986719
H	9.42439752002225	-0.60813328778761	-2.52556800937693
C	2.94766487329638	1.41540176844226	-4.34118851734966
H	2.23056664411680	1.59701355203706	-5.14597452895600
C	3.65647532938318	0.16906870008248	-2.40133202574073
H	3.49575977466683	-0.63699342792267	-1.68097592501166
O	8.18036932832135	9.72818795541208	-7.28510527845177
C	2.73648662083239	0.38159856649879	-3.42763585856642
H	1.85396692983283	-0.25709393305055	-3.51514730089782

Table S9 Gas phase optimized coordinates of **3** with doublet spin state (S_t = ½)

C	7.067443	4.188663	10.872968
Cl	9.442470	3.322487	14.214387
N	5.561273	4.549198	12.625786
P	6.695131	1.689800	14.224674
Ru	7.198814	3.872982	13.628341
C	7.473601	4.323388	9.517134
Cl	6.578054	4.620605	15.872910
N	4.233276	5.784419	14.100587
O	4.079585	2.578526	11.406802
P	7.625313	7.997641	16.212201
Ru	5.965586	6.826062	15.064977
C	6.728119	5.104631	8.674585
Cl	7.734187	6.298662	13.456360
N	3.124463	3.311756	11.508420
O	2.131445	3.260239	10.816515
C	5.552709	5.758929	9.141496
Cl	4.688924	7.029824	16.994288
C	5.110330	5.617612	10.433831
Cl	5.173842	8.697741	13.948831
C	5.852021	4.811423	11.339641
C	4.306335	4.882187	13.107826
C	3.123308	4.336530	12.562920
C	1.879129	4.752940	13.016369
C	1.832890	5.705665	14.020245
C	3.031580	6.189711	14.530055
C	7.108430	1.143637	15.939554
C	8.069335	1.783920	16.728858
C	8.386761	1.278611	17.990104
C	7.747594	0.143909	18.480901
C	6.771024	-0.486076	17.708683
C	6.452062	0.010080	16.448307
C	4.900144	1.270941	14.202384
C	4.349755	0.171914	13.533918
C	2.996910	-0.137409	13.679844
C	2.186349	0.635659	14.508264
C	2.727907	1.736168	15.173553
C	4.073074	2.060469	15.015589
C	7.512588	0.437464	13.167960
C	7.113490	0.254786	11.834995
C	7.736766	-0.711496	11.046263
C	8.785893	-1.473593	11.562664
C	9.213229	-1.264150	12.871886
C	8.577229	-0.317361	13.673197
C	8.869033	8.977373	15.270321
C	10.116469	9.264396	15.843175
C	10.983983	10.164641	15.229630
C	10.617351	10.790667	14.038852
C	9.381435	10.505730	13.462961
C	8.510023	9.603948	14.072407
C	8.587742	6.810638	17.212507
C	8.110662	6.400937	18.465201
C	8.763124	5.386088	19.161072
C	9.887163	4.768844	18.610744

C	10.342859	5.147759	17.349719
C	9.690020	6.158304	16.647078
C	7.067115	9.312106	17.373588
C	5.956942	10.095575	17.037522
C	5.602372	11.183919	17.831520
C	6.345894	11.499823	18.967700
C	7.454626	10.724845	19.304949
C	7.819500	9.639733	18.508883
H	8.393656	3.837170	9.185000
H	7.052113	5.258197	7.642925
H	4.999089	6.403672	8.455249
H	4.225123	6.154536	10.778397
H	0.985882	4.317427	12.566510
H	0.888258	6.080731	14.415922
H	3.045719	6.931824	15.330784
H	8.584759	2.666321	16.348080
H	9.141489	1.789668	18.592039
H	8.010549	-0.252086	19.465083
H	6.249694	-1.367418	18.089909
H	5.682684	-0.491878	15.857842
H	4.976714	-0.464185	12.906957
H	2.579519	-0.997593	13.150750
H	1.135295	0.370795	14.649324
H	2.100732	2.344589	15.829391
H	4.493901	2.916489	15.552138
H	6.299646	0.854586	11.416985
H	7.392437	-0.878061	10.022380
H	9.273477	-2.227401	10.939663
H	10.042579	-1.846099	13.281177
H	8.912157	-0.162255	14.700334
H	10.412552	8.790815	16.781382
H	11.948115	10.388796	15.692877
H	11.297144	11.501865	13.562754
H	9.082354	10.993389	12.532145
H	7.533211	9.403940	13.628678
H	7.216267	6.864677	18.888287
H	8.378739	5.063290	20.131712
H	10.403464	3.979901	19.164439
H	11.191843	4.638227	16.889372
H	10.031061	6.420258	15.644674
H	5.373463	9.854296	16.146792
H	4.735047	11.788738	17.555878
H	6.060991	12.350988	19.591284
H	8.046072	10.968750	20.190816
H	8.694821	9.045204	18.780723
N	7.707910	3.526057	11.828633
H	8.540836	2.987650	11.578809

Table S10 Optimized coordinates of **3** with doublet spin state in CH_2Cl_2 solution (S_t = ½)

C	6.986780	4.171915	10.868888
Cl	9.431804	3.367073	14.209146
N	5.512837	4.547994	12.645643
P	6.684347	1.678458	14.197963
Ru	7.164908	3.872645	13.623229
C	7.367202	4.286115	9.501143
Cl	6.560828	4.638722	15.878499
N	4.214210	5.809681	14.133681
O	3.993259	2.594899	11.453276
P	7.646329	8.000889	16.229006
Ru	5.960601	6.841902	15.086222
C	6.604918	5.058099	8.667092
Cl	7.690505	6.317660	13.447808
N	3.053935	3.347754	11.562855
O	2.062684	3.318142	10.864587
C	5.436545	5.720163	9.151251
Cl	4.707947	7.062845	17.040135
C	5.017718	5.597265	10.452989
Cl	5.172337	8.734644	13.982588
C	5.779565	4.802044	11.354472
C	4.266438	4.898885	13.147212
C	3.070775	4.363609	12.621276
C	1.834249	4.787449	13.089262
C	1.808731	5.745034	14.088887
C	3.017461	6.224595	14.574376
C	7.062307	1.160105	15.931027
C	8.019612	1.805406	16.722666
C	8.319248	1.320181	17.996970
C	7.663951	0.198133	18.499570
C	6.692117	-0.437796	17.724756
C	6.392528	0.038988	16.450661
C	4.905107	1.216757	14.115993
C	4.405825	0.100744	13.435259
C	3.052389	-0.230473	13.523151
C	2.192342	0.535582	14.307916
C	2.684816	1.649118	14.990741
C	4.030550	1.994956	14.889119
C	7.576727	0.447054	13.178481
C	7.216729	0.232109	11.839125
C	7.891637	-0.722229	11.077905
C	8.951997	-1.443023	11.631361
C	9.339085	-1.203906	12.949245
C	8.651069	-0.268219	13.721931
C	8.892704	8.967635	15.275618
C	10.151035	9.238367	15.834685
C	11.022963	10.129369	15.210858
C	10.650669	10.762384	14.024296
C	9.402654	10.495566	13.462665
C	8.527518	9.603925	14.083511
C	8.599466	6.808024	17.230414
C	8.126941	6.411379	18.489546
C	8.772583	5.393599	19.188883
C	9.888914	4.761948	18.637085

C	10.344584	5.133750	17.373313
C	9.696033	6.144905	16.666765
C	7.110544	9.327939	17.388491
C	6.007500	10.126480	17.059914
C	5.672760	11.223377	17.852864
C	6.432654	11.534238	18.981472
C	7.535786	10.745758	19.310650
C	7.879794	9.652105	18.514707
H	8.278059	3.790811	9.158000
H	6.904029	5.197166	7.625880
H	4.866903	6.351748	8.465740
H	4.131309	6.131589	10.799831
H	0.925490	4.358551	12.665063
H	0.872070	6.125562	14.497233
H	3.036694	6.975895	15.364445
H	8.545014	2.678970	16.335040
H	9.072529	1.832018	18.600780
H	7.912450	-0.183771	19.493050
H	6.161109	-1.310441	18.112913
H	5.629728	-0.472121	15.859379
H	5.068255	-0.532818	12.843508
H	2.673975	-1.103384	12.985298
H	1.139043	0.257849	14.398919
H	2.016673	2.251272	15.610986
H	4.410544	2.864043	15.434986
H	6.393132	0.793569	11.389456
H	7.576996	-0.913000	10.048788
H	9.478878	-2.189020	11.031179
H	10.173244	-1.756708	13.388394
H	8.954579	-0.095450	14.756305
H	10.455392	8.763612	16.769765
H	11.995253	10.339855	15.663440
H	11.334558	11.464474	13.540545
H	9.098773	10.988809	12.536117
H	7.542355	9.420501	13.651669
H	7.245723	6.891062	18.922359
H	8.392946	5.083314	20.165635
H	10.399468	3.970914	19.192831
H	11.194471	4.620266	16.918487
H	10.041211	6.403153	15.665050
H	5.412739	9.890977	16.175307
H	4.811240	11.839516	17.583097
H	6.165093	12.391657	19.604214
H	8.140275	10.985564	20.188857
H	8.752926	9.051901	18.781234
N	7.646533	3.518344	11.814117
H	8.464335	2.971326	11.532001

Table S11 Gas phase optimized coordinates of **3**$^{-}$ with singlet spin state (S_t = 0)

C	7.03511159242563	4.17917764518490	10.84920671161191
Cl	9.48138653582702	3.31754066013447	14.18751012876083
N	5.55619913057758	4.54453750096798	12.62703227917708
P	6.69733343429905	1.69495505446149	14.20927028840674
Ru	7.20663676585747	3.87583570372326	13.60270938983602
C	7.41754753190915	4.30570477113941	9.48560449600127
Cl	6.61147753480135	4.62881702361854	15.84074041421602
N	4.25821285290628	5.80619168318382	14.11089907996836
O	4.02808035092900	2.58910915483186	11.43508513025095
P	7.60034098685282	7.93192028754924	16.21969118959727
Ru	5.95846930645660	6.81498854602449	15.06964503437195
C	6.66165365535149	5.08983018844617	8.65182272242102
Cl	7.71869962442516	6.28481749844395	13.38631616074004
N	3.10236410364732	3.36296062063389	11.52158140742773
O	2.12569646506665	3.34370685434669	10.79852519954051
C	5.49858934954809	5.75238817179982	9.13765821880705
Cl	4.60648028737988	7.07295293518804	17.05227390538524
C	5.07850056115766	5.61605313450240	10.43992541328630
Cl	5.06535721964006	8.77245383289039	13.96663162104497
C	5.83175414193106	4.80841491267389	11.33653678865089
C	4.30964696469099	4.89896927521245	13.12132617508013
C	3.11412689729921	4.38119981923854	12.57221396176895
C	1.87486974969466	4.82289762352509	13.01748542639465
C	1.84998090759721	5.77932004050077	14.01886853955492
C	3.05768778710627	6.23773489855494	14.52983226078119
C	7.09441285878910	1.16219819887272	15.93576632657763
C	8.04679593454902	1.81632446721254	16.72563520969753
C	8.35942795260125	1.32805809918010	17.99585576370831
C	7.72031966988830	0.19611563318096	18.49757608237174
C	6.75154467793689	-0.44770841438109	17.72533632606982
C	6.44069303869499	0.03183193177072	16.45479476766774
C	4.90887146310728	1.25230058509452	14.16255167724260
C	4.38312467869691	0.13048170932639	13.51171815700605
C	3.02662409817058	-0.18012019033051	13.62471663120115
C	2.18814826399496	0.61412871314928	14.40512509175427
C	2.70604488877341	1.73565446819506	15.05529457869418
C	4.05488290051140	2.06058943300745	14.92787821074557
C	7.54408671975092	0.43064560270445	13.18649204401182
C	7.16542635714731	0.22126713648369	11.85155354480682
C	7.80862237698339	-0.75044676529056	11.08457443912089
C	8.85909107716144	-1.49446769354621	11.62609613633572
C	9.26748490584584	-1.26008085235727	12.93842452273303
C	8.60983051197236	-0.30693429006627	13.71637664760162
C	8.85018561422491	8.94733038867356	15.29966163594886
C	10.11657875961802	9.23312566938150	15.83002074089134
C	10.95837863905167	10.15115562757002	15.20159584740681
C	10.54613823342787	10.79837579517433	14.03567662795256
C	9.28860042536998	10.51798132844856	13.50116284997030
C	8.44597690179034	9.59811431658579	14.12743715161771
C	8.60067045280155	6.77517821478026	17.23438132944587
C	8.13969582338439	6.36984944403157	18.49452790752337
C	8.80309102407694	5.36580558269043	19.19835013106261
C	9.92894721842683	4.74967134542198	18.64816780893757

C	10.37263979611192	5.12463321942968	17.38075713691714
C	9.70544216175547	6.12373288948856	16.67366547056648
C	7.09553401576743	9.27165344436439	17.39468380777343
C	5.99432248760023	10.06659735048539	17.05042965907951
C	5.65303322728340	11.17343211417457	17.82745198418937
C	6.40073870076894	11.49650537798204	18.96152453084972
C	7.50064234736850	10.71090300479934	19.30844379993551
C	7.85180024447392	9.60931502660724	18.52469461483970
H	8.32673699614173	3.80846604957350	9.13954411305468
H	6.96768494504966	5.23640337232995	7.61335849199257
H	4.93453465330349	6.39718513401925	8.45958121740379
H	4.19689210169034	6.15388200937053	10.79340751350195
H	0.96774366477517	4.40700379473237	12.57766726060275
H	0.91225255204682	6.17410664224529	14.41198361596008
H	3.08928447374127	6.97918379625449	15.33011662323968
H	8.55291132874709	2.70233837796673	16.34036919836045
H	9.10736157213027	1.84907571451512	18.59864747396538
H	7.97784883176368	-0.18628383140902	19.48871986816853
H	6.23123950695604	-1.32705066308652	18.11322276901259
H	5.67943207867985	-0.48344843293128	15.86477204699149
H	5.02876588380655	-0.52250505490782	12.92195523971658
H	2.62819437827270	-1.05769573923021	13.10904012255892
H	1.13243636495477	0.35310196848545	14.51694067416736
H	2.05439320786499	2.36376084141447	15.66754184087884
H	4.45617258163925	2.93991956949456	15.44151963745873
H	6.35157647940372	0.80447997137242	11.41177864465407
H	7.47846729279744	-0.93531052809155	10.05911437931888
H	9.36172215138597	-2.25344415802912	11.02128499607364
H	10.09543094348460	-1.82929362269188	13.36862672981392
H	8.93018203786297	-0.13618877051946	14.74591344698260
H	10.44949070799377	8.74721876405601	16.75008972026661
H	11.93736743823843	10.37383051200629	15.63467651221493
H	11.20519289001055	11.52155441087185	13.54777027618715
H	8.95309327147142	11.02413862934826	12.59195860926007
H	7.44680622364080	9.40193203624982	13.72790131949199
H	7.24510250826061	6.83177252288278	18.92028929382279
H	8.42810648434090	5.05096403185548	20.17597703199732
H	10.45290101345973	3.96774483305848	19.20492009419708
H	11.22592948025772	4.61954023793202	16.92207573434768
H	10.03792157156543	6.38008367476213	15.66684584280132
H	5.41541135770317	9.81154497589391	16.15828719929583
H	4.79483368966149	11.78861952267947	17.54295319835623
H	6.12719937277190	12.36067013151649	19.57283974511448
H	8.09684778651071	10.96057075905473	20.19014821020801
H	8.72396048086600	9.01247996484079	18.80312599634604
N	7.68979064021291	3.51038082426213	11.79315306180511
H	8.49877323128086	2.95387927878043	11.50808510507373

Table S12 Gas phase optimized coordinates of $\mathbf{3}^{2-}$ with doublet spin state (S_t = ½)

C	7.161424	4.009076	10.847645
Cl	9.617768	3.301993	14.284051
N	5.657067	4.534277	12.596673
P	6.732332	1.769966	14.226462
Ru	7.330455	3.893708	13.666057
C	7.557595	4.042686	9.495383
Cl	6.670331	4.616733	15.923619
N	4.341600	5.738625	14.106100
O	4.094666	2.559822	11.384972
P	7.569325	7.940343	16.247984
Ru	5.995281	6.794464	15.116445
C	6.810548	4.752953	8.565550
Cl	7.794383	6.316367	13.430883
N	3.174603	3.346162	11.466277
O	2.171343	3.276499	10.769556
C	5.653720	5.432111	8.972666
Cl	4.605588	7.023245	17.090283
C	5.226633	5.378892	10.296971
Cl	5.062667	8.745798	14.015274
C	5.945471	4.644308	11.255875
C	4.431688	4.877105	13.053265
C	3.216920	4.409352	12.455414
C	1.979730	4.902587	12.860591
C	1.940274	5.814152	13.897411
C	3.146944	6.183687	14.495362
C	7.162342	1.128902	15.917821
C	8.121211	1.762112	16.715262
C	8.460082	1.227882	17.960040
C	7.840888	0.072732	18.429866
C	6.863478	-0.549988	17.651697
C	6.527504	-0.023621	16.406712
C	4.918230	1.388096	14.269321
C	4.310338	0.290932	13.648864
C	2.951484	0.033734	13.835080
C	2.186997	0.865235	14.651506
C	2.781951	1.972497	15.257757
C	4.134935	2.240429	15.062346
C	7.424704	0.447501	13.147756
C	7.002070	0.352040	11.812319
C	7.535217	-0.628733	10.976559
C	8.524074	-1.496687	11.443770
C	8.979985	-1.375538	12.755295
C	8.431276	-0.412062	13.601572
C	8.790754	9.023872	15.353599
C	10.038817	9.360602	15.893422
C	10.845141	10.318528	15.279548
C	10.412811	10.954369	14.115576
C	9.175930	10.617002	13.568318
C	8.368903	9.655972	14.178098
C	8.629981	6.824561	17.253838
C	8.188522	6.387364	18.510125
C	8.881427	5.388345	19.190617
C	10.011465	4.801920	18.617547

C	10.427686	5.198649	17.347863
C	9.734958	6.197154	16.665571
C	7.032032	9.262178	17.442509
C	5.897130	10.010125	17.101688
C	5.515305	11.099217	17.883024
C	6.244750	11.448689	19.020192
C	7.372230	10.705312	19.366788
C	7.766592	9.622685	18.577587
H	8.485566	3.539248	9.208472
H	7.148520	4.811431	7.526206
H	5.087699	6.028797	8.252332
H	4.343452	5.943539	10.602948
H	1.087679	4.529361	12.356853
H	1.004898	6.239452	14.264780
H	3.170663	6.873465	15.344054
H	8.615459	2.662412	16.343280
H	9.210446	1.740217	18.567754
H	8.117285	-0.342071	19.403969
H	6.352518	-1.445257	18.017616
H	5.756030	-0.513679	15.807560
H	4.898608	-0.375340	13.014225
H	2.489367	-0.822664	13.335661
H	1.127250	0.649562	14.817249
H	2.189836	2.645389	15.883056
H	4.598278	3.112871	15.537154
H	6.245295	1.044407	11.432124
H	7.173427	-0.710973	9.947946
H	8.946114	-2.257204	10.780574
H	9.768273	-2.035548	13.129023
H	8.793201	-0.321768	14.627394
H	10.381891	8.873551	16.809572
H	11.811392	10.580924	15.721356
H	11.042909	11.709682	13.635599
H	8.825076	11.108602	12.656540
H	7.383866	9.407326	13.766926
H	7.272341	6.807663	18.933694
H	8.513058	5.040071	20.159995
H	10.550284	4.011971	19.150217
H	11.260462	4.695538	16.851714
H	10.028337	6.454778	15.646297
H	5.328963	9.731519	16.206938
H	4.630721	11.676087	17.597830
H	5.934152	12.298838	19.635762
H	7.955427	10.972464	20.253384
H	8.657089	9.052301	18.854411
N	7.848278	3.445937	11.859627
H	8.710379	2.950465	11.642683