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Tracking the Role of *trans*–Ligands on Ruthenium–NO Bond Lability: A Computational Insight

Renato Pereira Orenha,[a*] Graziele Cappato Guerra Silva,[a] Ana Paula de Lima Batista,[b] Antonio Gustavo Sampaio de Oliveira Filho,[b] Nelson Henrique Morgon,[c] Vanessa Borges Silva,[a] Saulo Samuel Pereira Furtado,[a] Giovanni Finoto Caramori,[d] Maurício Jeomar Piotrowski[e] and Renato Luis Tame Parreira[a*]

Supplementary Material

[a.] *Núcleo de Pesquisas em Ciências Exatas e Tecnológicas, Universidade de Franca, Franca, SP, Brazil. E–mail: rpo9@hotmail.com / renato.parreira@unifran.edu.br*
[b.] *Departamento de Química, Faculdade de Filosofia, Ciências e Letras de Ribeirão Preto, Universidade de São Paulo, Ribeirão Preto, Brazil.*
[c.] *Instituto de Química, Universidade Estadual de Campinas, CP 6154, 13083–970, Campinas, SP, Brazil.*
[d.] *Departamento de Química, Universidade Federal de Santa Catarina, Campus Universitário Trindade, CP 476, Florianópolis, SC, 88040–900, Brazil.*
[e.] *Department of Physics, Federal University of Pelotas, P.O. Box 354, Pelotas, Brazil.*

Table S1. Optimized Cartesian coordinates of the compounds investigated in this paper from the ZORA–BP86/TZ2P computational model.

Complex		**1**[a]	
Atom	X	Y	Z
Ru	–0.085026	0.002717	0.002464
N	–2.267673	0.064570	–0.013198
N	–0.135188	1.540893	1.554798
N	–0.236956	–1.544638	–1.532433
N	–0.185492	–1.533109	1.554905
N	–0.101024	1.559741	–1.529820
H	–2.675688	0.894934	0.440770
H	–2.674358	0.063481	–0.960229
H	–2.722861	–0.732099	0.455870
H	–0.550732	2.434737	1.257399
H	–0.658476	1.269691	2.398953
H	0.800885	1.793851	1.901882
H	–1.021785	–2.196660	–1.395552
H	0.597634	–2.146362	–1.580251
H	–0.353464	–1.188139	–2.491311
H	0.581019	–1.449361	2.237863
H	–1.041847	–1.522671	2.125845
H	–0.111858	–2.497546	1.201721
H	0.419323	2.402719	–1.247790
H	–1.032942	1.902609	–1.800374
H	0.343496	1.271309	–2.412989
N	1.690556	–0.049421	–0.018076
O	2.826494	–0.082934	–0.043370
Complex		**1**[b]	
Atom	X	Y	Z
Ru	–0.081416	0.003218	0.004068
N	–2.256535	0.069335	–0.018520
N	–0.138628	1.534606	1.550045
N	–0.247069	–1.538820	–1.524292
N	–0.184749	–1.524947	1.551793
N	–0.097763	1.553974	–1.522772
H	–2.663777	0.898208	0.438412
H	–2.657835	0.074195	–0.967587
H	–2.715315	–0.729061	0.443527
H	–0.529167	2.436004	1.242464
H	–0.689323	1.270966	2.378807
H	0.793068	1.768258	1.920799
H	–0.980390	–2.235833	–1.334733
H	0.615514	–2.089832	–1.636807
H	–0.454185	–1.185467	–2.468669
H	0.523229	–1.385103	2.286422
H	–1.078515	–1.576176	2.059232

H	–0.016231	–2.480951	1.208827
H	0.458447	2.378668	–1.256372
H	–1.026881	1.926673	–1.760749
H	0.307775	1.251909	–2.419740
N	1.693982	–0.058180	–0.017960
O	2.829800	–0.103332	–0.049118

Complex		**1**[c]	
Atom	X	Y	Z
Ru	–0.078236	0.004288	0.004192
N	–2.253514	0.060360	–0.018099
N	–0.141958	1.534727	1.548366
N	–0.234752	–1.535988	–1.523666
N	–0.189399	–1.523536	1.549578
N	–0.102924	1.554501	–1.519969
H	–2.665741	0.891273	0.431594
H	–2.656383	0.054642	–0.966994
H	–2.708140	–0.736354	0.451946
H	–0.539693	2.433770	1.241588
H	–0.687805	1.269266	2.380228
H	0.789406	1.775395	1.916567
H	–0.998894	–2.207481	–1.363797
H	0.612543	–2.117088	–1.598990
H	–0.390481	–1.180450	–2.477572
H	0.584983	–1.453723	2.225441
H	–1.040256	–1.495667	2.128497
H	–0.137448	–2.489564	1.196279
H	0.442174	2.386442	–1.251529
H	–1.035873	1.916301	–1.761777
H	0.309506	1.258846	–2.416428
N	1.695018	–0.050369	–0.018086
O	2.831906	–0.091278	–0.050292

Complex		**1**[d]	
Atom	X	Y	Z
Ru	–0.068449	0.001317	0.002378
N	–2.245268	0.068379	–0.018268
N	–0.133086	1.526098	1.542908
N	–0.243131	–1.535863	–1.516397
N	–0.175675	–1.519910	1.545470
N	–0.098149	1.549031	–1.517556
H	–2.648797	0.889686	0.435680
H	–2.643320	0.075628	–0.959117
H	–2.702657	–0.722754	0.437742
H	–0.517036	2.419245	1.231727
H	–0.695903	1.264084	2.353219
H	0.778869	1.765478	1.935433

H	–1.002518	–2.195218	–1.341702
H	0.587017	–2.122824	–1.614128
H	–0.416114	–1.182665	–2.458229
H	0.522543	–1.395257	2.280445
H	–1.063897	–1.560788	2.046086
H	–0.021593	–2.470706	1.207032
H	0.446499	2.374439	–1.262297
H	–1.025457	1.911398	–1.741420
H	0.292529	1.258738	–2.415207
N	1.685475	–0.052531	–0.019886
O	2.792152	–0.086694	–0.046836

Complex		**2**	
Atom	X	Y	Z
Ru	–0.114258	–0.002586	–0.016504
N	–2.206383	0.056649	0.958824
N	0.870977	0.224873	1.896480
N	–1.037161	–0.237865	–1.989405
N	–0.087731	–2.169284	0.256690
N	–0.188927	2.170985	–0.215447
H	–2.205158	0.233974	1.969103
H	–2.821678	0.777919	0.565717
H	–2.737073	–0.814512	0.846606
H	0.665915	1.095446	2.400152
H	0.692917	–0.522324	2.577346
H	1.891655	0.226207	1.756102
H	–1.633921	–1.063935	–2.110046
H	–0.290779	–0.331999	–2.689441
H	–1.614829	0.547662	–2.309342
H	0.849469	–2.500103	0.514601
H	–0.713925	–2.531623	0.984154
H	–0.320757	–2.696788	–0.592310
H	0.703109	2.605185	0.049090
H	–0.901237	2.644208	0.351236
H	–0.350097	2.486483	–1.178688
N	1.568165	–0.046858	–0.766201
O	2.705425	–0.007157	–0.438285

Complex		**3**	
Atom	X	Y	Z
Ru	–0.112895	0.003045	0.014917
N	–2.071897	0.108903	0.101900
N	–0.307525	–1.837672	1.135508
N	–0.163032	1.860965	–1.094013
N	–0.339913	–1.071793	–1.850212
N	–0.105342	1.085993	1.888959
H	–1.224915	–1.832353	1.597801

H	–0.266863	–2.703401	0.585899
H	0.396810	–1.955654	1.872449
H	–1.082834	1.961390	–1.539293
H	0.535040	1.918483	–1.844110
H	–0.024421	2.710328	–0.534739
H	–0.124430	–2.074500	–1.811428
H	–1.315791	–0.993424	–2.160554
H	0.239550	–0.706204	–2.614207
H	0.472083	0.653647	2.618790
H	–1.069436	1.101632	2.244048
H	0.210698	2.061382	1.844216
H	–2.707980	–0.660135	–0.110899
H	–2.607453	0.974050	0.178664
N	1.684501	–0.095525	–0.055474
O	2.836252	–0.149679	–0.145519

Complex		**4**	
Atom	X	Y	Z
Ru	–0.107212	0.020503	0.025203
N	–2.167538	–0.028684	–0.016425
N	–0.116474	1.512275	1.599374
N	–0.023948	–1.469864	–1.509788
N	–0.362444	–1.526477	1.502904
N	–0.149194	1.560746	–1.483868
H	–0.397312	2.453864	1.309170
H	–0.737542	1.273750	2.378475
H	0.832203	1.598963	1.982183
H	–0.471902	–2.358400	–1.264593
H	0.969814	–1.673672	–1.693886
H	–0.444317	–1.194028	–2.402606
H	–0.011181	–1.320131	2.441997
H	–1.392641	–1.565392	1.532817
H	–0.000828	–2.455851	1.269277
H	0.213337	2.471136	–1.185671
H	–1.138515	1.684356	–1.728059
H	0.362003	1.333767	–2.342608
H	–2.745457	0.758285	0.288656
H	–2.695193	–0.507888	–0.748413
N	1.756153	–0.060010	0.016388
O	2.624915	–0.619552	–0.612802

Complex		**5**	
Atom	X	Y	Z
Ru	–0.059704	–0.014044	–0.030887
O	–2.200455	0.069923	–0.071006
N	–0.145557	1.519626	1.518418
N	–0.206609	–1.539893	–1.582775

N	–0.246362	–1.566769	1.481477
N	–0.067648	1.546454	–1.546696
H	–0.673964	2.359065	1.240066
H	–0.575447	1.207784	2.401086
H	0.781612	1.874905	1.793889
H	–0.822895	–2.326114	–1.330963
H	0.696944	–1.979897	–1.810395
H	–0.560980	–1.194758	–2.486329
H	0.182945	–1.330530	2.387427
H	–1.230611	–1.788056	1.689794
H	0.186537	–2.463267	1.217303
H	0.422512	2.407201	–1.264268
H	–1.023091	1.842664	–1.792579
H	0.377045	1.276855	–2.435746
H	–2.784422	0.540615	0.561851
H	–2.795477	–0.351011	–0.728155
N	1.691387	–0.081874	0.001661
O	2.827613	–0.125121	0.022401

Complex		**6**	
Atom	X	Y	Z
Ru	–0.066781	0.009608	0.005319
O	–2.406596	0.103684	–0.045640
N	–0.107839	1.532425	1.583849
N	–0.026274	–1.491324	–1.548017
N	–0.289845	–1.550994	1.499354
N	–0.100564	1.567421	–1.507686
H	–0.514121	2.436406	1.317243
H	–0.597960	1.264860	2.444951
H	0.856166	1.740091	1.870951
H	–0.497850	–2.373818	–1.317778
H	0.948080	–1.750721	–1.757903
H	–0.429500	–1.203291	–2.447259
H	0.125223	–1.309925	2.406308
H	–1.276815	–1.763284	1.685590
H	0.148845	–2.443206	1.244098
H	0.355639	2.436580	–1.208700
H	–1.059294	1.824676	–1.769402
H	0.373974	1.314778	–2.382111
H	–2.999755	0.661814	0.493566
H	–2.998898	–0.414867	–0.622127
N	1.752031	–0.071754	0.034645
O	2.650913	–0.628889	–0.490943

Complex		**7**	
Atom	X	Y	Z
Ru	–0.026689	0.025285	–0.243355

H	–0.202240	0.192135	–1.861279
N	–1.063251	1.923276	–0.181634
N	0.958711	–1.823064	–0.787431
N	–1.935678	–0.982649	–0.387259
N	1.830631	1.081524	–0.585114
H	–1.028306	2.386556	–1.096199
H	–2.059750	1.854460	0.053165
H	–0.674198	2.587688	0.496830
H	0.725361	–2.090059	–1.750008
H	0.704346	–2.620811	–0.194143
H	1.983481	–1.782221	–0.754484
H	–2.594983	–0.733658	0.358662
H	–2.400085	–0.757318	–1.273743
H	–1.876910	–2.006734	–0.360642
H	1.797793	2.081357	–0.356867
H	2.098549	1.035036	–1.574226
H	2.624368	0.711305	–0.050307
N	0.170176	–0.161158	1.569249
O	0.293446	–0.277294	2.703802

Complex		**8**	
Atom	X	Y	Z
Ru	–0.219711	0.004427	–0.228986
H	–0.892651	0.020904	–1.780833
N	1.685123	–0.119245	–1.202454
N	–2.124609	0.128258	0.793663
N	–0.172146	2.152541	–0.421656
N	–0.419162	–2.139750	–0.360665
H	1.796957	–0.944794	–1.798343
H	1.892817	0.673147	–1.817358
H	2.428873	–0.154727	–0.489900
H	–2.663528	0.969342	0.567238
H	–1.981273	0.130776	1.811599
H	–2.758463	–0.648624	0.584360
H	0.771102	2.553943	–0.421895
H	–0.608748	2.411396	–1.310362
H	–0.676093	2.651819	0.317310
H	0.471463	–2.646658	–0.334975
H	–0.872404	–2.373112	–1.248106
H	–0.986300	–2.555733	0.384085
N	0.762079	–0.030184	1.402813
O	1.916249	–0.095092	1.732135

Complex		**9**	
Atom	X	Y	Z
Ru	–0.089385	–0.003960	0.008050
C	–2.177085	0.099124	0.007353

N	–0.146228	1.544395	1.560257
N	–0.297474	–1.539180	–1.544182
N	–0.233617	–1.553299	1.554034
N	–0.079066	1.552151	–1.537978
H	–0.622834	2.408638	1.265482
H	–0.635877	1.252897	2.418290
H	0.787019	1.846711	1.873872
H	–0.855781	–2.352958	–1.249148
H	0.601718	–1.930878	–1.858439
H	–0.756920	–1.201272	–2.401886
H	0.267076	–1.304109	2.419135
H	–1.191635	–1.781167	1.854960
H	0.176437	–2.451995	1.261828
H	0.415584	2.406852	–1.244745
H	–1.009795	1.871839	–1.840992
H	0.396967	1.255568	–2.402064
N	1.711988	–0.092905	0.008583
O	2.841077	–0.148472	0.008826
O	–3.301893	0.154172	0.006977

Complex		**10**	
Atom	X	Y	Z
Ru	–0.202372	–0.039797	–0.041301
C	–2.178860	0.120467	0.026250
N	–0.048193	1.485709	1.495765
N	–0.259521	–1.581764	–1.588167
N	–0.281492	–1.591348	1.498034
N	–0.136998	1.500881	–1.591920
H	–0.466933	2.385557	1.233647
H	–0.510201	1.236079	2.377817
H	0.927736	1.695009	1.743140
H	–0.771822	–2.428145	–1.315646
H	0.686993	–1.891219	–1.842498
H	–0.704025	–1.280396	–2.462609
H	0.154864	–1.313371	2.384822
H	–1.231299	–1.892805	1.741284
H	0.216887	–2.443361	1.216255
H	0.284223	2.383567	–1.279768
H	–1.056544	1.753886	–1.969591
H	0.426246	1.212351	–2.400129
O	–3.290116	0.333550	0.188872
N	1.717618	–0.113234	–0.024576
O	2.657644	0.353604	0.490041

Complex		**11**	
Atom	X	Y	Z
Ru	–0.035253	–0.002487	0.002107

C	–2.047470	0.112451	0.016780
N	–0.119486	1.526645	1.539079
N	–0.315234	–1.511318	–1.531569
N	–0.292959	–1.525763	1.525194
N	–0.140543	1.540957	–1.519010
H	–1.068940	1.918333	1.579480
H	0.081903	1.185773	2.486089
H	0.520838	2.315512	1.393239
H	–1.303202	–1.793795	–1.556526
H	0.234716	–2.367124	–1.394700
H	–0.091873	–1.194924	–2.482143
H	0.314831	–1.417758	2.345270
H	–1.261545	–1.505061	1.868543
H	–0.134575	–2.484708	1.195170
H	0.134582	2.474887	–1.193951
H	–1.110918	1.633315	–1.845153
H	0.435706	1.362617	–2.349485
N	–3.215747	0.178751	0.024847
N	1.774030	–0.105208	–0.011086
O	2.917439	–0.169539	–0.019206

Complex		**12**	
Atom	X	Y	Z
Ru	–0.124312	–0.044787	–0.040966
C	–2.166061	0.161288	0.074592
N	0.033009	1.461214	1.481033
N	–0.297797	–1.564472	–1.576618
N	–0.327995	–1.557882	1.493916
N	–0.192895	1.503903	–1.552147
H	–0.399372	2.349684	1.209733
H	–0.442659	1.201755	2.350707
H	1.014470	1.657180	1.715882
H	–0.844052	–2.376205	–1.272849
H	0.621364	–1.911414	–1.874417
H	–0.780878	–1.229942	–2.415838
H	0.182136	–1.354012	2.358941
H	–1.321107	–1.635704	1.738491
H	–0.014963	–2.490300	1.208166
H	0.338623	2.347931	–1.317289
H	–1.170884	1.786701	–1.677569
H	0.155648	1.210748	–2.469542
N	–3.313651	0.356128	0.217862
N	1.762465	–0.122951	–0.035718
O	2.689860	0.389985	0.518122

Complex		**$[Ru(NH_3)_5]^{2+}$**	
Atom	X	Y	Z

Ru	–0.164119	0.005016	0.005174
N	–2.244691	0.072732	0.002525
N	–0.010906	1.526226	1.545795
N	–0.112008	–1.524556	–1.535960
N	–0.117297	–1.539187	1.530338
N	–0.004379	1.539915	–1.522831
H	–2.622171	1.018060	0.142099
H	–2.663758	–0.257327	–0.875668
H	–2.674730	–0.500735	0.738680
H	–0.444182	2.432063	1.328643
H	–0.402548	1.271674	2.460448
H	0.971808	1.756036	1.743732
H	–0.685381	–2.358269	–1.358744
H	0.840173	–1.891820	–1.662484
H	–0.390822	–1.217823	–2.475724
H	0.849911	–1.772842	1.790172
H	–0.568797	–1.303645	2.422660
H	–0.533000	–2.439848	1.263685
H	–0.229142	2.494238	–1.217078
H	–0.581167	1.400493	–2.361216
H	0.956949	1.608998	–1.881559
Complex		$[Ru(NH_2)(NH_3)_4]^+$	
Atom	X	Y	Z
Ru	–0.118113	0.007477	–0.000731
N	–2.122366	0.074969	0.250783
N	–0.305924	–1.809259	1.134555
N	–0.105549	1.855990	–1.088896
N	–0.300561	–1.075230	–1.843182
N	–0.127750	1.061746	1.873271
H	–1.279176	–1.762518	1.470453
H	–0.208080	–2.702514	0.640807
H	0.292565	–1.898867	1.961693
H	–1.074364	2.161025	–1.260536
H	0.339029	1.825668	–2.012937
H	0.351614	2.639509	–0.609290
H	0.045682	–2.040864	–1.818150
H	–1.295805	–1.141672	–2.101023
H	0.165054	–0.656367	–2.655681
H	0.436877	0.665652	2.631314
H	–1.115882	0.980376	2.156487
H	0.097936	2.061823	1.871359
H	–2.624963	–0.581253	–0.365761
H	–2.527906	0.987592	–0.006087
Complex		$[Ru(H_2O)(NH_3)_4]^{2+}$	
Atom	X	Y	Z

Ru	–0.126729	–0.003360	–0.039612
O	–2.228843	–0.022467	0.016157
N	–0.004463	1.498845	1.519900
N	–0.064647	–1.531086	–1.577722
N	–0.224677	–1.544640	1.468291
N	0.016474	1.545215	–1.555554
H	–0.315015	2.442009	1.257047
H	–0.530913	1.281529	2.374953
H	0.964464	1.628300	1.839979
H	–0.604582	–2.379569	–1.367901
H	0.894740	–1.867827	–1.733247
H	–0.388045	–1.241947	–2.508816
H	0.218471	–1.300967	2.362038
H	–1.196215	–1.783924	1.703372
H	0.217278	–2.432975	1.203530
H	0.551965	2.368018	–1.252475
H	–0.882887	1.922805	–1.877711
H	0.494118	1.240719	–2.412653
H	–2.699013	0.766990	0.350190
H	–2.719024	–0.305683	–0.780976

Complex		$[RuH(NH_3)_4]^+$	
Atom	X	Y	Z
Ru	–0.036168	0.034209	–0.334075
H	–0.204654	0.193900	–1.885477
N	–1.052075	1.915848	–0.051533
N	0.974971	–1.842731	–0.658210
N	–1.928220	–0.997643	–0.256716
N	1.850293	1.072223	–0.453615
H	–0.818321	2.566041	–0.808913
H	–2.075611	1.855304	–0.069815
H	–0.829859	2.405724	0.822693
H	0.560470	–2.341373	–1.452309
H	0.948375	–2.496056	0.133040
H	1.968039	–1.755410	–0.898544
H	–2.408422	–0.962086	0.649801
H	–2.581149	–0.599970	–0.939822
H	–1.881304	–1.994159	–0.494130
H	1.772962	2.094602	–0.474381
H	2.337746	0.832818	–1.323200
H	2.509534	0.870127	0.306768

Complex		$[Ru(CO)(NH_3)_4]^{2+}$	
Atom	X	Y	Z
Ru	–0.208522	0.001928	0.008062
C	–2.002920	0.090430	0.007295
N	–0.008345	1.514625	1.540105

N	–0.156973	–1.523135	–1.524100
N	–0.158615	–1.534785	1.528562
N	–0.005934	1.526011	–1.512340
H	–0.555887	2.363752	1.356220
H	–0.309403	1.215236	2.475075
H	0.961687	1.836222	1.660285
H	–0.779970	–2.317862	–1.337243
H	0.778443	–1.933352	–1.648889
H	–0.433664	–1.197142	–2.457695
H	0.787435	–1.702112	1.897123
H	–0.737164	–1.322222	2.349983
H	–0.490606	–2.454393	1.214655
H	–0.249292	2.473383	–1.199772
H	–0.599153	1.369595	–2.335907
H	0.953141	1.601515	–1.877478
O	–3.157432	0.147384	0.006861

Complex		$[Ru(CN)(NH_3)_4]^+$	
Atom	X	Y	Z
Ru	–0.208522	0.001928	0.008062
C	–2.002920	0.090430	0.007295
N	–0.008345	1.514625	1.540105
N	–0.156973	–1.523135	–1.524100
N	–0.158615	–1.534785	1.528562
N	–0.005934	1.526011	–1.512340
H	–0.555887	2.363752	1.356220
H	–0.309403	1.215236	2.475075
H	0.961687	1.836222	1.660285
H	–0.779970	–2.317862	–1.337243
H	0.778443	–1.933352	–1.648889
H	–0.433664	–1.197142	–2.457695
H	0.787435	–1.702112	1.897123
H	–0.737164	–1.322222	2.349983
H	–0.490606	–2.454393	1.214655
H	–0.249292	2.473383	–1.199772
H	–0.599153	1.369595	–2.335907
H	0.953141	1.601515	–1.877478
O	–3.157432	0.147384	0.006861

Complex		NO^+	
Atom	X	Y	Z
N	1.725484	–0.050451	–0.018854
O	2.795915	–0.082032	–0.042689

Complex		**NO**	
Atom	X	Y	Z
N	1.678268	–0.049059	–0.017802
O	2.837252	–0.083251	–0.043609

[a] Geometry optimized from the ZORA–BP86/TZ2P computational model; [b] Geometry optimized from the ZORA–BP86–D3BJ/TZ2P computational model; [c] Geometry optimized from the ZORA–PBE–D3BJ/TZ2P computational model; [d] Geometry optimized from the wB97XD/Def2–TZVP computational model.

Table S2. Theoretical and experimental geometric parameters to $[Ru(NO)(NH_3)_5]^{3+}$: **1** and $\mathbf{1_{EXP}}$, respectively.

Complex	$\mathbf{1}^{[a]}$	$\mathbf{1}^{[b]}$	$\mathbf{1}^{[c]}$	$\mathbf{1}^{[d]}$	$\mathbf{1_{EXP}}$	$\mathbf{1}^{[a]}-\mathbf{1_{EXP}}$	$\mathbf{1}^{[b]}-\mathbf{1_{EXP}}$	$\mathbf{1}^{[c]}-\mathbf{1_{EXP}}$	$\mathbf{1}^{[d]}-\mathbf{1_{EXP}}$	$(\mathbf{1}^{[a]}-\mathbf{1_{EXP}})/\mathbf{1_{EXP}}$ x 100%	$(\mathbf{1}^{[b]}-\mathbf{1_{EXP}})/\mathbf{1_{EXP}}$ x 100%	$(\mathbf{1}^{[c]}-\mathbf{1_{EXP}})/\mathbf{1_{EXP}}$ x 100%	$(\mathbf{1}^{[d]}-\mathbf{1_{EXP}})/\mathbf{1_{EXP}}$ x 100%
Bond distances [Å]													
Ru–NO	1.776	1.777	1.774	1.755	1.771	0.005	0.006	0.003	–0.016	0.282	0.316	0.183	–0.910
N–O	1.137	1.137	1.138	1.108	1.172	–0.035	–0.035	–0.034	–0.064	–2.986	–2.974	–2.894	–5.501
$Ru–NH_{3(trans)}$[e]	2.184	2.176	2.176	2.178	2.017	0.167	0.159	0.159	0.161	8.280	7.895	7.888	7.980
$Ru–NH_{3(cis)}$[f,g]	2.186	2.177	2.175	2.169	2.093	0.093	0.085	0.083	0.076	4.468	4.039	3.946	3.649
Bond angles [˚]													
Ru–N–O	179.4	179.1	179.1	179.3	172.9	6.5	6.2	6.2	6.4	3.8	3.6	3.6	3.7
$NH_{3(trans)}$–Ru–NO	178.9	179.3	178.7	178.7	175.4	3.5	3.9	3.3	3.3	2.0	2.2	1.9	1.9
$NH_{3(cis)}$–Ru–NO[g]	92.1	92.3	92.4	92.5	90.8	1.3	1.5	1.6	1.7	1.5	1.6	1.7	1.9
$NH_{3(trans)}$–Ru–$NH_{3(cis)}$[g]	87.9	87.7	87.7	87.5	89.3	–1.4	–1.5	–1.6	–1.8	–1.5	–1.7	–1.8	–2.0

[a] Geometry optimized from the ZORA–BP86/TZ2P computational model; [b] Geometry optimized from the ZORA–BP86–D3BJ/TZ2P computational model; [c] Geometry optimized from the ZORA–PBE–D3BJ/TZ2P computational model; [d] Geometry optimized from the wB97XD/Def2–TZVP computational model; [e] $Ru–L_{trans}$ is the Ru–L chemical bond in *trans* position in relation to Ru–NO bond. [f] $Ru–NH_{3(cis)}$ is the $Ru–NH_3$ chemical bond in *cis* position in relation to Ru–NO bond. [g] Average value.

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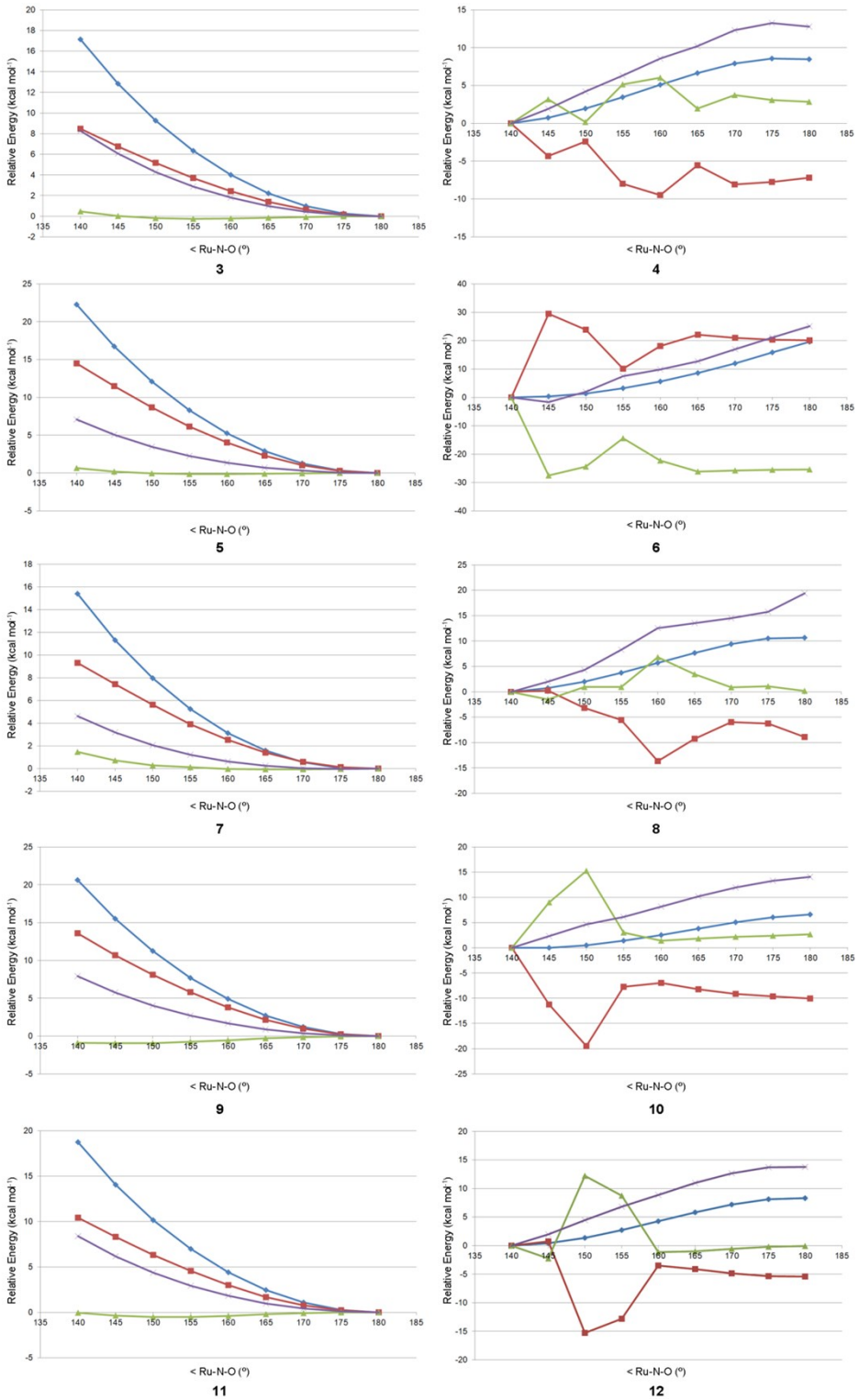

Figure S1. Relative values of the EDA components, obtained through of the change of the Ru–N–O bond angle from 140 to 180°, to **3**–**12**. Color code: $\Delta\Delta E_{int}$ (blue), $\Delta\Delta V_{elstat}$ (red), $\Delta\Delta E_{Pauli}$ (green) and $\Delta\Delta E_{oi}$ (purple).

Table S3. Relative values of the EDA components in the Ru–N–O angles (140–180°) of **1**–**8**.

		1					**3**		
<	$\Delta\Delta E_{int}$	$\Delta\Delta V_{elstat}$	$\Delta\Delta E_{Pauli}$	$\Delta\Delta E_{oi}$	<	$\Delta\Delta E_{int}$	$\Delta\Delta V_{elstat}$	$\Delta\Delta E_{Pauli}$	$\Delta\Delta E_{oi}$
140	20.68	12.85	0.26	7.57	140	17.14	8.46	0.45	8.25
145	15.46	10.19	–0.21	5.48	145	12.83	6.75	0.03	6.06
150	11.99	8.60	–0.22	3.61	150	9.26	5.16	–0.18	4.29
155	7.54	5.43	–0.45	2.56	155	6.33	3.70	–0.24	2.88
160	4.71	3.44	–0.30	1.58	160	4.00	2.43	–0.21	1.79
165	3.01	2.32	–0.05	0.75	165	2.22	1.39	–0.15	0.99
170	1.07	0.80	–0.12	0.39	170	0.98	0.63	–0.07	0.43
175	0.22	0.17	–0.05	0.10	175	0.25	0.16	–0.02	0.11
180	0.00	0.00	0.00	0.00	180	0.00	0.00	0.00	0.00
		2					**4**		
<	$\Delta\Delta E_{int}$	$\Delta\Delta V_{elstat}$	$\Delta\Delta E_{Pauli}$	$\Delta\Delta E_{oi}$	<	$\Delta\Delta E_{int}$	$\Delta\Delta V_{elstat}$	$\Delta\Delta E_{Pauli}$	$\Delta\Delta E_{oi}$
140	0.00	0.00	0.00	0.00	140	0.00	0.00	0.00	0.00
145	0.47	–13.73	10.42	3.78	145	0.74	–4.34	3.19	1.90
150	1.68	–16.82	11.54	6.96	150	1.93	–2.42	0.17	4.20
155	3.49	–13.24	6.91	9.81	155	3.45	–7.97	5.13	6.31
160	5.84	–10.55	3.34	13.05	160	5.07	–9.50	6.01	8.57
165	8.60	–7.14	–0.59	16.33	165	6.64	–5.54	1.97	10.22
170	11.56	–4.49	–3.49	19.54	170	7.90	–8.09	3.72	12.29
175	14.35	–4.64	–3.73	22.72	175	8.56	–7.75	3.06	13.26
180	15.63	–5.26	–3.73	24.62	180	8.45	–7.17	2.84	12.80
		5					**7**		
<	$\Delta\Delta E_{int}$	$\Delta\Delta V_{elstat}$	$\Delta\Delta E_{Pauli}$	$\Delta\Delta E_{oi}$	<	$\Delta\Delta E_{int}$	$\Delta\Delta V_{elstat}$	$\Delta\Delta E_{Pauli}$	$\Delta\Delta E_{oi}$
140	22.24	14.49	0.67	7.08	140	15.38	9.30	1.45	4.62
145	16.72	11.47	0.20	5.05	145	11.30	7.42	0.71	3.18
150	12.08	8.67	–0.05	3.46	150	7.95	5.62	0.26	2.06
155	8.28	6.15	–0.13	2.25	155	5.24	3.91	0.11	1.22
160	5.26	4.02	–0.13	1.36	160	3.12	2.52	–0.03	0.63
165	2.93	2.30	–0.09	0.72	165	1.57	1.40	–0.08	0.24
170	1.29	1.03	–0.05	0.31	170	0.55	0.60	–0.08	0.02
175	0.33	0.27	–0.01	0.07	175	0.03	0.12	–0.04	–0.05
180	0.00	0.00	0.00	0.00	180	0.00	0.00	0.00	0.00
		6					**8**		
<	$\Delta\Delta E_{int}$	$\Delta\Delta V_{elstat}$	$\Delta\Delta E_{Pauli}$	$\Delta\Delta E_{oi}$	<	$\Delta\Delta E_{int}$	$\Delta\Delta V_{elstat}$	$\Delta\Delta E_{Pauli}$	$\Delta\Delta E_{oi}$
140	0.00	0.00	0.00	0.00	140	0.00	0.00	0.00	0.00
145	0.30	29.47	–27.50	–1.67	145	0.71	0.26	–1.50	1.97
150	1.39	23.77	–24.35	1.98	150	2.00	–3.21	0.95	4.27
155	3.20	10.14	–14.46	7.51	155	3.72	–5.52	0.96	8.29
160	5.61	18.05	–22.27	9.83	160	5.68	–13.62	6.78	12.54
165	8.58	22.02	–26.19	12.74	165	7.66	–9.25	3.43	13.50
170	12.01	20.89	–25.80	16.92	170	9.42	–5.95	0.88	14.50
175	15.86	20.29	–25.56	21.13	175	10.54	–6.26	1.05	15.76
180	19.62	20.03	–25.43	25.02	180	10.62	–8.91	0.16	19.38

Table S4. Relative values of the EDA components in the Ru–N–O angles (140–180°) of **9**–**12**.

		9					**11**		
<	$\Delta\Delta E_{int}$	$\Delta\Delta V_{elstat}$	$\Delta\Delta E_{Pauli}$	$\Delta\Delta E_{oi}$	<	$\Delta\Delta E_{int}$	$\Delta\Delta V_{elstat}$	$\Delta\Delta E_{Pauli}$	$\Delta\Delta E_{oi}$
140	20.62	13.57	–0.88	7.93	140	18.72	10.41	–0.06	8.37
145	15.52	10.71	–0.95	5.77	145	14.06	8.29	–0.38	6.15
150	11.24	8.12	–0.93	4.05	150	10.15	6.32	–0.51	4.35
155	7.71	5.79	–0.77	2.70	155	6.96	4.55	–0.50	2.92
160	4.90	3.79	–0.56	1.67	160	4.41	3.01	–0.41	1.81
165	2.73	2.14	–0.29	0.89	165	2.46	1.67	–0.19	0.97
170	1.21	0.97	–0.14	0.39	170	1.09	0.76	–0.10	0.42
175	0.30	0.25	–0.04	0.09	175	0.28	0.21	–0.03	0.10
180	0.00	0.00	0.00	0.00	180	0.00	0.00	0.00	0.00
		10					**12**		
<	$\Delta\Delta E_{int}$	$\Delta\Delta V_{elstat}$	$\Delta\Delta E_{Pauli}$	$\Delta\Delta E_{oi}$	<	$\Delta\Delta E_{int}$	$\Delta\Delta V_{elstat}$	$\Delta\Delta E_{Pauli}$	$\Delta\Delta E_{oi}$
140	0.00	0.00	0.00	0.00	140	0.00	0.00	0.00	0.00
145	0.02	–11.26	8.98	2.30	145	0.43	0.71	–2.25	1.96
150	0.53	–19.44	15.28	4.68	150	1.38	–15.29	12.22	4.46
155	1.41	–7.71	3.01	6.10	155	2.69	–12.81	8.71	6.79
160	2.56	–6.97	1.38	8.15	160	4.24	–3.49	–1.12	8.84
165	3.82	–8.22	1.85	10.20	165	5.83	–4.13	–0.99	10.95
170	5.05	–9.10	2.18	11.97	170	7.21	–4.85	–0.59	12.65
175	6.06	–9.62	2.41	13.27	175	8.11	–5.37	–0.23	13.71
180	6.64	–10.08	2.65	14.07	180	8.28	–5.40	–0.07	13.75

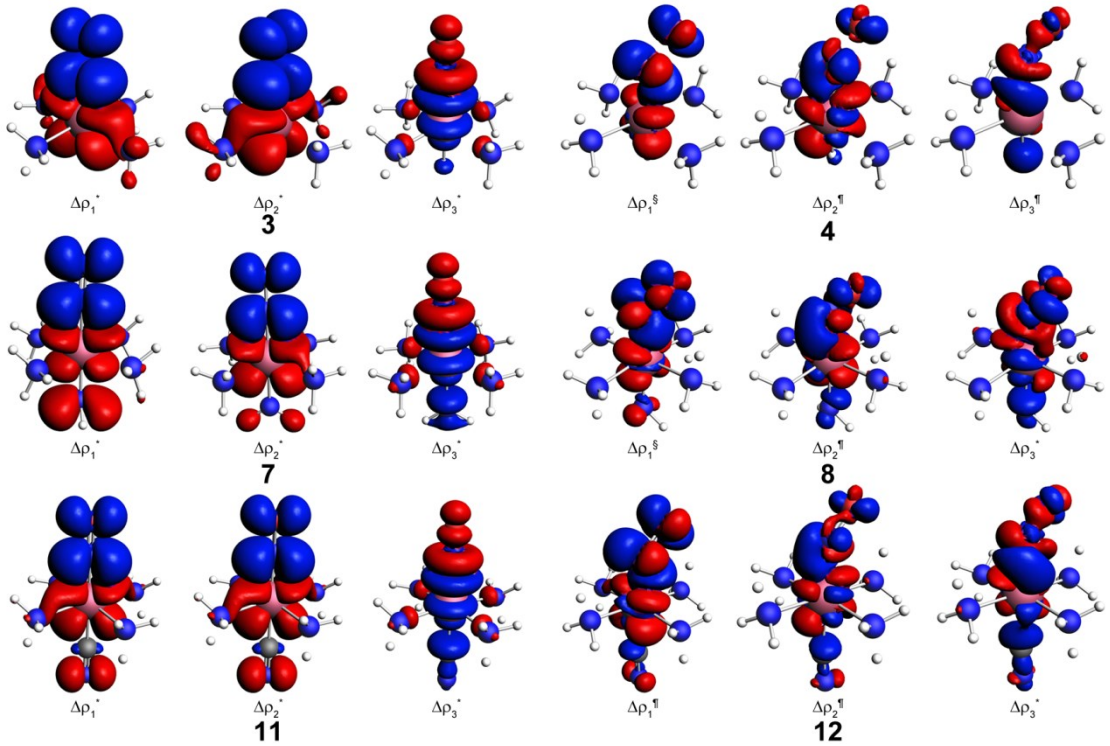

Figure S2. Selected density deformation channels surface plots, $\Delta\rho_i$, for interacting fragments: i) $[RuL_{trans}(NH_3)_4]^{2+}$ – NO^+ (**3**, **7** and **11**); and ii) $[RuL_{trans}(NH_3)_4]^{+}$ – NO^0 (**4**, **8** and **12**). Red and blue regions indicate the electronic density outflow and inflow, respectively. Choose contour values: *=0.001; ¶=0.002; §=0.005 a.u.

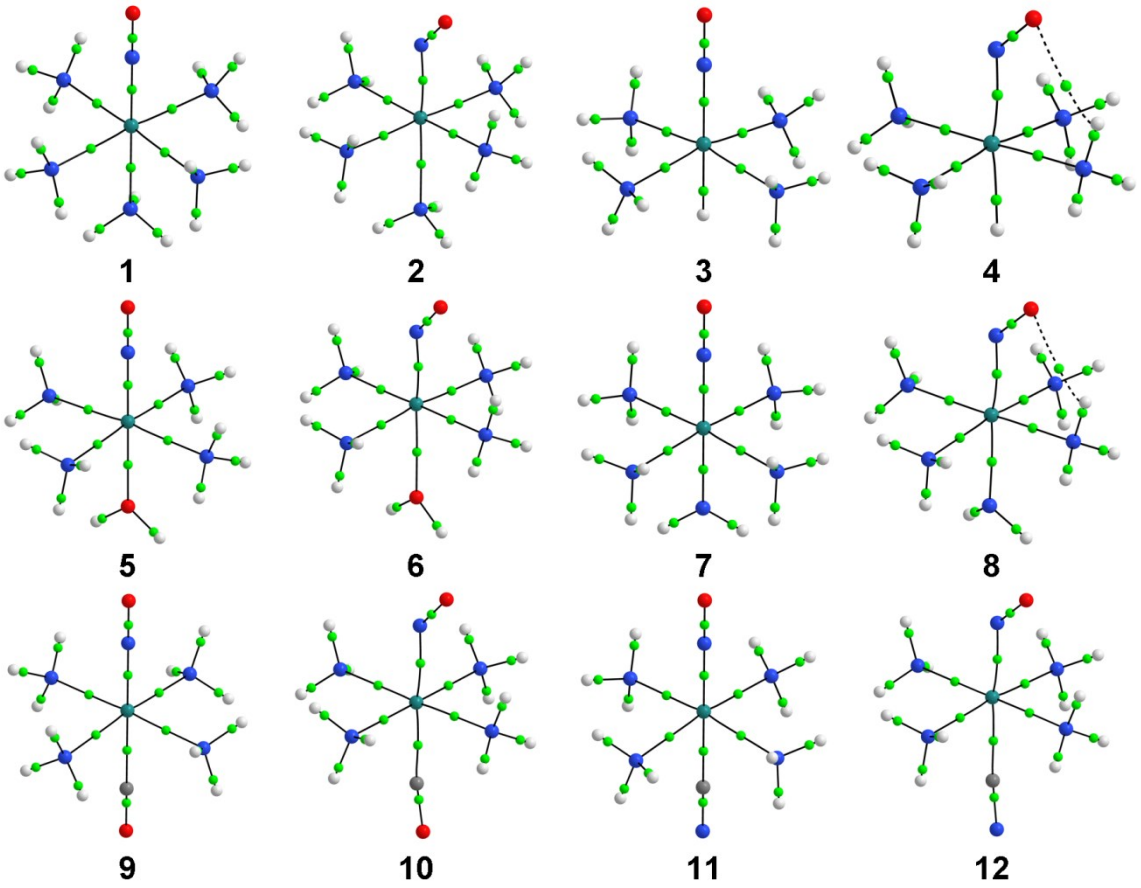

Figure S3. Topological map containing the bond paths (continuous or dashed lines connecting the cores) and bond critical points (small green points) for the structures studied in this paper. Atoms color: H (white), C (gray), N (blue), O (red) and Ru (turquoise).

Table S5. Density of total energy, H_b, and electron density, ρ_b, in the Ru–NO BCP of the compounds investigated. The values of all the parameters are in a.u.

Complex	H_b	ρ_b
1	–0.088	0.184
2	–0.081	0.174
3	–0.065	0.159
4[a]	–0.056	0.148
5	–0.101	0.196
6	–0.093	0.185
7	–0.076	0.171
8[b]	–0.070	0.163
9	–0.074	0.171
10	–0.047	0.138
11	–0.071	0.167
12	–0.059	0.152

[a] To compound **4**, there is one BCP related to N–H···O–N interaction with values of H_b and ρ_b equal to 0.003 and 0.014 a.u, respectively. [b] To compound **8**, there is one BCP related to N–H···O–N interaction with values of H_b and ρ_b equal to 0.003 and 0.015 a.u, respectively.