The Influence of L Ligands on the $\{RuNO\}^{6/7}$ Bonding Situation in *cis*-$[Ru(NO)(NO_2)L_{1-4}]^q$ Complexes: A Theoretical Insight

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Supporting Information

Table S1. Calculated vibrational frequencies (cm^{-1}), bond lengths (Å), angles (°) for isomers at GS (**1a-4a**) and at MS1(**1b-4b)**, prior reduction at BP86/TZVP level of theory.

Geometric			GS			MS1		
Parameters	**1a**	**2a**	**3a**	**4a**	**1b**	**2b**	**3b**	**4b**
Symmetry	C_1	C_1	C_1	C_1	C_1	C_1	C_1	C_1
ν_a(NO)	1978	1930	1946[b]	1945	1847	1836	1857	1854
ν_a(NO_2)	1521	1519	1508[b]	1505	1492	1484	1477	1473
N(1)–O(1)	1.143	1.151	1.149[b]/*1.130*[a]	1.149	1.143	1.149	1.146	1.147
Ru–N(1)	1.730	1.731	1.732[b]/*1.769*[a]	1.731				
Ru–O(1)					1.843	1.851	1.851	1.846
Ru–N(2)	2.064	2.115	2.116[b]/*2.088*[a]	2.084	2.016	2.039	2.083	2.048
N(2)–O(2)	1.223	1.225	1.232[b]/*1.236*[a]	1.225	1.240	1.235	1.239	1.233
N(2)–O(3)	1.235	1.233	1.226[b]/*1.232*[a]	1.233	1.228	1.235	1.228	1.234
Ru–N(3)	2.146	2.123	2.096[b]/*2.079*[a]	2.081	2.143	2.115	2.088	2.074
Ru–N(4)	2.259	2.284	2.127[b]/*2.079*[a]	2.147	2.270	2.278	2.119	2.145
Ru–N(5)	2.177	2.177	2.114[b]/*2.077*[a]	2.122	2.116	2.108	2.037	2.048
Ru–N(6)	2.147	2.122	2.069[b]/*2.072*[a]	2.099	2.142	2.128	2.058	2.089
∠Ru–N(1)–O(1)	178.52	172.69	177.73[b]/*174.50*[a]	178.58	175.68	169.11	174.67	176.29
∠Ru–N(2)–O(2)	118.37	120.78	117.36[b]	118.05	117.41	114.47	115.93	116.60
∠O(2)–N(2)–O(3)	125.39	124.32	124.60[b]	125.24	124.95	123.83	124.17	124.68

[a]Experimental values are taken fromm ref.61 [b]Theoretical values are taken from ref. 41.

Table S2. Selected pairwise steric energies, dE(i,j) and associated overlap S(i,j) for disjoint interactions, obtained by NBO analysis for complexes **1a** and **2a,** at M06/Def2-SVP level of theory.

NLMO (i)	NLMO (j)	PNLMO S(i,j)	dE(i,j) kcal/mol
1a			
BD (1) Ru–N2	LP (2) O2	-0.1751	15.25
BD (1) Ru–N2	LP (2) O3	-0.1802	13.67
BD (1) O2–N2	LP (3) O3	-0.1530	16.19
BD (2) O2–N2	LP (2) O3	0.1392	7.82
BD (1) N2–O3	LP (2) O2	0.1540	9.27
Total Pairwise Steric Energy			145.61
2a			
BD (1) N5–Ru	BD (1) N1–O1	0.1635	11.35
BD (1) Ru–N2	LP (2) O2	-0.1800	15.49
BD (1) Ru–N2	LP (2) O3	-0.1920	17.73
BD (2) N2–O2	LP (3) O3	0.1618	17.70
BD (1) N2–O3	LP (2) O2	0.1598	11.52
Total Pairwise Steric Energy			612.35

Table S3. Calculated vibrational frequencies (cm^{-1}), bond lengths (Å), angles (°) for **1a'-4b'** isomers after reduction at BP86/TZVP level of theory.

Geometric	GS				MS1			
Parameters	**1a'**	**2a'**	**3a'**	**4a'**	**1b'**	**2b'**	**3b'**	**4b'**
Symmetry	C_1	C_1	C_1	C_1	C_1	C_1	C_1	C_1
$\nu_{a(}$NO)	1704	1621	1706[a]	1703	1577	1550	1635	1632
$\nu_a(NO_2)$	1412	1407	1430[a]	1437	1391	1372	1393	1295
N(1)–O(1)	1.185	1.202	1.184[a]	1.184	1.192	1.200	1.182	1.182
Ru–N(1)	1.802	1.798	1.809[a]	1.807				
Ru–O(1)					1.965	1.967	2.068	2.055
Ru–N(2)	1.974	2.036	2.076[a]	2.037	1.939	1.993	2.010	1.995
N(2)–O(2)	1.240	1.242	1.242[a]	1.234	1.245	1.247	1.250	1.243
N(2)–O(3)	1.260	1.247	1.240[a]	1.249	1.265	1.254	1.243	1.249
Ru–N(3)	2.136	2.139	2.061[a]	2.073	2.140	2.125	2.076	2.041
Ru–N(4)	2.274	2.263	2.093[a]	2.124	2.267	2.255	2.103	2.128
Ru–N(5)	2.260	2.269	2.154[a]	2.163	2.142	2.141	1.987	2.001
Ru–N(6)	2.156	2.124	2.069[a]	2.072	2.126	2.104	2.026	2.069
∠Ru–N(1)–O(1)	143.46	142.64	145.34[a]	144.57	137.85	140.17	136.30	138.49
∠Ru–N(2)–O(2)	121.55	122.28	119.89[a]	120.00	120.99	123.87	120.64	118.34
∠O(2)–N(2)–O(3)	121.33	121.08	122.04[a]	122.68	121.12	120.33	121.59	121.98

[a] Theoretical values are taken from ref. 41

To evaluate the scalar relativistic effect into the bonding scheme of NO^+ complexation, we carried out a population analysis of the relevant NO^+ levels, namely, 1π, 1σ and 2π*, at both, scalar relativistic (Rel.) and non-relativistic (NoRel.) level of theory (Table S4). In order to obtain a clear evaluation of the differences in the population of such levels, we included a simple difference comparison (=NoRel.-Rel.). The results suggest a small influence of the scalar relativistic effect into the charge transfer in the studied Ruthenium complexes, however it can be roughly estimated to increases the population of the 2π* level in an amount of ~0.05e, due to the expansion of the 4*d* shell which allows to increase the metal-ligand interaction.

Table S4. Population of the 1π, 1σ and 2π*, NO^+-levels at the non-relativistic (NonRel.) and scalar relativistic (Rel.) level of theory. The difference it is included for a clear comparison.

	Rel.				**NoRel.**				**Difference** (NoRel.-Rel.)		
		NO^+				NO^+					
$[Ru(NO)(NO_2)L]^{2+}$	1π	1σ	2π*		1π	1σ	2π*		1π	1σ	2π*
1a	3.95	1.85	1.09		3.88	1.78	1.05		-0.07	-0.07	-0.04
2a	3.84	1.93	1.12		3.75	1.86	1.04		-0.09	-0.07	-0.08
3a	3.67	1.86	1.08		3.67	1.82	1.00		0.00	-0.04	-0.08
4a	3.78	1.63	1.03		3.76	1.58	0.98		-0.02	-0.05	-0.05
1b	3.85	1.95	0.86		3.84	1.89	0.80		-0.01	-0.06	-0.06
2b	3.80	1.83	0.89		3.77	1.78	0.80		-0.03	-0.05	-0.09
3b	3.83	1.78	0.91		3.80	1.74	0.86		-0.03	-0.04	-0.05
4b	3.81	1.96	0.92		3.79	1.89	0.89		-0.02	-0.07	-0.03
$[Ru(NO)(NO_2)L]^{+}$											
1a'	3.82	1.70	1.30		3.80	1.70	1.27		-0.02	0.00	-0.03
2a'	3.69	1.62	1.29		3.65	1.60	1.23		-0.04	-0.02	-0.06
3a'	3.66	1.59	1.21		3.58	1.58	1.17		-0.08	-0.01	-0.04
4a'	3.61	1.77	1.39		3.60	1.70	1.34		-0.01	-0.07	-0.05
1b'	3.81	1.86	1.20		3.79	1.85	1.13		-0.02	-0.01	-0.07
2b'	3.66	1.82	1.09		3.63	1.82	1.05		-0.03	0.00	-0.04
3b'	3.66	1.77	1.10		3.65	1.80	1.08		-0.01	0.03	-0.02
4b'	3.67	1.75	1.29		3.67	1.75	1.20		0.00	0.00	-0.09

Table S5. Bond orders and natural atomic charges, obtained by NBO analysis for complexes **1a-4a,** at M06/Def2-SVP level of theory.

Compound	Bond	Bond orders	Atomic charges	
		B	Atom group	q^{NPA}
	Ru–N(1)	1.459	Ru	0.687
	N(1)–O(1)	1.894	N(1)O(1)	0.355
	Ru–N(2)	0.606	N(2)	0.404
1a	Ru–N(3)	0.649	N(3)	-0.999
	Ru–N(4)	0.529	N(4)	-1.051
	Ru–N(5)	0.630	N(5)	-1.054
	Ru–N(6)	0.638	N(6)	-1.000
	Ru–N(1)	1.479	Ru	0.695
	N(1)–O(1)	1.852	N(1)O(1)	0.307
	Ru–N(2)	0.578	N(2)	0.401
2a	Ru–N(3)	0.520	N(3)	-0.504
	Ru–N(4)	0.466	N(4)	-0.514
	Ru–N(5)	0.548	N(5)	-0.527
	Ru–N(6)	0.551	N(6)	-0,483
	Ru–N(1)	1.479	Ru	0.695
	N(1)–O(1)	1.852	N(1)O(1)	0.307
	Ru–N(2)	0.578	N(2)	0.401
3a[a]	Ru–N(3)	0.520	N(3)	-0.504
	Ru–N(4)	0.466	N(4)	-0.514
	Ru–N(5)	0.548	N(5)	-0.527
	Ru–N(6)	0.551	N(6)	-0,483
	Ru–N(1)	1.495	Ru	0.696
	N(1)–O(1)	1.845	N(1)O(1)	0.304
	Ru–N(2)	0.583	N(2)	0.406
4a	Ru–N(3)	0.534	N(3)	-0.481
	Ru–N(4)	0.460	N(4)	-0.516
	Ru–N(5)	0.533	N(5)	-0.525
	Ru–N(6)	0.519	N(6)	-0.498

*b Wiberg bond order, q^{NPA} Natural charge from NPA analysis. [a] Theoretical values are taken from ref. 41.

Table S6. Bond orders and natural atomic charges, obtained by NBO analysis for complexes **1b-4b,** at M06/Def2-SVP level of theory.

Compound	Bond	Bond orders	Atomic charges	
		B	Atom group	q^{NPA}
	Ru–O(1)	0.637	Ru	0.742
	O(1)–N(1)	1.916	O(1)N(1)	0.368
	Ru–N(2)	0.646	N(2)	0.394
1b	Ru–N(3)	0.634	N(3)	-1.007
	Ru–N(4)	0.516	N(4)	-1.066
	Ru–N(5)	0.680	N(5)	-1.005
	Ru–N(6)	0.625	N(6)	-1.008
	Ru–O(1)	0.637	Ru	0.742
	O(1)–N(1)	1.892	O(1)N(1)	0.317
	Ru–N(2)	0.594	N(2)	0.387
2b	Ru–N(3)	0.522	N(3)	-0.511
	Ru–N(4)	0.478	N(4)	-0.520
	Ru–N(5)	0.608	N(5)	-0.471
	Ru–N(6)	0.546	N(6)	-0.483
	Ru–O(1)	0.637	Ru	0.742
	O(1)–N(1)	1.892	O(1)N(1)	0.317
	Ru–N(2)	0.594	N(2)	0.387
3b	Ru–N(3)	0.522	N(3)	-0.511
	Ru–N(4)	0.478	N(4)	-0.520
	Ru–N(5)	0.608	N(5)	-0.471
	Ru–N(6)	0.546	N(6)	-0.483
	Ru–O(1)	0.827	Ru	0.750
	O(1)–N(1)	1.480	O(1)N(1)	0.013
	Ru–N(2)	0.583	N(2)	0.393
4b	Ru–N(3)	0.524	N(3)	-0.504
	Ru–N(4)	0.466	N(4)	-0.524
	Ru–N(5)	0.589	N(5)	-0.471
	Ru–N(6)	0.526	N(6)	-0.483

*bWiberg bond order, q^{NPA}Natural charge from NPA analysis.

Table S7. Bond critical points properties (in a.u): electron densities (ρ), Laplacian ($\nabla^2\rho$), bond ellipticity (ε) for Ru−N(1-6) and N(1)–O(1) bonds on $\{RuNO\}^6$ and $\{RuON\}^6$ cores at M06/Def2-SVP level of theory.

				GS			
BCP Properties	Ru–N(1)	N(1)–O(1)	Ru–N(2)	Ru–N(3)	Ru–N(4)	Ru–N(5)	Ru–N(6)
ρ_b	0.210	0.595	0.115	0.087	0.067	0.080	0.087
1a $\nabla^2\rho_b$	1.018	-1.805	0.350	0.351	0.282	0.319	0.353
ε	0.064	0.001	0.216	0.328	0.386	0.025	0.297
ρ_b	0.213	0.583	0.102	0.098	0.067	0.084	0.097
2a $\nabla^2\rho_b$	0.944	-1.734	0.331	0.349	0.257	0.308	0.341
ε	0.132	0.004	0.110	0.367	0.184	0.027	0.212
ρ_b	0.194	0.540	0.101	0.100	0.094	0.095	0.105
3a[a] $\nabla^2\rho_b$	1.148	-1.349	0.295	0.359	0.339	0.334	0.386
ε	0.061	0.003	0.271	0.150	0.156	0.074	0.425
ρ_b	0.210	0.586	0.110	0.097	0.088	0.092	0.101
4a $\nabla^2\rho_b$	1.016	-1.770	0.340	0.390	0.359	0.356	0.406
ε	0.066	0.002	0.259	0.191	0.207	0.052	0.417
				MS1			
ρ_b	0.131	0.565	0.127	0.086	0.065	0.092	0.086
1b $\nabla^2\rho_b$	1.083	-1.727	0.402	0.373	0.287	0.362	0.371
ε	0.110	0.005	0.219	0.200	0.310	0.029	0.220
ρ_b	0.132	0.557	0.120	0.094	0.067	0.098	0.098
2b $\nabla^2\rho_b$	1.006	-1.693	0.400	0.364	0.269	0.354	0.359
ε	0.191	0.083	0.195	0.316	0.130	0.023	0.202
ρ_b	0.129	0.561	0.108	0.098	0.092	0.113	0.106
3b $\nabla^2\rho_b$	1.053	-1.708	0.366	0.420	0.394	0.416	0.445
ε	0.150	0.040	0.265	0.094	0.122	0.044	0.339
ρ_b	0.130	0.560	0.117	0.098	0.086	0.110	0.101
4b $\nabla^2\rho_b$	1.074	-1.690	0.385	0.420	0.374	0.410	0.430
ε	0.104	0.024	0.259	0.087	0.103	0.043	0.356

*All values are in a.u. One atomic unit of ρ_b =6.748 eÅ^{-3}, of $\nabla^2\rho_b$ =24.10 eÅ^{-5}, and energy = e^2/a_0 = 627.51 kcal mol^{-1} = 27.21 eV. [a]Theoretical values are taken from ref. 41.

Table S8. Bond orders and natural atomic charges, obtained by NBO analysis for complexes **1a'-4a',** at M06/Def2-SVP level of theory.

Compound	Bond	Bond orders	Atomic charges	
		B	Atom group	q^{NPA}
	Ru–N(1)	1.202	Ru	0.573
	N(1)–O(1)	1.785	N(1)O(1)	-0.044
	Ru–N(2)	0.674	N(2)	0.386
1a'	Ru–N(3)	0.587	N(3)	-1.002
	Ru–N(4)	0.468	N(4)	-1.042
	Ru–N(5)	0.505	N(5)	-1.063
	Ru–N(6)	0.556	N(6)	-1.005
	Ru–N(1)	1.349	Ru	0.594
	N(1)–O(1)	1.668	N(1)O(1)	-0.119
	Ru–N(2)	0.605	N(2)	0.391
2a'	Ru–N(3)	0.499	N(3)	-0.673
	Ru–N(4)	0.475	N(4)	-0.735
	Ru–N(5)	0.473	N(5)	-0.730
	Ru–N(6)	0.532	N(6)	-0.677
	Ru–N(1)	1.210	Ru	0.555
	N(1)–O(1)	1.789	N(1)O(1)	-0.022
	Ru–N(2)	0.585	N(2)	0.382
3a'[a]	Ru–N(3)	0.505	N(3)	-0.474
	Ru–N(4)	0.456	N(4)	-0.486
	Ru–N(5)	0.441	N(5)	-0.502
	Ru–N(6)	0.490	N(6)	-0.465
	Ru–N(1)	1.234	Ru	0.561
	N(1)–O(1)	1.776	N(1)O(1)	-0.026
	Ru–N(2)	0.601	N(2)	0.393
4a'	Ru–N(3)	0.480	N(3)	-0.463
	Ru–N(4)	0.443	N(4)	-0.488
	Ru–N(5)	0.421	N(5)	-0.500
	Ru–N(6)	0.494	N(6)	-0.470

*b Wiberg bond order, q^{NPA} Natural charge from NPA analysis. [a]Theoretical values are taken from ref. 41.

Table S9. Bond orders and natural atomic charges, obtained by NBO analysis for complexes **1b'-4b',** at M06/Def2-SVP level of theory.

Compound	Bond	Bond orders	Atomic charges	
		B	Atom group	q^{NPA}
	Ru–O(1)	0.549	Ru	0.589
	O(1)–N(1)	1.757	O(1)N(1)	-0.055
	Ru–N(2)	0.730	N(2)	0.387
1b'	Ru–N(3)	0.560	N(3)	-1.004
	Ru–N(4)	0.467	N(4)	-1.047
	Ru–N(5)	0.588	N(5)	-1.033
	Ru–N(6)	0.579	N(6)	-1.004
	Ru–O(1)	0.434	Ru	0.562
	O(1)–N(1)	1.872	O(1)N(1)	0.019
	Ru–N(2)	0.644	N(2)	0.381
2b'	Ru–N(3)	0.486	N(3)	-0.479
	Ru–N(4)	0.453	N(4)	-0.489
	Ru–N(5)	0.601	N(5)	-0.421
	Ru–N(6)	0.548	N(6)	-0.452
	Ru–O(1)	0.434	Ru	0.562
	O(1)–N(1)	1.872	O(1)N(1)	0.019
	Ru–N(2)	0.644	N(2)	0.381
3b'	Ru–N(3)	0.486	N(3)	-0.479
	Ru–N(4)	0.453	N(4)	-0.489
	Ru–N(5)	0.601	N(5)	-0.421
	Ru–N(6)	0.548	N(6)	-0.452
	Ru–O(1)	0.451	Ru	0.569
	O(1)–N(1)	1.868	O(1)N(1)	0.007
	Ru–N(2)	0.636	N(2)	0.389
4b'	Ru–N(3)	0.520	N(3)	-0.454
	Ru–N(4)	0.441	N(4)	-0.492
	Ru–N(5)	0.570	N(5)	-0.421
	Ru–N(6)	0.491	N(6)	-0.469

*b Wiberg bond order, q^{NPA} Natural charge from NPA analysis.

Table S10. Bond critical points properties (in a.u): electron densities (ρ), Laplacian ($\nabla^2\rho$), bond ellipticity (ε) for Ru−N(1-6) and N(1)–O(1) bonds on $\{RuNO\}^7$ and $\{RuON\}^7$ cores at M06/Def2-SVP level of theory.

				GS			
BCP Properties	Ru–N(1)	N(1)–O(1)	Ru–N(2)	Ru–N(3)	Ru–N(4)	Ru–N(5)	Ru–N(6)
ρ_b	0.189	0.536	0.134	0.809	0.060	0.063	0.085
1a'$\nabla^2\rho_b$	0.684	-1.487	0.500	0.381	0.300	0.298	0.401
ε	0.120	0.022	0.187	0.244	0.441	0.250	0.154
ρ_b	0.191	0.515	0.115	0.090	0.066	0.064	0.093
2a'$\nabla^2\rho_b$	0.693	-1.366	0.453	0.360	0.293	0.288	0.380
E	0.136	0.031	0.072	0.213	0.205	0.318	0.464
ρ_b	0.172	0.491	0.106	0.104	0.097	0.085	0.102
3a'[a]$\nabla^2\rho_b$	0.798	-1.032	0.366	0.436	0.406	0.351	0.428
ε	0.078	0.020	0.252	0.091	0.040	0.158	0.409
ρ_b	0.185	0.536	0.116	0.098	0.087	0.079	0.098
4a'$\nabla^2\rho_b$	0.697	-1.507	0.429	0.464	0.420	0.376	0.458
ε	0.115	0.028	0.222	0.030	0.025	0.256	0.413
				MS1			
ρ_b	0.098	0.515	0.145	0.085	0.060	0.082	0.082
1b'$\nabla^2\rho_b$	0.737	-1.551	0.545	0.425	0.317	0.405	0.415
ε	0.012	0.044	0.141	0.004	0.348	0.342	0.045
ρ_b	0.099	0.505	0.127	0.092	0.067	0.085	0.096
2b'$\nabla^2\rho_b$	0.732	-1.463	0.497	0.379	0.297	0.394	0.411
ε	0.120	0.009	0.134	0.202	0.379	0.266	0.387
ρ_b	0.078	0.479	0.120	0.099	0.094	0.111	0.123
3b'$\nabla^2\rho_b$	0.517	-1.031	0.454	0.437	0.414	0.485	0.494
ε	0.216	0.050	0.225	0.247	0.170	0.255	0.149
ρ_b	0.075	0.531	0.127	0.105	0.085	0.118	0.097
4b'$\nabla^2\rho_b$	0.584	-1.656	0.486	0.511	0.425	0.519	0.489
ε	0.188	0.058	0.146	0.220	0.180	0.125	0.305

*All values are in a.u. One atomic unit of ρ_b =6.748 eÅ^{-3}, of $\nabla^2\rho_b$ =24.10 eÅ^{-5}, and energy = e^2/a_0 = 627.51 kcal mol^{-1} = 27.21 eV. [a]Theoretical values are taken from ref. 41.