Supporting Information for

"Charge and Geometrical Effects on the Catalytic N_2O Reduction by Rh_6^- and Rh_6^+ Clusters"

Héctor Francisco[1], Virineya Bertin[1*], Jorge R. Soto[2], and Miguel Castro[3]*

[1]Departamento de Química, Universidad Autónoma Metropolitana-Iztapalapa, San Rafael Atlixco 186, Col. Vicentina, México, D. F. 09340, México.
[2]Departamento de Física, Facultad de Ciencias, Universidad Nacional Autónoma de México (UNAM), CP 04510, México, D. F, México.
[3]Departamento de Física y Química Teórica, DEPg. Facultad de Química, UNAM, Del. Coyoacán, México D.F., 04510, México

Figure S1. Energy profile diagram for the reaction **(**$Rh_6)^+$ (octahedral) + $N_2O \rightarrow (Rh_6O)^+ + N_2$ reaction, including reactants, local minima intermediates, transition structures and products.

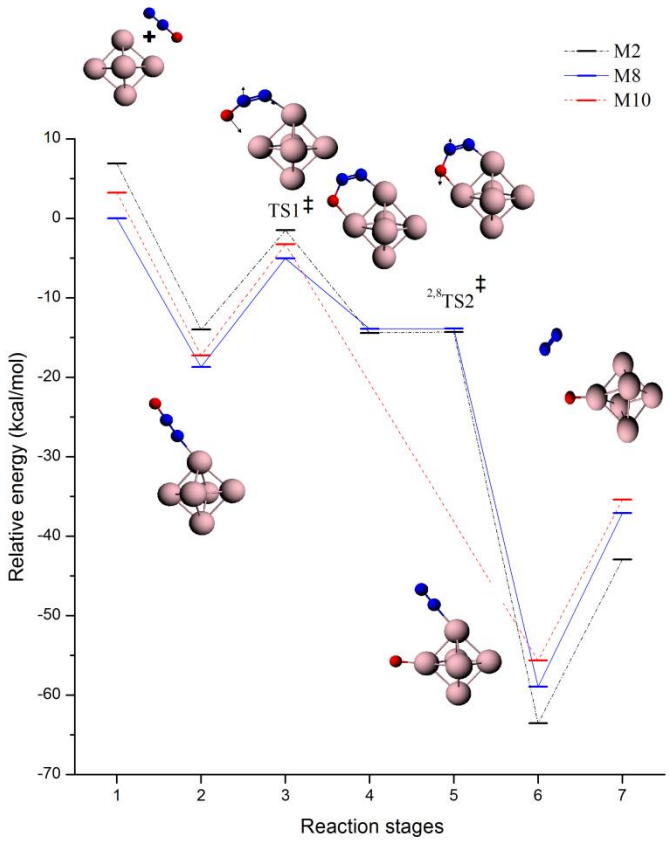

Figure S2. Energy profile diagram corresponding to the **(**$Rh_6)^+$ (prism) + $N_2O \rightarrow (Rh_6O)^+ + N_2$ reaction, including reactants, local minima intermediates, transition structures and products.

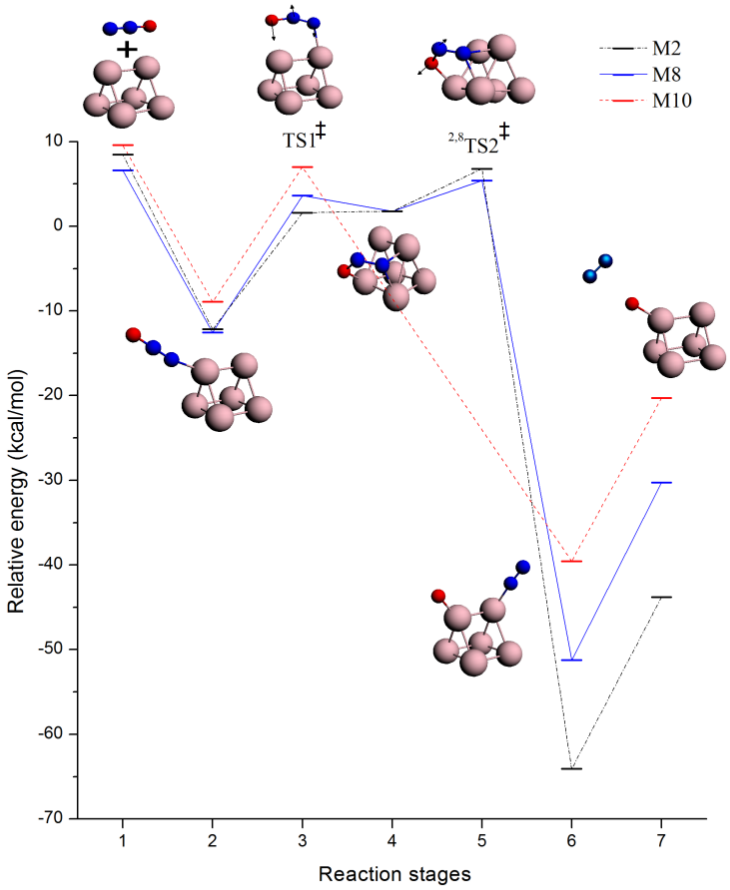

Table S1. Bond lengths (Å) and Hirshfeld charges of the complex Rh_6^{+1}(octahedral) + N_2O in the different reaction stages for M = 8

Geometry at Stage #	Rh-N	Rh-O	N-N	N-O	Rh-Rh	q(N1)	q(N2)	q(O)	q(Rh(N))	q(Rh(O))
1	----	-----	1.14	1.19		-0.08	0.20	-0.12	---	---
2	2.02	----	1.14	1.19	----	-0.06	0.22	-0.04	0.09	---
3	2.05	2.78	1.16	1.21	2.67	-0.07	0.17	-0.09	0.13	0.17
4	1.91	1.96	1.20	1.39	2.56	-0.09	0.07	-0.14	0.18	0.22
5	1.91	1.93	1.19	1.44	2.55	-0.08	0.06	-0.14	0.19	0.23
6	1.97	1.70	1.12	----	2.53	0.02	0.06	-0.19	0.13	0.23

Table S2. Bond lengths (Å) and Hirshfeld charges of the complex Rh_6^{+1}(prism) + N_2O in different M = 8 reaction stages.

Geometry at Stage #	Rh-N	Rh-O	N-N	N-O	Rh-Rh	q(N1)	q(N2)	q(O)	q(Rh(N))	q(Rh(O))
1	---	---	1.14	1.19	---	-0.08	0.20	-0.12	---	---
2	2.03	----	1.14	1.18	----	-0.06	0.23	-0.03	0.08	---
3	2.12	2.56	1.16	1.22	2.42	-0.06	0.18	-0.07	0.13	0.14
4	1.99	2.04	1.24	1.32	2.45	-0.12	0.05	-0.13	0.25	0.21
5	2.01	1.89	1.20	1.60	2.45	-0.09	0.03	-0.17	0.25	0.23
6	1.99	1.71	1.11	---	2.46	0.02	0.06	-0.20	0.12	0.23

Figure S3. Energy profile diagram corresponding to the **(**$Rh_6)^-$ (octahedral) + $N_2O \rightarrow (Rh_6O)^-$ + N_2 reaction, including reactants, local minima intermediates, transition structures and products.

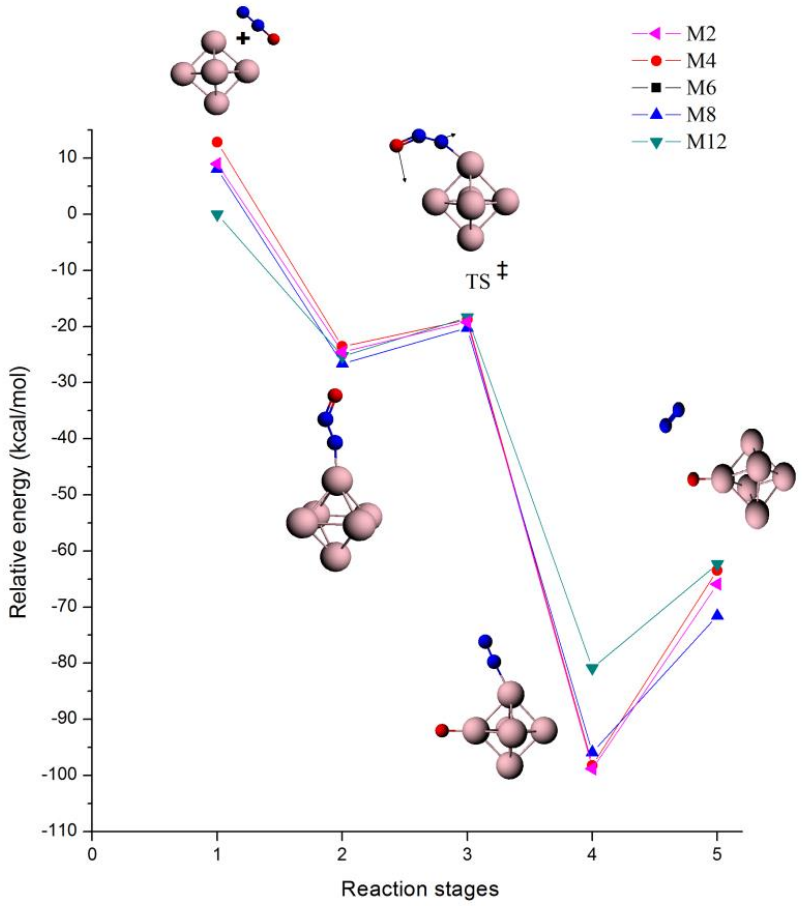

Figure S4. Energy profile diagram corresponding to the **(**$Rh_6)^-$ (prism) + $N_2O \rightarrow (Rh_6O)^-$ + N_2 reaction, including reactants, local minima intermediates, transition structures and products.

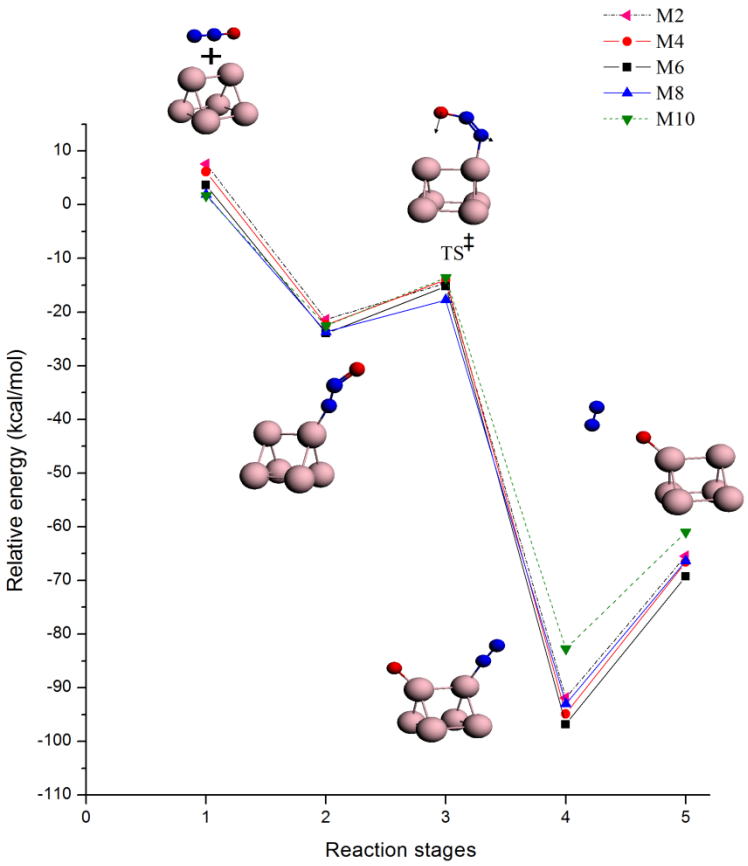

Table S3. Bond lengths (Å) and Hirshfeld charges of the complex Rh_6^{-1}(octahedral) + N_2O in the different reaction stages for M = 12

Geometry at Stage #	Rh-N	Rh-O	N-N	N-O	Rh-Rh	q(N1)	q(N2)	q(O)	q(Rh(N))	q(Rh(O))
1	----	-----	1.14	1.19		-0.08	0.20	-0.12	---	---
2	1.90	----	1.17	1.24	----	-0.12	0.09	-0.24	-0.08	---
3	1.90	3.50	1.18	1.26	2.59	-0.15	0.04	-0.27	-0.04	-0.06
4	1.93	1.76	1.13	----	2.59	-0.05	-0.12	-0.39	-0.05	0.03

Table S4. Bond lengths (Å) and Hirshfeld charges of the complex Rh_6^{-1}(prism) + N_2O in the different reaction stages for M = 10

Geometry at Stage #	Rh-N	Rh-O	N-N	N-O	Rh-Rh	q(N1)	q(N2)	q(O)	q(Rh(N))	q(Rh(O))
1	---	---	1.14	1.19	---	-0.08	0.20	-0.12	---	---
2	1.94	----	1.15	1.22	----	-0.09	0.14	-0.19	-0.08	---
3	1.96	3.31	1.20	1.26	2.39	-0.18	0.03	-0.25	0.01	-0.04
4	1.91	1.75	1.13	----	2.49	-0.05	-0.12	-0.36	-0.06	0.07