J. Braz. Chem. Soc., Vol. 22, No. 3, S1-S7, 2011.
Printed in Brazil - ©2011 Sociedade Brasileira de Química
0103 - 5053 $6.00+0.00

Supplementary Information

Quantum Mechanics/Molecular Mechanics Investigation of the Ethene Polymerization Mechanism Catalyzed by a Bulky Diimine-Ni(II) Complex

Daví A. C. Ferreira,[a] Simoni M. P. Meneghetti,[a] Marçal de Oliveira Neto,[b] Willian R. Rocha[c] and Mario R. Meneghetti*[,a]

[a]Instituto de Química e Biotecnologia, Universidade Federal de Alagoas, Campus A.C. Simões, Av. Lourival de Melo Mota, 57072-970 Maceió-AL, Brazil

[b]Instituto de Química, Universidade de Brasília, Campus Universitário Darcy Ribeiro, Asa Norte, 70910-900 Brasília-DF, Brazil

[c]Laboratório de Química Computacional e Modelagem Molecular, Departamento de Química - ICEX, Universidade Federal de Minas Gerais, 31270-901 Belo Horizonte-MG, Brazil

The figures below depict complementary views of the different molecular species modeled on this work. Also, a series of tables are presented displaying the main molecular parameter of some significant chemical species modeled, *i.e*. bond distances and angles.

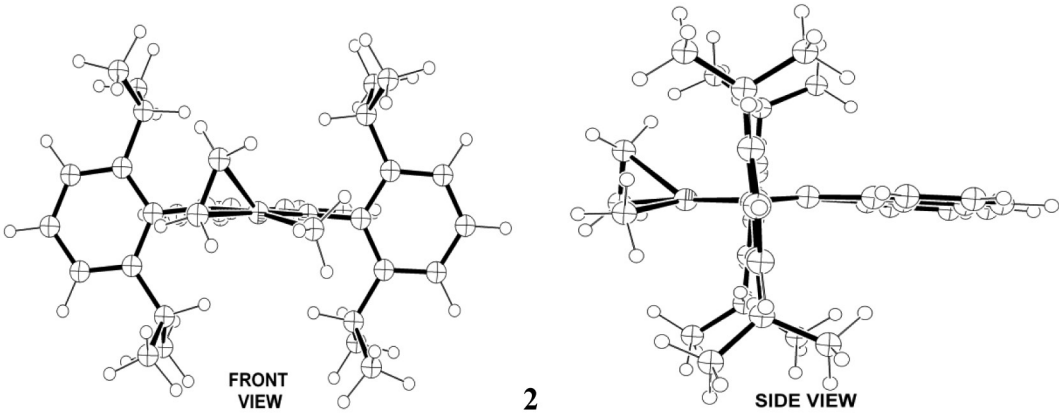

Figure S1. Front and side views of the molecular geometry of the π-complex **2**.

*e-mail: mrm@qui.ufal.br

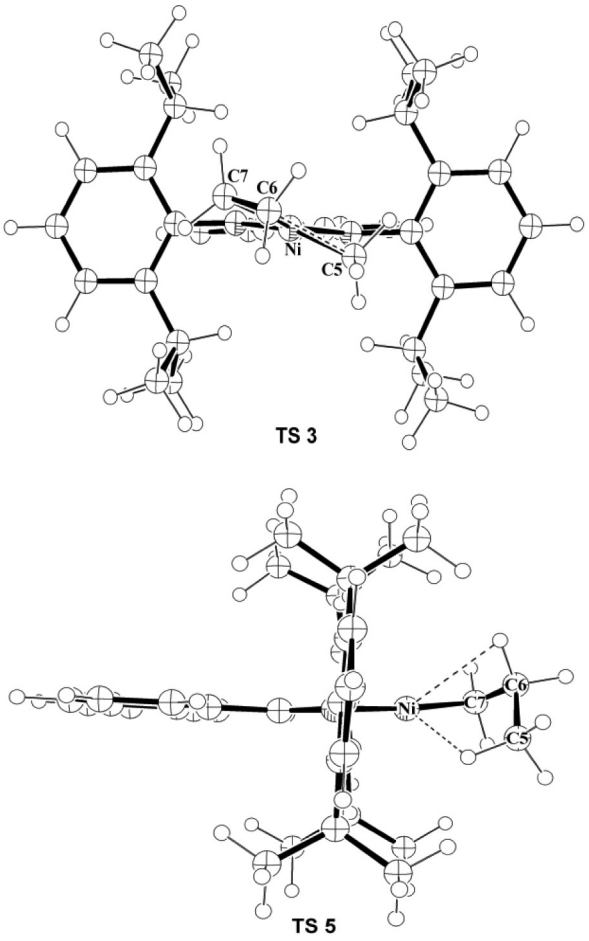

Figure S2. Front and side views of the molecular geometries of the migratory insertion TS **3** and TS **5**, respectively.

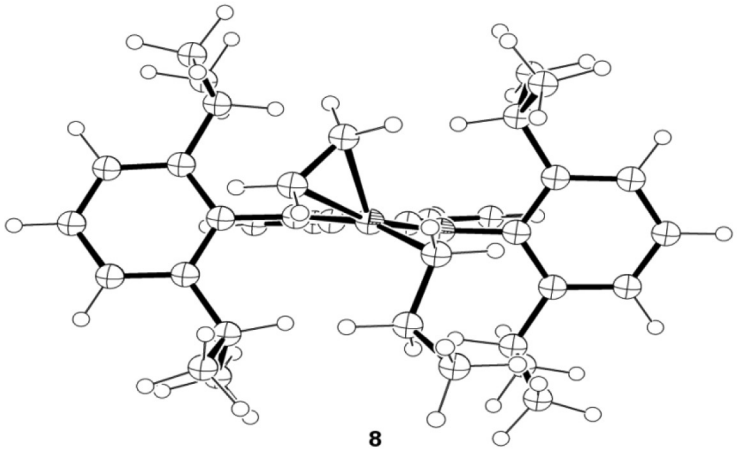

Figure S3. Front view of the molecular geometries of the π-complex **8**.

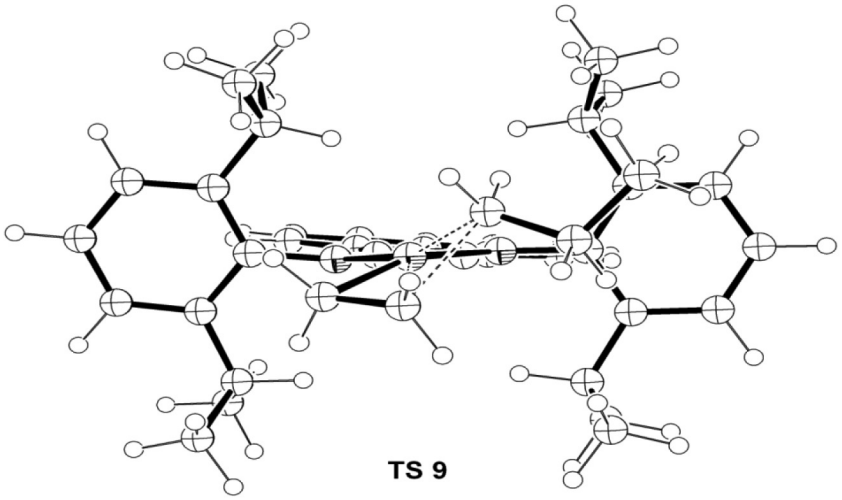

Figure S4. Front view of the molecular geometry of the migratory insertion TS **9**.

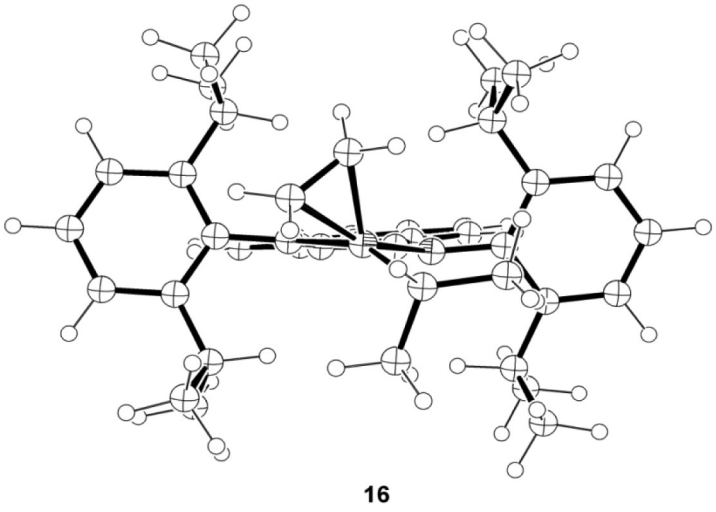

Figure S5. Front view of the molecular geometry of the π-complex **16**.

Table S1. Relevant bond lengths (Å) of computed diimine complexes during stage I

Bond	**1**	**2**	**3**	**4**	**5**	**6**
C1–C1'	1.479	1.481	1.472	1.476	1.476	1.477
N–C1	1.295	1.292	1.292	1.289	1.291	1.291
N'–C1'	1.289	1.290	1.294	1.297	1.298	1.295
Ni–N	1.929	2.056	2.118	2.108	2.081	2.044
Ni–N'	2.082	2.162	2.044	1.940	1.925	1.947
Ni–C7	-	2.129	2.011	1.902	1.884	1.902
Ni–C6	-	2.161	2.287	-	2.319	2.210
Ni–C5	1.867	1.923	2.030	-	2.594	-
C5–C6	-	-	2.249	1.570	1.567	1.541
C6–C7	-	1.388	1.405	1.532	1.535	1.501
Ni–H5*	2.244	2.499	2.281	2.151	2.137	-
Ni–H6*	-	-	-	-	2.471	1.731
C5–H5	1.115	1.095	1.098	1.109	1.108	1.095
C6–H6	-	-	-	1.096	1.105	1.188

* Hydrogen atoms with agostic interactions or hydrogen atom closest to the metal. # Average distance.

Table S2. Relevant bond lengths (Å) of computed diimine complexes during stage II

Bond length	**8**	**9**	**10**	**11**	**12**
C1–C1'	1.480	1.474	1.475	1.475	1.479
N–C1	1.289	1.295	1.298	1.299	1.296
N'–C1'	1.294	1.292	1.289	1.291	1.292
Ni–N	2.152	2.012	1.941	1.923	1.946
Ni–N'	2.076	2.127	2.096	2.065	2.029
C8–C9	1.393	1.427	1.534	1.535	1.498
C6–H6*	1.100	-	-	-	-
C7–H7*	1.096	1.101	1.115	1.109	1.099
C8–H8*	1.087	1.089	1.098	1.115	1.194
Ni–C7	1.931	2.092	2.266	2.680	-
Ni–C8	2.134	2.162	2.551	2.254	2.196
Ni–C9	2.111	1.977	1.904	1.882	1.906
Ni–H7*	2.548	2.111	2.093	2.236	3.239
Ni–H8*	2.673	2.599	–	2.282	1.708

* Hydrogen atoms with agostic interactions or hydrogen atom closest to the metal. # Average distance.

Table S3. Relevant bond lengths (Å) of computed diimine complexes during stage III

Bond length	**13**	**14**	**16**	**17**	**18**	**19**	**20**	**21**	**22**
C1–C1'	1.481	1.477	1.484	1.496	1.475	1.479	1.475	1.475	1.476
N–C1	1.293	1.291	1.289	1.302	1.297	1.297	1.298	1.299	1.295
N'–C1'	1.291	1.296	1.292	1.284	1.289	1.291	1.291	1.292	1.292
Ni–N	1.963	2.053	2.165	1.956	1.959	1.941	1.929	1.924	1.947
Ni–N'	2.148	1.961	2.168	2.662	2.098	2.121	2.081	2.068	2.040
C6–C7	1.387	1.511	1.536	1.551	1.543	1.547	1.542	1.544	1.547
C8–C9	-	-	1.398	1.445	1.539	1.529	1.531	1.534	1.498
C6–H6	1.090	1.093	1.095	1.089	1.099	1.133	1.126	1.119	1.101
C7–H7*	1.087[#]	1.166	1.099	1.109	1.106	1.097	-	-	-
C8–H8*	-		1.086	1.089	1.102	-	1.103	1.110	1.193
Ni–C6	2.259	1.913	1.959	2.121	3.131	2.503	2.545	2.605	-
Ni–C7	2.099	2.187	1.959	2.313	2.329	3.128	3.608	-	-
Ni–C8	-	-	2.118	2.194	2.824	2.588	2.371	2.279	2.207
Ni–C9	-	-	2.088	1.931	1.936	1.908	1.892	1.886	1.906
Ni–H6*	2.695	2.502	2.486	-	-	1.901	1.945	2.078	-
Ni–H7*	-	1.758	2.700	2.061	2.166	2.818	3.522	-	-
Ni–H8*	-	-	-	-	-	-	-	2.374	1.716
Ni–H6	1.451	–	–	–	–	–	–	–	–

* Hydrogen atoms with agostic interactions or hydrogen atom closest to the metal. # Average distance.

Table S4. Relevant angles (º) of computed diimine complexes during stage I

Angle (º)	**1**	**2**	**3**	**4**	**5**	**6**
N–Ni–N'	85.20	81.38	81.63	84.08	84.91	84.97
N'–Ni–π *	98.11	-	111.12	-	-	-
N–Ni–π *	-	164.47	162.32	-	-	-
N–Ni–C5	100.10	92.53	90.13	-	-	-
N'–Ni–C5	174.62	170.14	164.75	-	-	-
C5–Ni–π *	-	89.83	79.93	-	-	-
C5–C6–C7	–	–	113.61	109.33	112.13	117.02

* π correspond to middle point of C=C bond.

Table S5. Relevant bond angles (º) of computed diimine complexes during stage II

Bond angle (º)	**8**	**9**	**10**	**11**	**12**
N–Ni–N'	81.24	82.04	84.13	85.02	85.06
N'–Ni–C7	96.87	95.65	-	-	-
N'–Ni–π *	146.70	150.93	-	-	-
N–Ni–C7	-	158.48	-	-	-
C9–C8–C7	-	109.08	109.41	114.03	118.22
N–Ni–π *	99.33	115.13	-	-	-
Ni–C9–C8	78.76	76.98	95.20	81.87	79.33

* π correspond to middle point of C=C bond.

Table S6. Relevant angles (º) of computed diimine complexes during stage III

Bond angle (º)	**13**	**14**	**16**	**17**	**18**	**19**	**20**	**21**	**22**
N–Ni–N'	83.07	84.87	79.72	75.33	83.82	83.97	84.73	85.03	84.96
N'–Ni–π *	107.28	105.25	102.05	101.37	-	-	-	-	-
N`–Ni–C7	100.87	147.65	-	87.39	175.29	-	-	-	-
N–Ni–π *	107.28	-	-	-	-	-	-	-	-
N'–Ni–π *	-	-	142.56	138.94	-	-	-	-	-
N–Ni–π *	–	–	101.26	119.45	–	–	–	–	–

* π correspond to middle point of C=C bond.

Table S7. Relevant dihedral angles (º) of computed diimine complexes during stage I

Dihedral angle (º)	**1**	**2**	**3**	**4**	**5**	**6**
N–C1–C1'–N'	0.11	6.53	8.67	1.56	1.58	1.07
C2'–N'–Ni–π *	-	27.30	21.57	-	-	-
C6–C7–Ni–C5	-	–92.11	3.81	-	-	-
C2–N–Ni–C5	2.68	–7.49	–20.96	-	-	-
C1–N–C2–C4	88.69	88.91	89.43	89.04	87.18	91.78
Ni–N–C2–C4	–93.19	–88.33	–79.71	–90.98	–99.50	–81.78
C1'–N'–C2'–C4'	–88.82	–89.21	–86.97	–88.83	–91.17	–88.10
Ni–N'–C2'–C4'	93.05	105.08	103.24	95.89	92.67	87.10
C3'–C2'–C2–C3	1.62	9.38	13.86	0.91	–6.85	3.61

* π correspond to middle point of C=C bond.

Table S8. Relevant dihedral angles (º) of computed diimine complexes during stage II

Dihedral angle (º)	**8**	**9**	**10**	**11**	**12**
N–C1–C1'–N'	11.06	9.23	0.29	–0.08	0.99
C2'–N'–Ni–C7	–23.12	–24.21	-	-	-
C2–N–Ni–π *	–43.79	34.61	-	-	-
C7–Ni–C9–C8	-	–35.12	-	-	-
C1–N–C2–C4	93.61	85.14	87.62	90.04	88.83
Ni–N–C2–C4	–74.91	–107.62	–89.06	–85.78	–82.11
C1'–N'–C2'–C4'	–84.17	–91.97	–88.97	–83.41	–84.98
Ni–N'–C2'–C4'	108.48	81.40	88.24	87.46	85.79
C3'–C2'–C2–C3	20.97	–16.16	2.64	8.36	8.85

* π correspond to middle point of C=C bond.

Table S9. Relevant dihedral angles (º) of computed diimine complexes during stage III

Dihedral angles(º)	**13**	**14**	**16**	**17**	**18**	**19**	**20**	**21**	**22**
N–C1–C1'–N'	1.02	2.75	10.81	16.57	–2.26	3.64	1.81	1.96	1.86
C2'–N'–C6–C7	75.77	–12.57	–113.14	-	-	-	-	-	-
C2'–N'–Ni–C6	–25.61	–7.38	–34.95	–48.22	-	-	-	-	-
Ni–C6–C8–C9	-	-	90.69	–10.10	-	-	-	-	-
C2–N–Ni–C9	-	-	–58.66	–43.05	2.33	7.51	–13.74	–14.63	1.62
N–Ni– C9–C8	-	-	-	161.12	–146.31	–166.18	–166.11	–170.15	174.74
Ni–C9–C8–C6	-	-	-	10.07	–52.68	–29.42	–53.95	–62.64	–111.53
C1–N–C2–C4	88.05	92.25	–84.18	–79.40	–90.28	–86.77	–87.78	–87.75	–87.27
Ni–N–C2–C4	–110.23	–76.85	99.78	104.47	90.46	85.89	101.51	101.63	91.72
C1'–N'–C2'–C4'	–85.81	–91.18	90.51	84.33	88.00	88.76	89.58	93.09	88.19
Ni–N'–C2'–C4'	104.96	86.51	–73.07	–62.37	–97.98	–75.13	–94.38	–92.94	–84.96
C3'–C2'–C2–C3	–2.23	1.22	21.80	25.27	–6.49	6.79	2.48	4.95	1.96