Electronic Supplementary Material (ESI) for RSC Advances.

The Siliconyl, Boronyl, and Iminoboryl Ligands as Analogues of the Well-known Carbonyl Ligand: Predicted Reactivity towards Dipolar Cyclooligomerization in Iron/Cobalt Carbonyl Complexes

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Supporting Information

1. Theoretical Methods

Morokuma Energy Decomposition Analyses (EDA)[1] were carried out for selected BP86 structures at the BP86/DZP level using the program package ADF.[2] The bonding dissociation energy is divided into two physically appealing entities:

$$\Delta E = \Delta E_{prep} + \Delta E_{int}$$

The preparation energy (ΔE_{prep}) is the energy required to promote the two fragments (A and B) from their isolated equilibrium geometry to the geometry that they have in the compound AB. The interaction energy (ΔE_{int}) is the interaction between the two prepared fragments in the molecule. In this study, ΔE_{prep} is sufficiently small to be neglected, so that only ΔE_{int} needs to be considered. This interaction energy can be separated into three major components:

$$\Delta E_{int} = \Delta E_{els} + \Delta E_{Pauli} + \Delta E_{orb}$$

In this equation the first term ΔE_{els} is the electrostatic interaction energy between the fragments, which is calculated using a frozen electron density distribution at the geometry of the complex. The second term ΔE_{Pauli} is the repulsive energy caused by Pauli repulsion. The last term ΔE_{orb} is the stabilization energy from relaxed orbital interaction between the prepared fragments. The ΔE_{orb} term can be further broken down into orbital contributions from different irreducible representations. This allows the prediction of separate energy contributions from σ and π interactions.

2. Complete list of monomer and oligomer structures

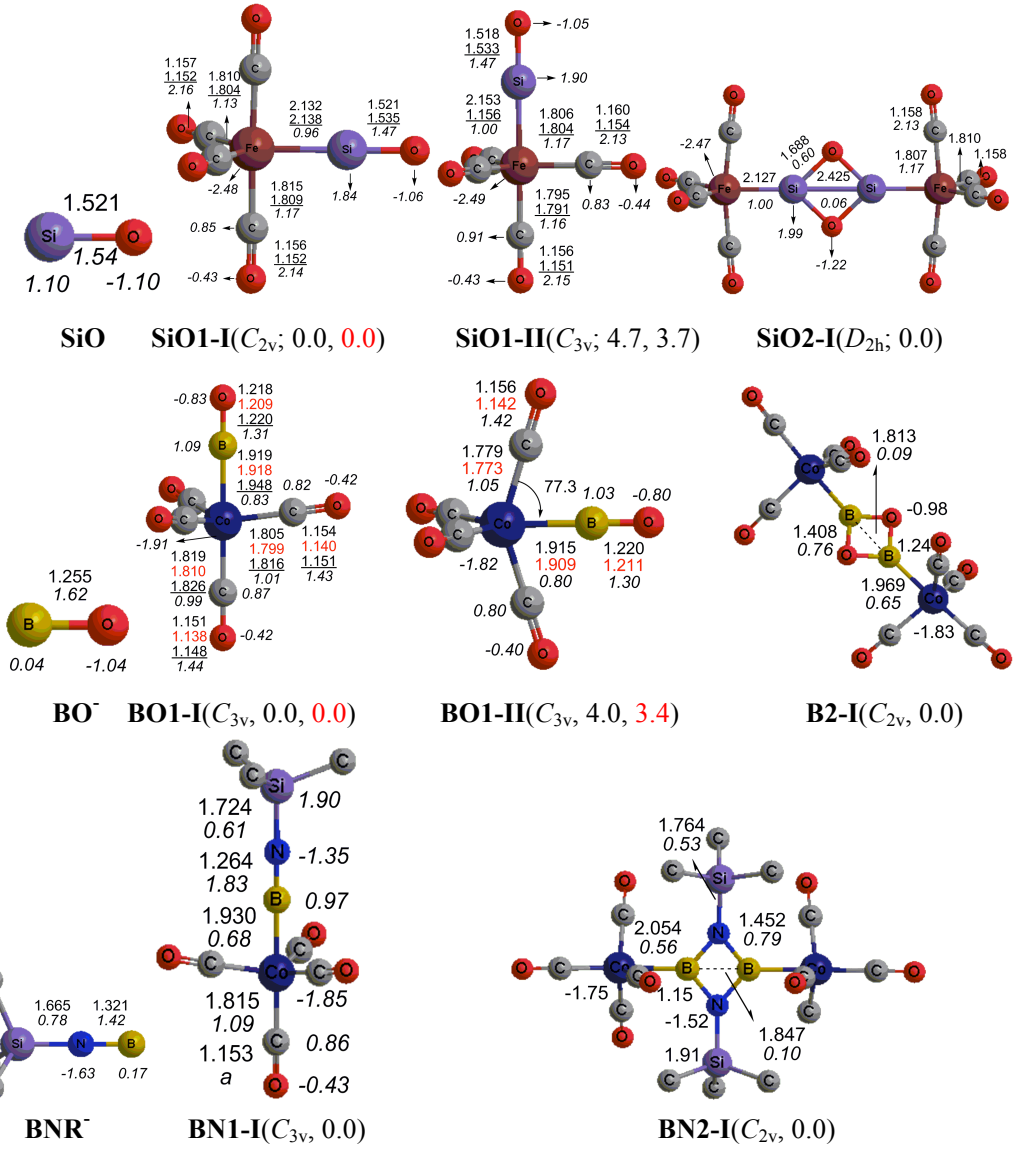


Figure S1. Optimized $Fe_n(CO)_{4n}(SiO)_n$, $Co_n(CO)_{4n}(BO)_n$, and $Co_n(CO)_{4n}(BNSiMe_3)_n$ (n =1, 2) structures. The symmetry and relative free energies (unit in kcal/mol) are given in parenthesis. Hydrogen atoms are omitted for clarity. The Wiberg bond indices (WBIs) as well as the Natural Charges are given in italics. The bond distances are given in Å. The red bond distances and red relative energies are given by M06L/TZ2P level's calculation. The earlier theoretical parameters of $Fe(CO)_4(SiO)$[3] and $Co(CO)_4(BO)$[4] are given in underlined.

The metastable structures, i.e. **SiO1-II**, and **BO1-II**, are found to be transition states, lying 4.7 kcal/mol and 4.0 kcal/mol above their global minima **SiO1-I**, and **BO1-I**, respectively. In addition, the M06L/TZ2P level optimized structures as well as relative energies are quite closed to that of M06L/DZP level (Fig. S1). Our predicted $Fe(CO)_4(SiO)$ structures parameters (**SiO1-I** and **SiO1-II** in Fig. S1) are well consistent with the MP2 values with averaged differences less than 0.01 Å.3

Moreover, our predicted **BO1-I** structure parameters are better than the earlier LDA parameters by averaged differences of ~0.02 Å.4

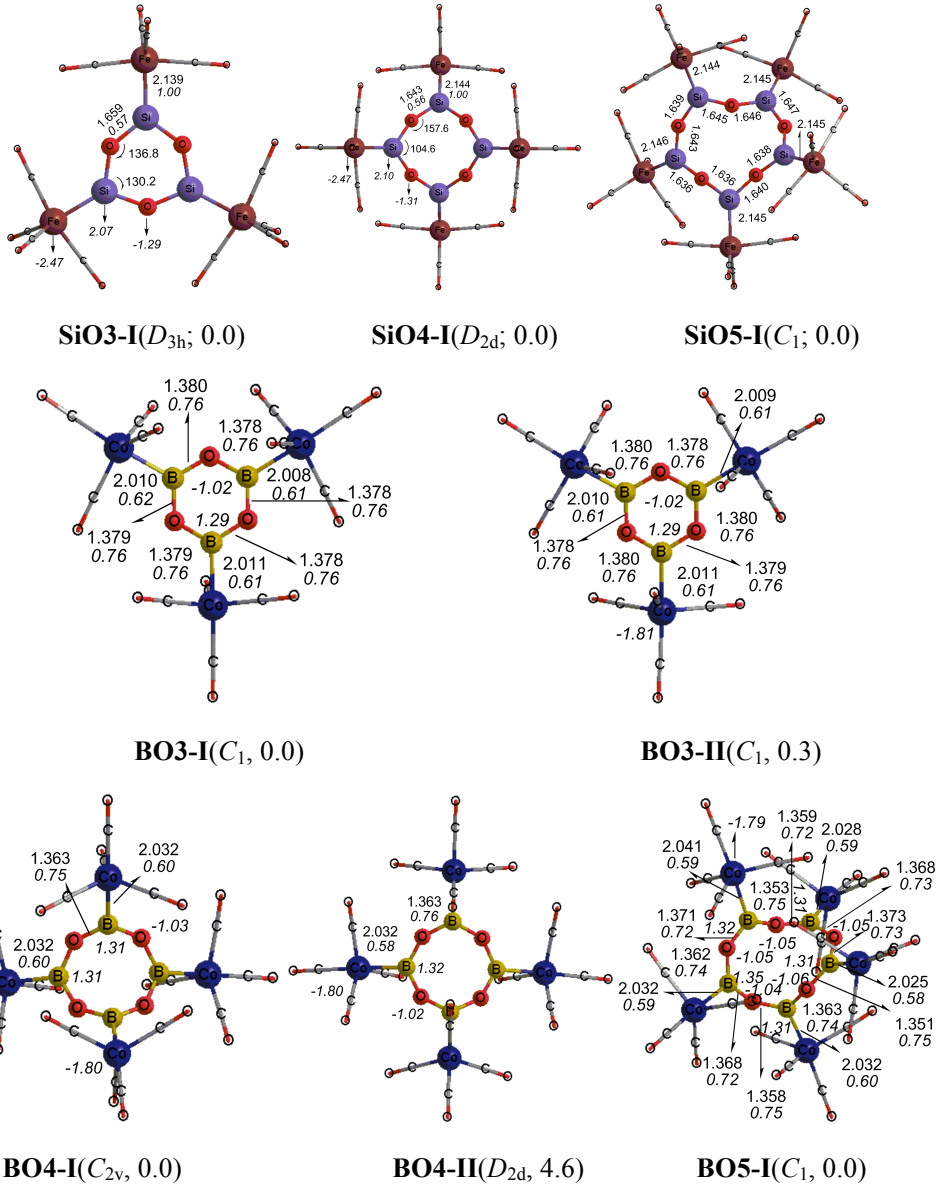


Figure S2. Optimized $Fe_n(CO)_{4n}(Si_nO_n)$, $Co_n(CO)_{4n}(B_nO_n)$, and (n = 3 ~ 5) structures. The symmetry and relative free energies (unit in kcal/mol) are given in parenthesis. Selected Wiberg bond indices (WBIs) are given in italics. The bond distances are given in Å.

The second lowest energy $Co_3(CO)_{12}(B_3O_3)$ and $Co_4(CO)_{16}(B_4O_4)$ structures, namely **BO3-II** and **BO4-II**, are analogous to the global minima structures **BO3-I** and **BO4-I**, but different with the arrangement of the three equatorial CO groups of $Co(CO)_4$ fragments. Such difference leads to a smaller relative energy of 0.3 kcal/mol and 4.6 kcal/mol above **BO3-I** and **BO4-I**. Thus, $Co_3(CO)_{12}(B_3O_3)$ and $Co_4(CO)_{16}(B_4O_4)$ molecules are potential fluxional systems.

3. Thermochemistry

In order to investigate the stability of $M_n(CO)_{4n}(L_n)$, several different reactions are reported in Table S1, including bond dissociation energies (BDEs) in terms of the ligand (BO^-, $BNSiMe_3^-$, and SiO) dissociation steps, as well as possible $M_n(CO)_{4n}(L_n)$ formation energies from mononuclear or smaller oligomers.

Table S1. Reaction energies (in kcal/mol) for the reported structures.

Reactions	L=SiO		L=BO^-		L=BNR^-	
	$-\Delta E_{zpe}$	$-\Delta G$	$-\Delta E_{zpe}$	$-\Delta G$	$-\Delta E_{zpe}$	$-\Delta G$
$2M(CO)_4(L) \rightarrow M_2(CO)_8(L_2)$	73.9	61.1	33.3	20.8	48.2	25.7
$3M(CO)_4(L) \rightarrow M_3(CO)_{12}(L_3)$	146.6	120.6	91.9	66.0	57.4	10.6
$4M(CO)_4(L) \rightarrow M_4(CO)_{16}(L_4)$	200.9	158.5	121.1	82.0	--	--
$5M(CO)_4(L) \rightarrow M_5(CO)_{20}(L_5)$	254.6	199.2	159.7	103.8	--	--
$M(CO)_4(L)+M_2(CO)_8(L_2) \rightarrow M_3(CO)_{12}(L_3)$	72.7	59.4	58.6	45.2	9.2	-15.1
$M(CO)_4(L)+M_3(CO)_{12}(L_3) \rightarrow M_4(CO)_{16}(L_4)$	54.3	38.0	29.1	16.0	--	--
$M(CO)_4(L)+M_4(CO)_{16}(L_4) \rightarrow M_5(CO)_{20}(L_5)$	53.7	40.7	38.6	21.8	--	--
$2M_2(CO)_8(L_2) \rightarrow M_4(CO)_{16}(L_4)$	53.1	36.2	54.4	40.4	--	--
$M_2(CO)_8(L_2)+M_3(CO)_{12}(L_3) \rightarrow M_5(CO)_{20}(L_5)$	34.1	17.5	34.4	17.0	--	--
$M(CO)_4 + L \rightarrow M(CO)_4(L)$	46.0	35.5	231.4	220.5	234.2	223.5

The $Fe(CO)_4 \leftarrow (SiO)$ bond dissociation energy (*BDE*) is predicted to be 46.0 kcal/mol, which is slightly stronger than the experimental value of 37.0 kcal/mol for the *BDE* of $Fe(CO)_4 \leftarrow (CO)$.[5] Furthermore, the $Co(CO)_4 \leftarrow L$ (L = BO^-, $BNSiMe_3^-$) are predicted to be 231.4 and 234.2 kcal/mol per cobalt atom, obviously indicating extremely strong $Co(CO)_4 \leftarrow L$ interactions arising from ionic interaction between $[Co(CO)_4]^+$ and L^- as well as the strong σ donation from L^- to $[Co(CO)_4]^+$ (for details see the **binding nature** in the ESI). Comparing with the $M \leftarrow CO$ interaction, the stronger $M \leftarrow L$ interactions (L = BO^-, $BNSiMe_3^-$) therefore suggest that the reactive L ligands are well captured in the metal complexes.

The free energies of formation for $M_n(CO)_{4n}(L_n)$ from monomers or smaller oligomers (Table S2) indicate the thermodynamic instability of mononuclear $M(CO)_4(L)$ or oligomers $M_{n-1}(CO)_{4n-1}(L_{n-1})$, since the formation of $M_n(CO)_{4n}(L_n)$ always release free energy. Note that the zero-point corrected total electronic energy of formation for $[Co(CO)_4]_3(B_3N_3Si_3Me_9)$ is predicted to be 9.2 kcal/mol. However the free energy of formation is found to require 15.1 kcal/mol compensation, since three bulky $SiMe_3$ groups in **BN3-I** increase the steric repulsion as well as entropy effect. Furthermore, the most likely oligomerization process might be $M(CO)_4(L) + M_{n-1}(CO)_{4n-1}(L_{n-1}) \rightarrow M_n(CO)_{4n}(L_n)$, because of the considerable free energy release and the smaller steric repulsion between mononuclear and smaller oligomers.

4 Electronic Structure and Bonding Nature

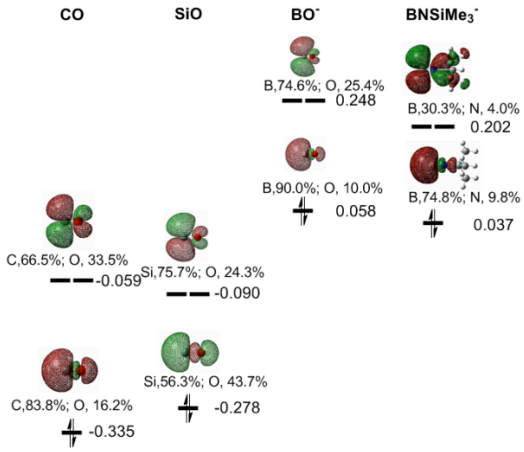


Figure S3. Comparing the frontier orbitals of CO, SiO, BO^-, and $BNSiMe_3^-$.

Table S3. Energy decomposition analysis of $Fe_n(CO)_{4n}(Si_nO_n)$, $Co_n(CO)_{n4}(B_nO_n)$, and $Co_n(CO)_{4n}(B_nN_nSi_nMe_{3n})$ (unit in kcal/mol).

	$Fe(CO)_5$	**SiO1-II**	**BO1-I**	**BN1-I**	**SiO2-I**	**BO2-I**	**SiO3-1**	**BO3-1**
ΔE_{int}	-55.0	-47.7	-252.2	-264.9	-63.7	-263.1	-65.4	-266.2
ΔE_{Paul}	128.8	108.7	260.9	289.2	150.6	258.3	148.7	236.1
ΔE_{els}	-91.9	-65.6	-335.3	-354.3	-113.4	-295.5	-113.2	-262.1
ΔE_{ster}	36.8	43.1	-74.4	-65.0	37.3	-37.2	35.6	-26.0
ΔE_{orb}	-89.5	-88.7	-175.1	-195.9	-96.5	-219.5	-95.1	-232.09
a_1*	-48.0	-58.4	-152.5	-165.4	-59.6	-211.3(a')	-58.9	---
b_2	0.0	-0.1	-0.2	-0.3	-11.7	-8.2(a'')	-11.1	---
e_1*	-41.5	-30.2	-22.4	-30.3	-24.9(b_1)	•••	-24.7(b_1)	---

The a_1 presents the M←L σ donation, and the e_1 term means the M→L π back donation.

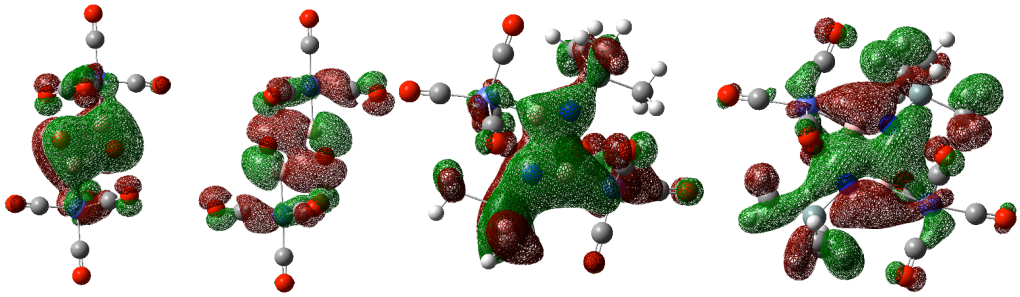
The frontier orbitals of CO, SiO, BO^-, and $BNSiMe_3^-$ are compared in both shape and energy (Figure S4). The HOMO of these ligands (CO, SiO, BO^-, BNR^-) should be viewed as mainly the lone pair electrons localized on the carbon (percentage of 83.8% for CO), silicon (percentage of 56.3% for SiO), and boron atoms (percentage of 90.0% for BO^-, and percentage of 74.8% for BNR^-). For the corresponding LUMOs, the contributions of the carbon, silicon, and boron atoms are found to be 66.5% for C(O), 75.7% for Si(O), 74.6% for B(O), and 30.3% for B(NR), respectively. The HOMO and LUMO energies of these ligands can be divided into positive and negative groups, where the neutral CO and SiO belong to the negative group, and the overcharged BO^- and BNR^- belong to the positive one.

In the trigonal bipyramidal $Co(CO)_4(BO)$, the boronyl prefers the more spatial axial position to accommodate the 90.0% lone-pair electrons locating on the B(O). In contrast, the siliconyl in $Fe(CO)_4(SiO)$ favors the equatorial position since the

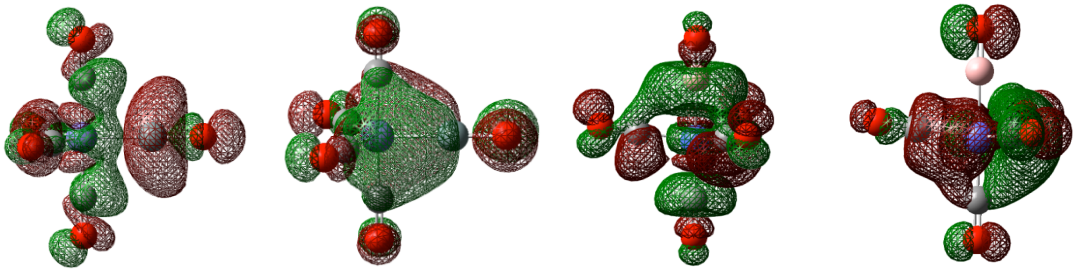
relatively smaller contribution of the lone pair electrons of 56.3% on Si(O) leads to the equatorial position with less *trans-influence*.

The *BDE*s of $Fe(CO)_5$ and $Fe(CO)_4(SiO)$ are essentially identical, as indicated by our predicted $Fe(CO)_4$←(SiO) *BDE* of 46.0 kcal/mol and the earlier MP2 $Fe(CO)_4$←(CO) *BDE* of 46.9 kcal/mol.[6] However, the M←L σ donation and M→L π* back donation in $Fe(CO)_5$ and $Fe(CO)_4(SiO)$ are obviously different from each other, since the ratio of σ donation/π* back donation in $Fe(CO)_5$ is predicted to be 1.16 (slightly stronger σ donation), but the ratio in $Fe(CO)_4(SiO)$ is found to be 1.93 (much stronger σ donation). Comparing with the carbon atom in carbonyl, the softer silicon atom in siliconyl can more readily donate than accept electrons. In addition, the binding nature between the positively charged $[Co(CO)_4]^+$ fragment and the negatively charged ligands (BO^- and BNR^-) are strongly different from that in $Fe(CO)_4$←(CO), since the ionic interactions as well as the [M]←(L) (L= BO^-, BNR^-) interactions lead to the much stronger interaction energies (E_{int}s). Actually, the E_{int}s of $[Co(CO)_4]$←(L) are reported to be –252.2 kcal/mol for $Co(CO)_4(BO)$, and –264.9 kcal/mol for $Co(CO)_4(BNR)$, which are nearly five times that of $Fe(CO)_5$ or $Fe(CO)_4(SiO)$. Thus the E_{int}s originated from the attractive steric interactions (E_{ster}s) (–70.0±5.0 kcal/mol) for $[Co(CO)_4]$←(L) rather than the repulsive E_{ster}s (40.0± 4.0 kcal/mol) for $Fe(CO)_5$ or $Fe(CO)_4(SiO)$, and stronger orbital interactions (E_{orb}s) (–185±10.0 kcal/mol) for $[Co(CO)_4]$←(L). The stronger E_{orb}s, nearly twice that of the E_{orb}s of $Fe(CO)_5$ or $Fe(CO)_4(SiO)$, mainly comes from the stronger σ donation instead of the weaker π* back donation.

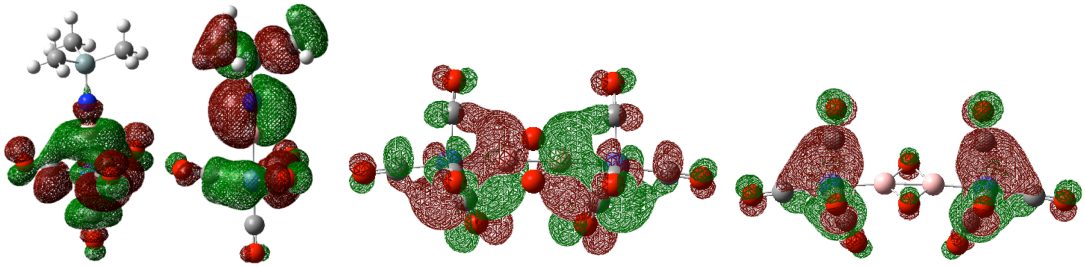
In the dimers (**SiO2-I** and **BO2-I**) and trimers (**SiO3-I** and **BO3-I**), the E_{int}s with respect to $[M_n(CO)_{4n}]$←(L) (M= Fe, Co; L = Si_nO_n, B_nO_n; n = 2, 3) increase further from –47.7 kcal/mol for $Fe(CO)_4(SiO)$ and –252.2 kcal/mol for $Co(CO)_4(BO)$ to –64.5±1.0 kcal/mol for $Fe_n(CO)_{4n}(Si_nO_n)$ and –264.7±1.0 for $Co_n(CO)_{4n}(B_nO_n)$, which mainly originat from the gradually increased σ donation of $[M_n(CO)_{4n}]$ ←(L) attributed to the more polarized Si-O/B-O bonds in the Si_nO_n/B_nO_n.



HOMO-12(-0.347) HOMO-13(-0.375) **BO2-ts** HOMO-14(-0.305) HOMO-17(-0.328) **BN2-ts**



LUMO (-0.104) HOMO+1(-0.244) **SiO1-I** LUMO (-0.107) HOMO (-0.259) **BO1-I**
(Si:43%,O:5%) (Si:3%,O:10%) (B:8%,O:1%) (B0%,O4%)



LUMO (-0.091) HOMO (-0.233) **BN1-I** LUMO (-0.099) HOMO (-0.241) **BO2-I**
(B:8%,N:1%) (B:7%,N:28%) (B:30%,O:0%) (B: 0%,O:1%)

Figure S4. Some important occupied orbitals for monomer, dimers, and transition states. The orbital energies are given in a. u. The partial atoms contribution are given in the sencond line parenthesis.

Table S4. The theoretical Cartesian coordinates (in Å) for the structure **SiO1-I** using the M06L/DZP method

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	26	0	0.000000	0.000000	0.250547
2	6	0	0.000000	1.580319	1.132656
3	6	0	0.000000	-1.580319	1.132656
4	6	0	1.814502	0.000000	0.216763
5	8	0	0.000000	2.582050	1.711786
6	8	0	-2.970630	0.000000	0.216246
7	8	0	0.000000	-2.582050	1.711786
8	8	0	0.000000	0.000000	-3.402140
9	8	0	2.970630	0.000000	0.216246
10	6	0	-1.814502	0.000000	0.216763
11	14	0	0.000000	0.000000	-1.881332

Sum of electronic and zero-point Energies= -2081.830214

Sum of electronic and thermal Free Energies= -2081.870280

Table S5. The theoretical Cartesian coordinates (in Å) for the structure **SiO1-II** using the M06L/DZP method

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	26	0	0.000000	0.000000	0.239874
2	6	0	0.000000	1.806312	0.224827
3	6	0	1.564312	-0.903156	0.224827
4	6	0	-1.564312	-0.903156	0.224827
5	6	0	0.000000	0.000000	2.035288
6	14	0	0.000000	0.000000	-1.913410
7	8	0	0.000000	2.965434	0.258949
8	8	0	0.000000	0.000000	-3.431121
9	8	0	-2.568141	-1.482717	0.258949
10	8	0	2.568141	-1.482717	0.258949
11	8	0	0.000000	0.000000	3.190824

Sum of electronic and zero-point Energies= -2081.823195

Sum of electronic and thermal Free Energies= -2081.863692

Table S6. The theoretical Cartesian coordinates (in Å) for the structure **BO1-I** using the M06L/DZP method

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	27	0	0.000000	0.000000	0.148017
2	6	0	0.000000	0.000000	1.967303
3	6	0	0.000000	1.789377	-0.092496
4	6	0	-1.549646	-0.894689	-0.092496
5	6	0	1.549646	-0.894689	-0.092496
6	8	0	-2.537819	-1.465211	-0.263291
7	8	0	0.000000	0.000000	3.118481
8	8	0	0.000000	2.930421	-0.263291
9	8	0	0.000000	0.000000	-2.988829
10	8	0	2.537819	-1.465211	-0.263291
11	5	0	0.000000	0.000000	-1.770718

Sum of electronic and zero-point Energies= -1936.279462

Sum of electronic and thermal Free Energies= -1936.318753

Table S7. The theoretical Cartesian coordinates (in Å) for the structure **BN1-I** using the M06L/DZP method

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	27	0	0.000000	0.000000	1.717281
2	6	0	0.000000	0.000000	3.532543
3	6	0	1.540242	-0.889259	1.434067
4	6	0	0.000000	1.778518	1.434067
5	6	0	-1.540242	-0.889259	1.434067
6	8	0	0.000000	2.914703	1.222114
7	8	0	0.000000	0.000000	4.685286
8	8	0	2.524207	-1.457352	1.222114
9	8	0	-2.524207	-1.457352	1.222114
10	5	0	0.000000	0.000000	-0.213007
11	7	0	0.000000	0.000000	-1.476840
12	14	0	0.000000	0.000000	-3.200905
13	6	0	1.531833	0.884404	-3.807040
14	1	0	2.444595	0.391827	-3.456810
15	1	0	1.571064	0.907054	-4.901639
16	1	0	1.561630	1.921168	-3.456810
17	6	0	-1.531833	0.884404	-3.807040
18	1	0	-1.571064	0.907054	-4.901639
19	1	0	-2.444595	0.391827	-3.456810
20	1	0	-1.561630	1.921168	-3.456810
21	6	0	0.000000	-1.768808	-3.807040
22	1	0	0.000000	-1.814108	-4.901639
23	1	0	0.882965	-2.312995	-3.456810
24	1	0	-0.882965	-2.312995	-3.456810

Sum of electronic and zero-point Energies= -1955.632736

Sum of electronic and thermal Free Energies= -1955.676345

Table S8. The theoretical Cartesian coordinates (in Å) for the structure **SiO2-I** using the M06L/DZP method

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	26	0	3.339134	0.000000	0.000000
2	26	0	-3.339134	0.000000	0.000000
3	6	0	-3.167682	1.797963	0.000000
4	6	0	-3.167682	-1.797963	0.000000
5	6	0	-4.330619	0.000000	1.512942
6	6	0	-4.330619	0.000000	-1.512942
7	6	0	4.330619	0.000000	1.512942
8	6	0	3.167682	1.797963	0.000000
9	6	0	4.330619	0.000000	-1.512942
10	6	0	3.167682	-1.797963	0.000000
11	8	0	-3.050733	2.949651	0.000000
12	8	0	-4.960701	0.000000	-2.484358
13	8	0	-4.960701	0.000000	2.484358
14	8	0	-3.050733	-2.949651	0.000000
15	8	0	4.960701	0.000000	2.484358
16	8	0	3.050733	2.949651	0.000000
17	8	0	4.960701	0.000000	-2.484358
18	8	0	3.050733	-2.949651	0.000000
19	14	0	-1.212371	0.000000	0.000000
20	14	0	1.212371	0.000000	0.000000
21	8	0	0.000000	1.174938	0.000000
22	8	0	0.000000	-1.174938	0.000000

Sum of electronic and zero-point Energies= -4163.778126

Sum of electronic and thermal Free Energies= -4163.837996

Table S9. The theoretical Cartesian coordinates (in Å) for the structure **BO2-I** using the M06L/DZP method

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	1.077333	0.000000	-0.220426
2	8	0	-1.077333	0.000000	-0.220426
3	5	0	0.000000	0.906373	-0.192416
4	5	0	0.000000	-0.906373	-0.192416
5	27	0	0.000000	-2.866711	-0.009959
6	27	0	0.000000	2.866711	-0.009959
7	6	0	0.000000	2.283118	1.675066
8	6	0	0.000000	4.665630	0.299313
9	6	0	-1.557436	2.786311	-0.922095
10	6	0	1.557436	2.786311	-0.922095
11	6	0	0.000000	-2.283118	1.675066
12	6	0	-1.557436	-2.786311	-0.922095
13	6	0	1.557436	-2.786311	-0.922095
14	6	0	0.000000	-4.665630	0.299313
15	8	0	0.000000	-1.878173	2.760831
16	8	0	2.560023	-2.729435	-1.492274
17	8	0	0.000000	-5.800820	0.500374
18	8	0	-2.560023	-2.729435	-1.492274
19	8	0	-2.560023	2.729435	-1.492274
20	8	0	2.560023	2.729435	-1.492274
21	8	0	0.000000	1.878173	2.760831
22	8	0	0.000000	5.800820	0.500374

Sum of electronic and zero-point Energies= -3872.612025

Sum of electronic and thermal Free Energies= -3872.670691

Table S10. The theoretical Cartesian coordinates (in Å) for the structure **BN2-I** using the M06L/DZP method

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	5	0	0.000000	0.923734	-0.059906
2	27	0	0.000000	2.973800	-0.187939
3	27	0	0.000000	-2.973800	-0.187939
4	6	0	0.000000	-2.498471	1.517425
5	6	0	1.479621	-2.832259	-1.209866
6	6	0	-1.479621	-2.832259	-1.209866
7	6	0	0.000000	2.498471	1.517425
8	6	0	1.479621	2.832259	-1.209866
9	6	0	-1.479621	2.832259	-1.209866
10	6	0	0.000000	4.779481	0.038432
11	8	0	0.000000	2.192438	2.640528
12	8	0	-2.415264	2.741517	-1.886570
13	8	0	0.000000	5.922406	0.203725
14	8	0	2.415264	2.741517	-1.886570
15	8	0	2.415264	-2.741517	-1.886570
16	8	0	-2.415264	-2.741517	-1.886570
17	8	0	0.000000	-2.192438	2.640528
18	8	0	0.000000	-5.922406	0.203725
19	7	0	1.119755	0.000000	-0.027698
20	7	0	-1.119755	0.000000	-0.027698
21	5	0	0.000000	-0.923734	-0.059906
22	14	0	2.848819	0.000000	0.324022
23	14	0	-2.848819	0.000000	0.324022
24	6	0	-3.252948	1.501946	1.364012
25	1	0	-2.689822	1.505325	2.303450
26	1	0	-3.070276	2.458055	0.864323
27	1	0	-4.317473	1.476472	1.626086
28	6	0	-3.252948	-1.501946	1.364012
29	1	0	-3.070276	-2.458055	0.864323
30	1	0	-2.689822	-1.505325	2.303450
31	1	0	-4.317473	-1.476472	1.626086
32	6	0	-3.863392	0.000000	-1.255227
33	1	0	-4.506688	-0.884026	-1.314025
34	1	0	-4.506688	0.884026	-1.314025
35	1	0	-3.235036	0.000000	-2.150648
36	6	0	3.863392	0.000000	-1.255227
37	1	0	4.506688	0.884026	-1.314025

38	1	0	4.506688	-0.884026	-1.314025
39	1	0	3.235036	0.000000	-2.150648
40	6	0	3.252948	-1.501946	1.364012
41	1	0	3.070276	-2.458055	0.864323
42	1	0	4.317473	-1.476472	1.626086
43	1	0	2.689822	-1.505325	2.303450
44	6	0	3.252948	1.501946	1.364012
45	1	0	3.070276	2.458055	0.864323
46	1	0	2.689822	1.505325	2.303450
47	1	0	4.317473	1.476472	1.626086
48	6	0	0.000000	-4.779481	0.038432

Sum of electronic and zero-point Energies= -4649.974668

Sum of electronic and thermal Free Energies= -4650.046306

Table S11. The theoretical Cartesian coordinates (in Å) for the structure **SiO3-I** using the M06L/DZP method

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	0.000000	1.501845	0.000000
2	8	0	-1.300636	-0.750922	0.000000
3	8	0	1.300636	-0.750922	0.000000
4	14	0	1.542345	0.890473	0.000000
5	14	0	-1.542345	0.890473	0.000000
6	14	0	0.000000	-1.780947	0.000000
7	26	0	3.394666	1.959911	0.000000
8	26	0	0.000000	-3.919823	0.000000
9	26	0	-3.394666	1.959911	0.000000
10	6	0	2.352729	3.434506	0.000000
11	6	0	4.255492	2.456910	1.509448
12	6	0	4.150734	0.320270	0.000000
13	6	0	4.255492	2.456910	-1.509448
14	6	0	1.798005	-3.754776	0.000000
15	6	0	0.000000	-4.913819	1.509448
16	6	0	-1.798005	-3.754776	0.000000
17	6	0	0.000000	-4.913819	-1.509448
18	6	0	-4.150734	0.320270	0.000000
19	6	0	-4.255492	2.456910	1.509448
20	6	0	-2.352729	3.434506	0.000000
21	6	0	-4.255492	2.456910	-1.509448
22	8	0	4.804495	2.773876	2.479032
23	8	0	1.680522	4.376991	0.000000
24	8	0	4.804495	2.773876	-2.479032
25	8	0	2.950324	-3.643870	0.000000
26	8	0	0.000000	-5.547753	-2.479032
27	8	0	0.000000	-5.547753	2.479032
28	8	0	-2.950324	-3.643870	0.000000
29	8	0	4.630846	-0.733121	0.000000
30	8	0	-4.630846	-0.733121	0.000000
31	8	0	-1.680522	4.376991	0.000000
32	8	0	-4.804495	2.773876	-2.479032
33	8	0	-4.804495	2.773876	2.479032

Sum of electronic and zero-point Energies= -6245.684092

Sum of electronic and thermal Free Energies= -6245.761151

Table S12. The theoretical Cartesian coordinates (in Å) for the structure **BO3-I** using the M06L/DZP method

Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	0.806190	1.097505	-0.031655
2	8	0	0.550409	-1.255020	-0.067023
3	8	0	-1.359288	0.142849	-0.060627
4	6	0	-2.971495	2.334588	-0.263230
5	6	0	-1.971211	4.814084	0.294888
6	6	0	-0.644370	2.876032	1.697887
7	6	0	-0.263529	3.399893	-1.300471
8	6	0	-3.166382	-1.791261	0.813245
9	6	0	-3.091033	-4.180812	-0.498379
10	6	0	-1.728105	-2.247091	-1.868841
11	6	0	-0.684720	-3.630594	0.674147
12	6	0	2.844024	-0.097865	1.744808
13	6	0	3.119784	-2.028585	-0.633081
14	6	0	3.406916	1.030174	-1.050830
15	6	0	5.170401	-0.516218	0.353720
16	8	0	-2.340964	5.897694	0.433533
17	8	0	-3.983827	1.825339	-0.485677
18	8	0	0.464070	3.568594	-2.184384
19	8	0	-3.900077	-1.159573	1.444442
20	8	0	0.174471	-4.181163	1.216351
21	8	0	-3.779719	-5.082791	-0.703663
22	8	0	-1.540297	-1.907693	-2.963589
23	8	0	-0.150227	2.707313	2.733786
24	8	0	2.475925	0.095600	2.828721
25	8	0	3.397894	1.945702	-1.756821
26	8	0	6.305198	-0.598657	0.542337
27	8	0	2.929732	-3.080530	-1.071082
28	5	0	1.381530	-0.154929	-0.034159
29	5	0	-0.562726	1.267919	-0.023991
30	5	0	-0.821166	-1.126953	-0.085800
31	27	0	3.374216	-0.378498	0.073121
32	27	0	-1.365891	3.106863	0.085829
33	27	0	-2.007556	-2.747397	-0.190960

Sum of electronic and zero-point Energies= -5808.984902

Sum of electronic and thermal Free Energies= -5809.061435

Table S13. The theoretical Cartesian coordinates (in Å) for the structure **BN3-I** using the M06L/DZP method

Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	27	0	1.582093	2.949805	0.451358
2	27	0	1.759422	-2.837487	0.474215
3	27	0	-3.343173	-0.099662	0.459316
4	6	0	1.392529	1.875615	1.893767
5	6	0	3.283188	3.481756	0.677174
6	6	0	1.478296	2.832705	-1.296037
7	6	0	0.684095	4.449615	0.928624
8	6	0	0.921388	-2.160559	1.930845
9	6	0	1.381923	-4.579269	0.686329
10	6	0	1.708826	-2.686895	-1.272987
11	6	0	3.506491	-2.806204	0.952969
12	6	0	-2.318225	0.286307	1.900630
13	6	0	-4.666228	1.093504	0.682711
14	6	0	-3.196479	-0.129793	-1.288485
15	6	0	-4.185564	-1.627243	0.951149
16	8	0	4.361064	3.880249	0.829028
17	8	0	1.291462	1.156328	2.795200
18	8	0	0.242897	5.471745	1.249982
19	8	0	0.351765	-1.740265	2.846642
20	8	0	4.609788	-2.945206	1.278962
21	8	0	1.197458	-5.714515	0.831309
22	8	0	1.790343	-2.789255	-2.444512
23	8	0	1.520372	2.944887	-2.467954
24	8	0	-1.648274	0.565425	2.802707
25	8	0	-3.323973	-0.149931	-2.459583
26	8	0	-4.851188	-2.513469	1.289467
27	8	0	-5.558729	1.817462	0.833862
28	7	0	-0.794316	1.248472	-0.724670
29	7	0	1.474577	0.066365	-0.720640
30	7	0	-0.684481	-1.308928	-0.724042
31	5	0	0.755632	-1.185834	-0.625679
32	5	0	-1.410222	-0.060457	-0.629343
33	5	0	0.649272	1.252956	-0.626557
34	14	0	-1.798844	2.814331	-0.809672
35	14	0	-1.533805	-2.963361	-0.810388
36	14	0	3.331734	0.148904	-0.812869
37	6	0	-1.822459	-3.619452	0.921407

38	1	0	-1.049395	-4.328846	1.225961
39	1	0	-1.866708	-2.836055	1.684287
40	1	0	-2.778791	-4.153228	0.950420
41	6	0	-0.660465	-4.251260	-1.866770
42	1	0	0.269043	-4.696825	-1.519533
43	1	0	-1.393538	-5.065644	-1.929743
44	1	0	-0.500454	-3.895164	-2.889063
45	6	0	-3.145303	-2.973105	-1.780200
46	1	0	-3.411337	-4.037643	-1.806723
47	1	0	-4.014012	-2.445896	-1.392483
48	1	0	-2.997120	-2.658961	-2.817740
49	6	0	4.051649	0.214828	0.916564
50	1	0	4.326571	1.229789	1.212323
51	1	0	3.377004	-0.183309	1.681117
52	1	0	4.966500	-0.386487	0.950173
53	6	0	4.140331	-1.243866	-1.787049
54	1	0	5.198316	-0.951213	-1.799816
55	1	0	4.103563	-2.265354	-1.414012
56	1	0	3.804427	-1.256387	-2.828278
57	6	0	4.007463	1.547318	-1.871928
58	1	0	3.927860	2.573115	-1.520018
59	1	0	5.078724	1.319804	-1.941858
60	1	0	3.610873	1.510007	-2.891127
61	6	0	-0.996720	4.222000	-1.769796
62	1	0	-1.779811	4.991708	-1.771175
63	1	0	-0.094353	4.699340	-1.393536
64	1	0	-0.822862	3.949554	-2.815140
65	6	0	-2.224924	3.391921	0.922032
66	1	0	-3.212456	3.053109	1.243539
67	1	0	-1.502738	3.064464	1.676353
68	1	0	-2.238159	4.487273	0.941429
69	6	0	-3.340122	2.704974	-1.879303
70	1	0	-4.198892	2.140115	-1.525738
71	1	0	-3.665764	3.749002	-1.967618
72	1	0	-3.107307	2.362061	-2.891976

Sum of electronic and zero-point Energies= -6974.938308

Sum of electronic and thermal Free Energies= -6975.024880

Table S14. The theoretical Cartesian coordinates (in Å) for the structure **SiO4-I** using the M06L/DZP method

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	1.299869	1.299869	0.000000
2	8	0	1.299869	-1.299869	0.000000
3	8	0	-1.299869	-1.299869	0.000000
4	8	0	-1.299869	1.299869	0.000000
5	14	0	2.148230	0.000000	0.538561
6	14	0	0.000000	-2.148230	-0.538561
7	14	0	0.000000	2.148230	-0.538561
8	14	0	-2.148230	0.000000	0.538561
9	26	0	0.000000	-3.941056	-1.713882
10	26	0	0.000000	3.941056	-1.713882
11	26	0	-3.941056	0.000000	1.713882
12	26	0	3.941056	0.000000	1.713882
13	6	0	1.796096	3.782531	-1.630863
14	6	0	0.000000	3.942347	-3.520732
15	6	0	-1.796096	3.782531	-1.630863
16	6	0	0.000000	5.603986	-0.998306
17	6	0	-3.942347	0.000000	3.520732
18	6	0	-3.782531	1.796096	1.630863
19	6	0	-5.603986	0.000000	0.998306
20	6	0	-3.782531	-1.796096	1.630863
21	6	0	-1.796096	-3.782531	-1.630863
22	6	0	0.000000	-3.942347	-3.520732
23	6	0	0.000000	-5.603986	-0.998306
24	6	0	1.796096	-3.782531	-1.630863
25	6	0	3.782531	-1.796096	1.630863
26	6	0	3.942347	0.000000	3.520732
27	6	0	5.603986	0.000000	0.998306
28	6	0	3.782531	1.796096	1.630863
29	8	0	3.656117	-2.946599	1.581099
30	8	0	6.666551	0.000000	0.538688
31	8	0	3.935079	0.000000	4.679241
32	8	0	3.656117	2.946599	1.581099
33	8	0	2.946599	3.656117	-1.581099
34	8	0	0.000000	3.935079	-4.679241
35	8	0	-2.946599	3.656117	-1.581099
36	8	0	0.000000	6.666551	-0.538688
37	8	0	2.946599	-3.656117	-1.581099

38	8	0	0.000000	-6.666551	-0.538688
39	8	0	0.000000	-3.935079	-4.679241
40	8	0	-2.946599	-3.656117	-1.581099
41	8	0	-3.656117	-2.946599	1.581099
42	8	0	-3.935079	0.000000	4.679241
43	8	0	-6.666551	0.000000	0.538688
44	8	0	-3.656117	2.946599	1.581099

Sum of electronic and zero-point Energies= -8327.640941

Sum of electronic and thermal Free Energies= -8327.733733

Table S15. The theoretical Cartesian coordinates (in Å) for the structure **BO4-I** using the M06L/DZP method

Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-1.187788	1.185616	-0.279943
2	8	0	-1.187788	-1.185616	-0.279943
3	8	0	1.187788	-1.185616	-0.279943
4	8	0	1.187788	1.185616	-0.279943
5	6	0	-1.529109	2.362195	2.233964
6	6	0	0.000000	4.594670	2.667671
7	6	0	1.529109	2.362195	2.233964
8	6	0	0.000000	3.897825	0.032343
9	6	0	5.040858	0.000000	-2.639832
10	6	0	3.883672	-1.550740	-0.719873
11	6	0	2.325609	0.000000	-2.867792
12	6	0	3.883672	1.550740	-0.719873
13	6	0	-1.529109	-2.362195	2.233964
14	6	0	0.000000	-3.897825	0.032343
15	6	0	0.000000	-4.594670	2.667671
16	6	0	1.529109	-2.362195	2.233964
17	6	0	-3.883672	1.550740	-0.719873
18	6	0	-5.040858	0.000000	-2.639832
19	6	0	-2.325609	0.000000	-2.867792
20	6	0	-3.883672	-1.550740	-0.719873
21	8	0	-4.066615	2.555462	-0.177908
22	8	0	-1.521044	0.000000	-3.704617
23	8	0	-5.975186	0.000000	-3.316400
24	8	0	-4.066615	-2.555462	-0.177908
25	8	0	-2.502987	1.857497	2.600337
26	8	0	0.000000	5.546486	3.318779
27	8	0	2.502987	1.857497	2.600337
28	8	0	0.000000	4.419489	-1.005257
29	8	0	2.502987	-1.857497	2.600337
30	8	0	0.000000	-5.546486	3.318779
31	8	0	0.000000	-4.419489	-1.005257
32	8	0	-2.502987	-1.857497	2.600337
33	8	0	4.066615	2.555462	-0.177908
34	8	0	5.975186	0.000000	-3.316400
35	8	0	1.521044	0.000000	-3.704617
36	8	0	4.066615	-2.555462	-0.177908
37	5	0	1.769150	0.000000	-0.627761

38	5	0	0.000000	1.645052	0.212153
39	5	0	0.000000	-1.645052	0.212153
40	5	0	-1.769150	0.000000	-0.627761
41	27	0	3.552427	0.000000	-1.589930
42	27	0	0.000000	3.104431	1.617153
43	27	0	-3.552427	0.000000	-1.589930
44	27	0	0.000000	-3.104431	1.617153

Sum of electronic and zero-point Energies= -7745.303379

Sum of electronic and thermal Free Energies= -7745.398613

Table S16. The theoretical Cartesian coordinates (in Å) for the structure **SiO5-I** using the M06L/DZP method

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	1.638196	-0.091474	0.002256
2	8	0	0.764493	2.178901	0.846429
3	8	0	-1.599282	1.389591	0.141742
4	8	0	-1.582107	-1.156311	-0.125703
5	8	0	0.617097	-2.290808	-0.860605
6	14	0	-0.786546	-2.586011	-0.051546
7	14	0	-2.612508	0.114299	-0.014952
8	14	0	1.955323	1.083474	1.109033
9	14	0	1.888692	-1.282731	-1.105738
10	14	0	-0.597006	2.681195	0.076530
11	26	0	-4.755993	0.131254	-0.088212
12	26	0	-1.369016	-4.441571	0.855833
13	26	0	3.512395	-1.532779	-2.485146
14	26	0	3.569967	1.233977	2.511857
15	26	0	-0.959605	4.609793	-0.791419
16	6	0	2.728175	2.739152	3.053069
17	6	0	5.071993	2.113305	2.022111
18	6	0	3.613800	0.561244	4.192002
19	6	0	4.113686	-0.305673	1.765856
20	6	0	4.940993	-2.519540	-1.981228
21	6	0	4.155808	-0.043139	-1.716688
22	6	0	3.620351	-0.844545	-4.155806
23	6	0	0.615117	5.050944	-0.023444
24	6	0	-2.402837	3.810430	-1.509769
25	6	0	-1.924015	5.836713	0.126515
26	6	0	-0.408310	5.201760	-2.407672
27	6	0	-4.602439	1.812218	0.545101
28	6	0	-5.807299	-0.384920	1.291861
29	6	0	-4.576344	-1.563052	-0.669965
30	6	0	-5.634565	0.682228	-1.571374
31	6	0	-2.467559	-5.563101	-0.045991
32	6	0	-2.715880	-3.483278	1.563363
33	6	0	-0.880257	-5.066097	2.480066
34	6	0	0.142058	-5.076244	0.096268
35	6	0	2.586281	-2.972451	-3.065726
36	8	0	-3.314999	3.267372	-1.978641
37	8	0	-0.052061	5.577371	-3.444047

38	8	0	-2.553081	6.609259	0.715964
39	8	0	1.631824	5.312829	0.466024
40	8	0	4.544680	0.912912	-1.183110
41	8	0	3.685958	-0.401394	-5.224011
42	8	0	5.850971	-3.145555	-1.634676
43	8	0	1.986680	-3.888711	-3.441460
44	8	0	6.029661	2.669171	1.684919
45	8	0	3.639690	0.126674	5.265357
46	8	0	2.175549	3.698060	3.393378
47	8	0	4.436141	-1.292571	1.244214
48	8	0	-3.567765	-2.842325	2.022175
49	8	0	1.119612	-5.468046	-0.385547
50	8	0	-0.563789	-5.464482	3.520760
51	8	0	-3.181194	-6.265298	-0.626622
52	8	0	-4.484280	2.888346	0.960698
53	8	0	-6.178641	1.054688	-2.523119
54	8	0	-6.468081	-0.733700	2.176291
55	8	0	-4.428449	-2.654048	-1.036864

Sum of electronic and zero-point Energies= -10409.556782

Sum of electronic and thermal Free Energies= -10409.668914

Table S17. The theoretical Cartesian coordinates (in Å) for the structure **BO5-I** using the M06L/DZP method

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-0.746743	-1.174262	0.576793
2	8	0	-1.756043	0.057673	-1.130509
3	8	0	-0.557180	2.065520	-0.601768
4	8	0	1.286266	0.605242	-0.781068
5	8	0	1.608202	-1.306706	0.541217
6	6	0	-2.054180	-2.044878	-2.957324
7	6	0	-3.522616	-2.111139	-0.281956
8	6	0	-3.239055	-4.285903	-1.925327
9	6	0	-0.895527	-3.702834	-0.626167
10	6	0	0.526978	-1.838573	5.031990
11	6	0	-1.263137	-2.433617	3.007901
12	6	0	0.575914	-0.021957	2.972503
13	6	0	-4.190891	1.293933	-1.603441
14	6	0	-2.608140	3.832949	-0.809811
15	6	0	-5.000514	3.097935	0.288666
16	6	0	-2.946132	1.526788	1.196038
17	6	0	1.721928	3.630647	-1.533373
18	6	0	2.944699	4.837596	0.577913
19	6	0	2.991947	2.126143	0.895677
20	6	0	0.461916	3.808586	1.230524
21	6	0	4.267737	-1.667430	-0.138447
22	6	0	3.857381	0.570590	-2.126946
23	6	0	4.708796	-1.951147	-2.820745
24	6	0	2.030470	-1.878606	-2.325170
25	6	0	1.722408	-2.940736	2.829433
26	8	0	-2.023155	4.782297	-1.115342
27	8	0	-2.592456	0.989873	2.164902
28	8	0	-5.967955	3.590357	0.678168
29	8	0	-4.636998	0.609694	-2.422477
30	8	0	-2.332557	-2.831273	2.822086
31	8	0	0.661990	1.121416	2.761481
32	8	0	0.607834	-1.870585	6.182146
33	8	0	2.543637	-3.707861	2.561194
34	8	0	-4.305663	-1.592731	0.401042
35	8	0	-3.843542	-5.199295	-2.286032
36	8	0	-1.900887	-1.507823	-3.968514
37	8	0	0.022126	-4.184696	-0.107113

38	8	0	4.056170	1.681102	-2.382128
39	8	0	1.039863	-2.333721	-2.734655
40	8	0	5.452648	-2.472571	-3.531273
41	8	0	4.746510	-1.968196	0.868350
42	8	0	1.578182	3.795659	-2.673105
43	8	0	-0.490697	4.044259	1.840697
44	8	0	3.607031	5.756985	0.792507
45	8	0	3.643374	1.253274	1.295623
46	5	0	-1.719014	1.366471	-0.734919
47	5	0	-1.462517	-1.150135	-0.583341
48	5	0	0.781725	1.815634	-0.447506
49	5	0	0.420166	-1.378133	1.226727
50	5	0	1.980434	-0.534821	-0.525115
51	27	0	-3.462363	2.318377	-0.306286
52	27	0	1.907956	3.382281	0.216679
53	27	0	3.512725	-1.152960	-1.701852
54	27	0	0.407993	-1.760716	3.215725
55	27	0	-2.297552	-2.835655	-1.349771

Sum of electronic and zero-point Energies= -9681.651766

Sum of electronic and thermal Free Energies= -9681.759257

Complete Gaussian 09 reference (Reference 48)

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