Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

The Use of Main-Group Elements to Mimic Catalytic Behavior of Transition Metals I: Reduction of Dinitrogen to Ammonia Catalyzed by Bis(Lewis Base)Borylenes

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Table S1. Molecular Orbital Energies (in eV), HOMO-LUMO Gap (in eV), and Singlet−triplet Energy Splitting (ΔE_{ST}, in kcal mol^{-1}) Computed at the B3LYP/6-311+G** Level of Theory for Borylene Molecules B−R

R	HOMO(eV)	LUMO(eV)	LUMO+1(eV)	Gap_{H-L}(eV)	ΔE_{ST}(kcal/mol)
F	-7.74	-1.16	-1.16	6.58	78.75
Cl	-7.34	-2.12	-2.12	5.22	53.59
Br	-7.24	-2.29	-2.29	4.94	49.44
Me_3Si	-5.19	-2.36	-2.36	2.82	8.25

Table S2. The FMO energies of the three bis(Lewis base) borylene in their triplet ground state have been calculated by using DFT-B3LYP functional with 6-311G** basis

SOL	HOMO(eV)		LUMO(eV)		LUMO+1(eV)		Gap_{H-L}(eV)		ΔE(kcal/mol)
	α	β	α	β	α	β	α	β	
C-B-C	-5.78	-5.80	-3.37	-3.69	-0.81	-2.89	2.41	2.11	13.50
Si-B-Si	-5.80	-7.15	-1.53	-3.11	-1.39	-2.63	4.27	4.03	12.70
P-B-P	-6.01	-7.45	-1.92	-3.16	-1.71	-3.01	4.08	4.29	4.60
Gas	HOMO(eV)		LUMO(eV)		LUMO+1(eV)		Gap_{H-L}(eV)		ΔE(kcal/mol)
	α	β	α	β	α	β	α	β	
C-B-C	-8.22	-8.02	-6.57	-6.95	-3.62	-6.24	1.65	1.07	9.20
Si-B-Si	-7.96	-9.43	-3.84	-5.29	-3.68	-4.67	4.12	4.14	13.23
P-B-P	-8.62	-9.85	-4.39	-5.70	-4.16	-5.60	4.23	4.16	8.38

Table S3. The NPA on the charge transfer the B center, N_2, and the bis(Lewis base)borylene ligand L in the bis(Lewis base)borylene-dinitrogen compounds studied here.

Parameters	$n_{\pi(B\rightarrow N2)}$	$n_{\pi(N2\rightarrow B)}$	$n_{\sigma(N2\rightarrow B)}$	$n_{N2,\ excess}$	n_B	n_{formal}	$n_{B,\ excess}$	n_L
2	0.444	0.074	0.426	-0.056	4.031	2	2.031	1.975
3	0.519	0.091	0.420	0.008	3.536	2	1.536	1.544

The Yoshizawa's equation was employed to further describe the electron transfer among the B center, the N_2 moiety, and the bis(Lewis base) ligands (L). The number of electrons (n_L) transferred from L to B center can be calculated by eq. 1:

$$n_L = n_{B,\,excess} + n_{N2,\,excess} \quad (1)$$

where $n_{B,\,excess}$and $n_{N2,\,excess}$ are defined by

$$n_{B,\,excess} = n_B - n_{B,formal} \quad (2)$$

$$n_{N2,\,excess} = n_{\pi(B\rightarrow N2)} - n_{\pi(N2\rightarrow B)} - n_{\sigma(N2\rightarrow B)} \quad (3)$$

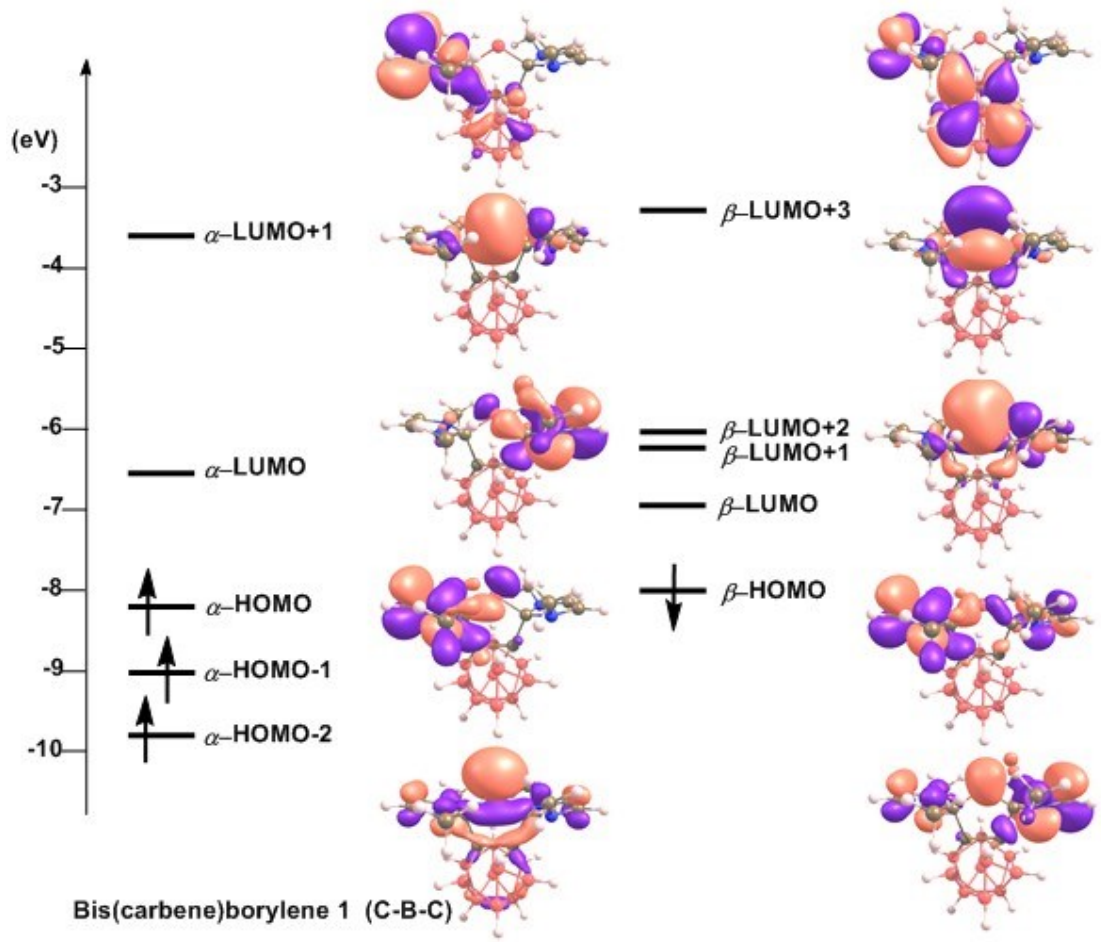
As shown in eq. 2, n_B is defined as the number of valence electrons of the B center, and nformal is the number of valence electrons of the B center with the formal charge. The excess electrons of the B center ($n_{B,\,excess}$) are thus expressed by the value of $n_B - n_{B,formal}$. As mentioned above, the number of electrons on the bonding N_2 moiety is determined by $\pi(B\rightarrow N_2)$, $\pi(N2\rightarrow B)$, and $\sigma(N_2\rightarrow B)$ electron transfer processes in the series of bis(Lewis base)borylene-dinitrogen compounds studied here. The number of electrons transferred of these processes was defined as $n_{\pi(B\rightarrow N2)}$, $n_{\pi(N2\rightarrow B)}$, and $n_{\sigma(N2\rightarrow B)}$ in eq. 3, respectively. And thus the excess electrons of the N_2 moiety ($n_{N2,\,excess}$) can be roughly estimated by using the value of $n_{\pi(B\rightarrow N2)} - n_{\pi(N2\rightarrow B)} - n_{\sigma(N2\rightarrow B)}$.

Table S4. The calculated adsorption energy ΔG value of reaction intermediates(ΔG, in kcal mol^{-1})

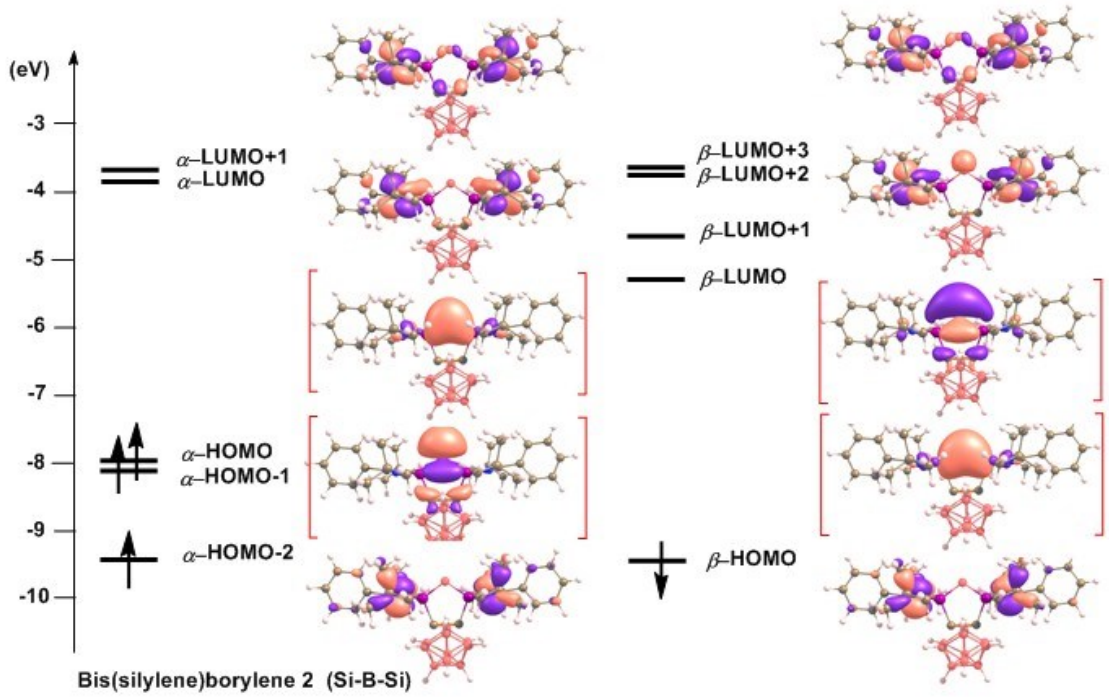
	$\Delta G_{(*N2H)}$	$\Delta G_{(*NH2)}$	$\Delta G_{(*NH3)}$
C-B-C	-67.73	-123.35	-46.26
Si-B-Si	-53.28	-96.15	-37.90
P-B-P	-57.43	-95.62	-35.29

Table S5. The calculated valence shell atomic orbitals population of B atoms

	$2p_x$	$2p_y$	$2p_z$
C-B-C	0.321	0.099	0.603
Si-B-Si	1.056	0.711	0.861
P-B-P	0.738	0.804	0.778



Bis(carbene)borylene 1 (C-B-C)



Bis(silylene)borylene 2 (Si-B-Si)

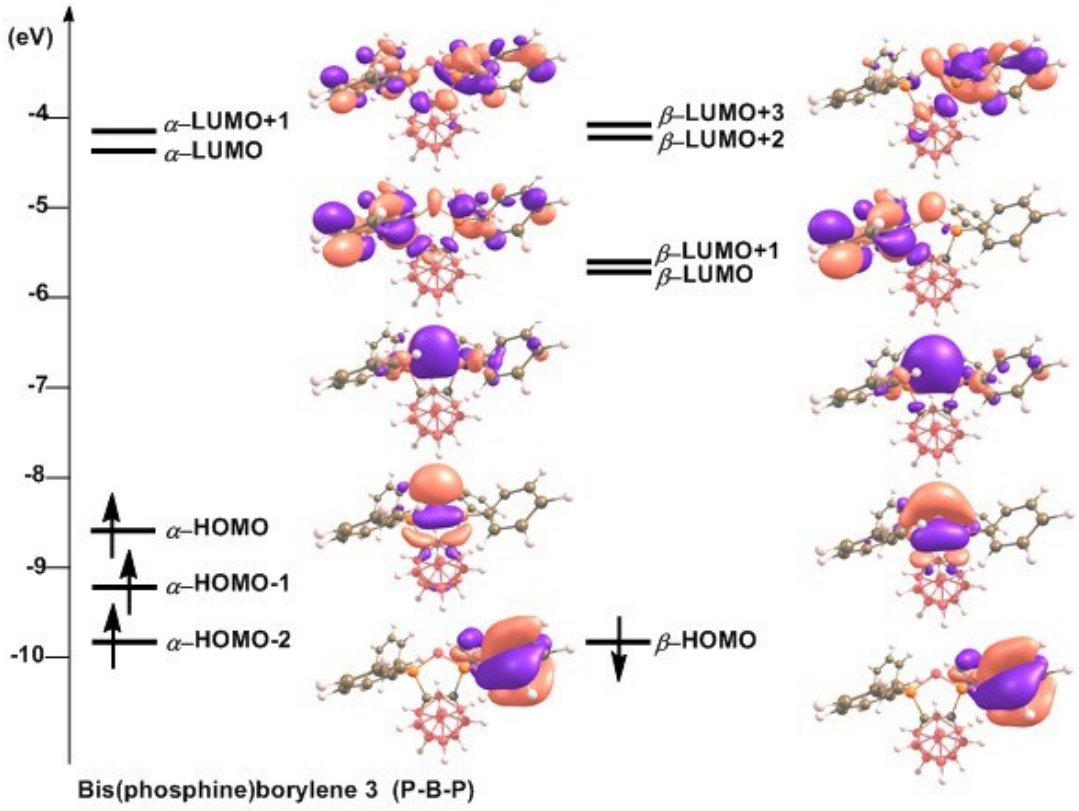


Figure S1. Frontier molecular orbitals of the *o*-carborane-based bis(Lewis base) borylene, **1**, **2**, and **3**, in triplet ground state, highlighting the two nearly degenerate SOMOs

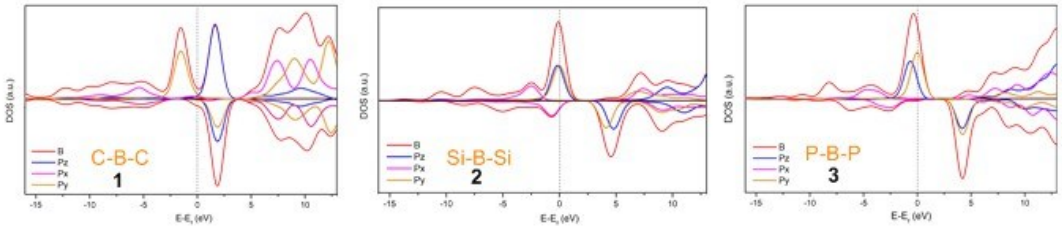


Figure S2. Projected electronic densities of states (PDOS) for boron orbitals of bis(Lewis base) borylene, **1**, **2**, and **3**, in triplet ground state. The top represents the alpha orbital, and the bottom represents the beta orbital.

Xyz coordinates

1

Atomic	Coordinates (Angstroms)		
	X	Y	Z
C	-0.73089100	0.95263600	-0.04622000
C	0.91185900	0.79112800	-0.03507000
B	0.13508600	1.27216000	-1.49250900
H	0.06744800	0.49390500	-2.36385500
B	-1.22186600	2.29193300	-1.00025600
H	-2.23517300	2.19526200	-1.60365900
B	-1.22098100	2.37720500	0.77140200
H	-2.23598400	2.33562000	1.37972600
B	0.13361100	1.40812500	1.36414700
H	0.05521800	0.70717500	2.29793200
B	1.66053900	2.00843100	-0.98033300
H	2.64316700	1.71101600	-1.57074400
B	0.30927700	3.00767000	-1.59167400
H	0.36891300	3.52831700	-2.65504200
B	-0.52861100	3.70999200	-0.17829200
H	-1.07427800	4.76087400	-0.23085600
B	0.30528000	3.14786800	1.29958700
H	0.36025700	3.76672100	2.30932400
B	1.66011400	2.09436200	0.79132000
H	2.64452600	1.85938600	1.40663600
B	1.25042600	3.53538300	-0.16642900
H	1.99218400	4.45885900	-0.20943300
B	-0.14490700	-1.46774600	0.08817700
N	2.23005300	-1.15333400	-1.07407100
N	2.18165900	-1.05547900	1.18762000
C	1.31737100	-0.74832100	0.01505300
C	3.45263700	-1.49357400	-0.58730600
C	3.41339100	-1.47030200	0.77943100
H	4.17658200	-1.76171800	1.48531100
H	4.26655500	-1.77418500	-1.23953700
N	-2.34816200	-0.70956100	-1.09808000
N	-2.41339800	-0.53921300	1.17148700
C	-1.43516300	-0.47506100	0.06568500
C	-3.64218500	-0.79954100	-0.66471000
C	-3.68271300	-0.64873800	0.69170700
H	-4.54053900	-0.63924900	1.34849500
H	-4.45372400	-1.00255400	-1.34763500
C	-2.01174700	-1.31113700	-2.39326000

H	-1.09502300	-0.89448000	-2.79411100
H	-1.92292900	-2.40268800	-2.32123100
H	-2.82359000	-1.07152200	-3.08447400
C	-2.09013900	-0.76189900	2.56695600
H	-1.25657300	-1.47488700	2.62152900
H	-1.81075300	0.15585500	3.08969400
H	-2.96127700	-1.19969600	3.06001900
C	1.82949800	-1.44784200	-2.43719000
H	1.76258300	-0.55083100	-3.05787600
H	2.56348500	-2.12772300	-2.87536000
H	0.85221500	-1.94410100	-2.41728400
C	1.85795900	-1.04173800	2.61465800
H	2.46460400	-1.80711000	3.10556200
H	2.07959100	-0.06879600	3.06210400
H	0.81094600	-1.28867000	2.77335100
N	-0.29205300	-2.86127100	0.06213200
N	-0.43346000	-3.99048000	0.02052900

2

Atomic	Coordinates (Angstroms)		
	X	Y	Z
Si	1.56209200	0.00008600	-0.15218400
Si	-1.56201900	0.00001200	-0.15244400
N	3.05340000	-1.08432800	-0.31931000
N	3.05346400	1.08459300	-0.31755000
N	-3.05330600	-1.08441600	-0.31956400
N	-3.05337400	1.08450200	-0.31789600
C	0.85134200	-0.00108300	1.63251500
C	-0.85152300	-0.00112200	1.63237400
C	3.36937400	-2.53044600	-0.57219400
C	3.65231300	-2.73726800	-2.07322000
H	4.55471300	-2.21044600	-2.39270100
H	3.80223800	-3.80291500	-2.27609400
H	2.80868000	-2.39317100	-2.68198600
C	4.55590900	-3.01122800	0.28311200
H	5.50403600	-2.56958800	-0.02677500
H	4.39058700	-2.78528200	1.34174000
H	4.64661600	-4.09767300	0.18109400
C	2.12989200	-3.34756100	-0.18415600
H	1.24094500	-3.01048800	-0.72746500
H	2.30005300	-4.39804400	-0.43851300
H	1.93554500	-3.28949600	0.88920800
C	3.84669000	0.00019000	-0.43886700

C	5.32607800	0.00033000	-0.61199200
C	5.91674100	0.00121200	-1.88332600
H	5.29782500	0.00178700	-2.77512800
C	7.30778400	0.00137600	-2.00362800
H	7.75983700	0.00209200	-2.99078000
C	8.11155700	0.00062500	-0.86243700
H	9.19299500	0.00075900	-0.95973500
C	7.52381100	-0.00028500	0.40535600
H	8.14504800	-0.00088700	1.29583900
C	6.13577600	-0.00041900	0.53459000
H	5.68027900	-0.00112200	1.52025400
C	3.36937500	2.53098900	-0.56899900
C	4.55649300	3.01069500	0.28609800
H	4.64711200	4.09727000	0.18539400
H	4.39188400	2.78340400	1.34454900
H	5.50443200	2.56947600	-0.02496500
C	3.65131300	2.73956700	-2.06997500
H	3.80148300	3.80541100	-2.27162200
H	4.55328000	2.21281300	-2.39079000
H	2.80709600	2.39656900	-2.67855200
C	2.13024900	3.34782800	-0.17921100
H	2.30047700	4.39858300	-0.43239900
H	1.24094000	3.01160900	-0.72245100
H	1.93647400	3.28849800	0.89418700
C	-3.36931100	-2.53054800	-0.57245200
C	-3.65223500	-2.73736000	-2.07348400
H	-3.80214700	-3.80300400	-2.27638200
H	-4.55464500	-2.21054400	-2.39295700
H	-2.80860400	-2.39325300	-2.68222700
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H	-2.29994700	-4.39815400	-0.43890100
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H	-1.93562200	-3.28975300	0.88897700
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H	-4.39057300	-2.78534600	1.34145100
H	-5.50398400	-2.56963700	-0.02709000
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C	-5.32602800	0.00026000	-0.61202900
C	-5.91686700	0.00117700	-1.88328400
H	-5.29807600	0.00172100	-2.77517400
C	-7.30793000	0.00147800	-2.00339300
H	-7.76012100	0.00225200	-2.99048400
C	-8.11154400	0.00086200	-0.86209000

H	-9.19299600	0.00113900	-0.95923300
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H	-8.14473400	-0.00053600	1.29618800
C	-6.13556500	-0.00037100	0.53466200
H	-5.67992700	-0.00104600	1.52026000
C	-3.36930600	2.53087800	-0.56940700
C	-2.13015400	3.34776100	-0.17978100
H	-2.30045600	4.39850900	-0.43294800
H	-1.93624200	3.28843800	0.89359000
H	-1.24089700	3.01158900	-0.72313500
C	-3.65135900	2.73934900	-2.07038000
H	-4.55338400	2.21262000	-2.39107300
H	-3.80148200	3.80518300	-2.27210100
H	-2.80721400	2.39625000	-2.67900200
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H	-5.50433900	2.56945400	-0.02523800
H	-4.39169900	2.78340500	1.34419100
H	-4.64695200	4.09722700	0.18499400
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H	2.44762500	1.49407700	2.82200600
B	-0.00014600	1.42245900	2.08779500
H	-0.00008700	2.33506400	1.34784500
B	-1.44312900	-0.88663800	2.97127000
H	-2.44795400	-1.49758900	2.82000600
B	-0.00021600	-1.44988300	3.85082400
H	-0.00025500	-2.48788000	4.42575100
B	0.88997100	-0.00258200	4.41149900
H	1.53698500	-0.00312500	5.40611200
B	-0.00026800	1.44525600	3.85240000
H	-0.00033300	2.48266400	4.42838700
B	-1.44316800	0.88294900	2.97227100
H	-2.44802300	1.49398100	2.82163600
B	-0.89052900	-0.00261300	4.41136600
H	-1.53771200	-0.00317800	5.40587100
B	0.00012300	0.00093100	-1.25093900
N	0.00027400	0.00242300	-2.66258700
N	0.00039600	0.00366500	-3.79049200

3

Atomic	Coordinates (Angstroms)		
	X	Y	Z
P	1.59291900	-0.05263300	-0.38711200
P	-1.58280800	-0.04909700	-0.30269600
B	0.02026700	1.43370300	1.81252500
H	-0.01822100	2.31248100	1.02538700
B	-1.38619600	0.85146100	2.74628000
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B	-1.33208800	-0.92833100	2.77898200
H	-2.32030100	-1.56703500	2.65779700
B	0.11736100	-1.44474600	1.87271400
H	0.15501300	-2.35803900	1.13011300
B	1.56014900	-0.83421200	2.71444300
H	2.57782600	-1.41114700	2.53548000
B	1.49248200	0.94221300	2.68471100
H	2.46329700	1.59030100	2.51671500
B	0.05467700	1.47321300	3.57997500
H	0.03451400	2.51808100	4.13883900
B	-0.77370700	0.00509200	4.18358000
H	-1.40143700	0.00471700	5.18897400
B	0.15116600	-1.42623100	3.63325000
H	0.19636700	-2.45186400	4.22561100
B	1.00237400	0.06162800	4.14539000
H	1.67392000	0.10424300	5.12121000
C	-0.79595500	-0.04575700	1.42159000
C	0.89852700	0.00764700	1.37972800
C	2.54350400	1.48440800	-0.70926800
C	3.63185200	1.90215000	0.07875500
H	3.92811200	1.34610700	0.96039700
C	4.33867900	3.05395500	-0.26335700
H	5.17142000	3.37404600	0.35542100
C	3.97865600	3.79196800	-1.39395500
H	4.53425900	4.68717900	-1.65671300
C	2.90654700	3.37759100	-2.18500200
H	2.62629500	3.94461100	-3.06754400
C	2.18825700	2.23098300	-1.84432200
H	1.35398200	1.91463400	-2.46316900
C	2.71954300	-1.48618600	-0.58489700
C	2.15861200	-2.74161100	-0.88216900
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C	2.98249000	-3.85107800	-1.06265900
H	2.54081100	-4.81517800	-1.29535800

C	4.36843400	-3.71995000	-0.95379200
H	5.00882900	-4.58505700	-1.09758000
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H	6.00966500	-2.36382800	-0.60499100
C	4.11607600	-1.35677200	-0.49614800
H	4.57550600	-0.39410500	-0.30995000
C	-2.81299900	-1.39180500	-0.54257200
C	-2.62137100	-2.69129800	-0.04148400
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C	-3.53069200	-3.70016100	-0.35196800
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C	-4.62251700	-3.43533300	-1.18246300
H	-5.32573700	-4.22645400	-1.42480000
C	-4.80460300	-2.15435300	-1.70321800
H	-5.64586200	-1.94255900	-2.35606500
C	-3.90936600	-1.13215200	-1.38522800
H	-4.07070400	-0.14178500	-1.79514700
C	-2.51433400	1.52093900	-0.46406400
C	-3.74250400	1.70496700	0.19761300
H	-4.16485200	0.91414200	0.80948200
C	-4.42911700	2.90943100	0.06072300
H	-5.37502700	3.04984900	0.57485500
C	-3.90378000	3.93070300	-0.73707600
H	-4.44498200	4.86616600	-0.84355400
C	-2.68868300	3.74917200	-1.39939500
H	-2.28300500	4.53981200	-2.02317100
C	-1.99242400	2.54739900	-1.26413500
H	-1.04669200	2.40467500	-1.77788200
B	-0.02195400	-0.23874800	-1.33012900
N	-0.06777900	-0.69881900	-2.65729500
N	-0.10490600	-1.07408200	-3.72213900