Carboranes as Lewis acids: Tetrel bonding in $CB_{11}H_{11}$ carbonium ylide

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SUPPLEMENTARY INFORMATION

Tables S1-S10. G4MP2 optimized geometries of (**1**) and complexes (**1**:***n***), *n* = 2-19, in cartesian coordinates (Å).

Table S1. (1) and (1:2)

$CB_{11}H_{11} \rightarrow$ (**1**) C_{5v}				$CB_{11}H_{12} \rightarrow H_{11}B_{11}C{:}H^{(-)} \rightarrow$ (**1**:**2**) C_{5v}			
Atom	X	Y	Z	Atom	X	Y	Z
C	0.000000	0.000000	1.324811	C	0.000000	0.000000	1.519851
B	-0.905846	1.246790	0.790301	B	0.000000	1.513716	0.734859
B	0.905846	1.246790	0.790301	B	1.439630	0.467764	0.734859
B	0.000000	1.539372	-0.731296	B	0.894246	1.230824	-0.770024
B	0.000000	0.000000	-1.604616	B	0.000000	0.000000	-1.703878
B	-0.904820	-1.245378	-0.731296	B	-1.446921	-0.470133	-0.770024
B	0.904820	-1.245378	-0.731296	B	0.000000	-1.521382	-0.770024
B	0.000000	-1.541117	0.790301	B	-0.889740	-1.224622	0.734859
B	1.465689	-0.476231	0.790301	B	0.889740	-1.224622	0.734859
B	-1.464030	0.475692	-0.731296	B	-0.894246	1.230824	-0.770024
H	-2.494485	0.810507	-1.204847	H	-1.526687	2.101304	-1.278248
H	2.374258	-0.771443	1.483631	H	1.470755	-2.024321	1.392843
H	0.000000	0.000000	-2.794830	H	0.000000	0.000000	2.601106
H	0.000000	2.622857	-1.204847	H	0.000000	0.000000	-2.894656
H	0.000000	-2.496442	1.483631	H	1.526687	2.101304	-1.278248
H	1.541677	-2.121936	-1.204847	H	-1.470755	-2.024321	1.392843
H	1.467372	2.019664	1.483631	H	0.000000	-2.597355	-1.278248
H	-1.541677	-2.121936	-1.204847	H	2.379732	0.773222	1.392843
H	-1.467372	2.019664	1.483631	H	-2.470231	-0.802627	-1.278248
B	1.464030	0.475692	-0.731296	H	0.000000	2.502199	1.392843
B	-1.465689	-0.476231	0.790301	B	1.446921	-0.470133	-0.770024
H	2.494485	0.810507	-1.204847	B	-1.439630	0.467764	0.734859
H	-2.374258	-0.771443	1.483631	H	2.470231	-0.802627	-1.278248
				H	-2.379732	0.773222	1.392843

Table S2. CH_2 (**1**:**3**) and CF_2 (**1**:**4**)

$H_{11}B_{11}C:CH_2 \rightarrow$ (**1**:**3**) C_s				$H_{11}B_{11}C:CF_2 \rightarrow$ (**1**:**4**) C_s			
Atom	X	Y	Z	Atom	X	Y	Z
C	0.626762	1.097131	0.000000	C	0.022740	0.681191	0.000000
B	-0.882355	0.950438	0.944964	B	-1.238974	-0.100181	0.926397
B	-0.882355	0.950438	-0.944964	B	-1.238974	-0.100181	-0.926397
B	-1.805471	-0.211815	0.000000	B	-1.539665	-1.572288	0.000000
B	-0.877445	-1.757287	0.000000	B	-0.025034	-2.530985	0.000000
B	0.650961	-1.493350	0.910660	B	1.219819	-1.616971	0.905824
B	0.650961	-1.493350	-0.910660	B	1.219819	-1.616971	-0.905824
B	1.623919	-0.339828	0.000000	B	1.573946	-0.143132	0.000000
B	0.650961	0.190047	-1.453793	B	0.476651	-0.115241	-1.464558
B	-0.858299	-0.745028	1.459788	B	-0.476666	-1.603119	1.455839
H	-1.388728	-1.029937	2.477937	H	-0.817238	-2.096837	2.475366
H	1.230275	0.663177	-2.370703	H	0.790719	0.564983	-2.377818
H	-1.452932	-2.791667	0.000000	H	-0.043313	-3.714114	0.000000
H	-2.986187	-0.128051	0.000000	H	-2.630980	-2.030686	0.000000
H	2.790281	-0.162646	0.000000	H	2.537762	0.540243	0.000000
H	1.201895	-2.326320	-1.545260	H	2.088504	-2.110312	-1.540208
H	-1.273400	1.909705	-1.513925	H	-2.007765	0.607087	-1.478718
H	1.201895	-2.326320	1.545260	H	2.088504	-2.110312	1.540208
H	-1.273400	1.909705	1.513925	H	-2.007765	0.607087	1.478718
B	-0.858299	-0.745028	-1.459788	B	-0.476666	-1.603119	-1.455839
B	0.650961	0.190047	1.453793	B	0.476651	-0.115241	1.464558
H	-1.388728	-1.029937	-2.477937	H	-0.817238	-2.096837	-2.475366
H	1.230275	0.663177	2.370703	H	0.790719	0.564983	2.377818
C	0.973129	2.436320	0.000000	C	0.010050	2.079833	0.000000
H	1.095860	2.985998	-0.930570	F	-0.001288	2.794207	1.050922
H	1.095860	2.985998	0.930570	F	-0.001288	2.794207	-1.050922

Table S3. CO (**1**:**5**) and N_2 (**1**:**6**)

$H_{11}B_{11}C:C\equiv O \rightarrow$ (**1**:**5**) C_{5v}				$H_{11}B_{11}C:N\equiv N \rightarrow$ (**1**:**6**) C_{5v}			
Atom	X	Y	Z	Atom	X	Y	Z
C	0.000000	0.000000	0.962561	C	0.000000	0.000000	0.961694
B	0.000000	1.557627	0.177767	B	0.000000	1.553060	0.196934
B	1.481391	0.481333	0.177767	B	1.477048	0.479922	0.196934
B	0.899529	1.238096	-1.308774	B	0.899059	1.237448	-1.291831
B	0.000000	0.000000	-2.236250	B	0.000000	0.000000	-2.219662
B	-1.455469	-0.472910	-1.308774	B	-1.454708	-0.472663	-1.291831
B	0.000000	-1.530370	-1.308774	B	0.000000	-1.529570	-1.291831
B	-0.915550	-1.260147	0.177767	B	-0.912866	-1.256452	0.196934
B	0.915550	-1.260147	0.177767	B	0.912866	-1.256452	0.196934
B	-0.899529	1.238096	-1.308774	B	-0.899059	1.237448	-1.291831
H	-1.532447	2.109233	-1.798133	H	-1.532370	2.109127	-1.779718
H	1.474691	-2.029738	0.877554	H	1.467404	-2.019708	0.907262
H	0.000000	0.000000	-3.419172	H	0.000000	0.000000	-3.402411
H	1.532447	2.109233	-1.798133	H	1.532370	2.109127	-1.779718
H	-1.474691	-2.029738	0.877554	H	-1.467404	-2.019708	0.907262
H	0.000000	-2.607155	-1.798133	H	0.000000	-2.607024	-1.779718
H	2.386100	0.775291	0.877554	H	2.374310	0.771460	0.907262
H	-2.479552	-0.805655	-1.798133	H	-2.479427	-0.805615	-1.779718
H	0.000000	2.508894	0.877554	H	0.000000	2.496497	0.907262
B	1.455469	-0.472910	-1.308774	B	1.454708	-0.472663	-1.291831
B	-1.481391	0.481333	0.177767	B	-1.477048	0.479922	0.196934
H	2.479552	-0.805655	-1.798133	H	2.479427	-0.805615	-1.779718
H	-2.386100	0.775291	0.877554	H	-2.374310	0.771460	0.907262
C	0.000000	0.000000	2.331397	N	0.000000	0.000000	3.444088
O	0.000000	0.000000	3.464346	N	0.000000	0.000000	2.336663

Table S4. NH_3 (**1**:**7**) and $N{=}HCH_2$ (**1**:**8**)

$H_{11}B_{11}C{:}NH_3 \rightarrow$ (**1**:**7**) C_s				$H_{11}B_{11}C{:}NH{=}CH_2 \rightarrow$ (**1**:**8**) C_s			
Atom	X	Y	Z	Atom	X	Y	Z
C	-1.132629	0.000756	0.000000	C	0.476248	0.773650	0.000000
B	-0.385663	-1.233885	0.896187	B	-0.973274	0.647504	0.896671
B	-0.385663	-1.233885	-0.896187	B	-0.973274	0.647504	-0.896671
B	1.110350	-1.530432	0.000000	B	-1.911084	-0.552181	0.000000
B	2.038923	-0.003231	0.000000	B	-0.968654	-2.074969	0.000000
B	1.114430	1.234729	0.898332	B	0.553691	-1.808975	0.895763
B	1.114430	1.234729	-0.898332	B	0.553691	-1.808975	-0.895763
B	-0.379761	1.524712	0.000000	B	1.484220	-0.602022	0.000000
B	-0.385663	0.471490	-1.449844	B	0.553691	-0.128562	-1.458314
B	1.111755	-0.474003	1.452930	B	-0.970469	-1.032396	1.451740
H	1.605858	-0.806175	2.476270	H	-1.487025	-1.317257	2.478264
H	-1.097905	0.765175	-2.353114	H	1.132991	0.360494	-2.367963
H	3.223099	-0.005294	0.000000	H	-1.508280	-3.128809	0.000000
H	1.604863	-2.606081	0.000000	H	-3.094013	-0.507327	0.000000
H	-1.103969	2.468139	0.000000	H	2.654210	-0.389121	0.000000
H	1.610767	2.102813	-1.532100	H	1.104989	-2.642350	-1.530435
H	-1.106214	-1.996892	-1.453669	H	-1.340412	1.622833	-1.464370
H	1.610767	2.102813	1.532100	H	1.104989	-2.642350	1.530435
H	-1.106214	-1.996892	1.453669	H	-1.340412	1.622833	1.464370
B	1.111755	-0.474003	-1.452930	B	-0.970469	-1.032396	-1.451740
B	-0.385663	0.471490	1.449844	B	0.553691	-0.128562	1.458314
H	1.605858	-0.806175	-2.476270	H	-1.487025	-1.317257	-2.478264
H	-1.097905	0.765175	2.353114	H	1.132991	0.360494	2.367963
N	-2.630325	0.006582	0.000000	N	1.189716	2.028984	0.000000
H	-2.982139	-0.473843	-0.832968	H	2.203919	1.921154	0.000000
H	-2.982139	-0.473843	0.832968	C	0.687126	3.201639	0.000000
H	-2.972811	0.971907	0.000000	H	-0.390856	3.310837	0.000000
				H	1.346880	4.061353	0.000000

Table S5. N≡CH (**1**:**9**) and $OH^{(-)}$ (**1**:**10**)

$H_{11}B_{11}C{:}N{\equiv}CH \rightarrow$ (**1**:**9**) C_{5v}				$H_{11}B_{11}C{:}OH^{(-)} \rightarrow$ (**1**:**10**) C_s			
Atom	X	Y	Z	Atom	X	Y	Z
C	0.000000	0.000000	0.952250	C	-0.044637	1.235279	0.000000
B	0.000000	1.542407	0.181298	B	-1.240799	0.406327	0.892217
B	1.466916	0.476630	0.181298	B	-1.240799	0.406327	-0.892217
B	0.897901	1.235855	-1.310911	B	-1.496689	-1.104759	0.000000
B	0.000000	0.000000	-2.239895	B	0.048614	-2.003409	0.000000
B	-1.452835	-0.472055	-1.310911	B	1.252501	-1.035951	0.895333
B	0.000000	-1.527601	-1.310911	B	1.252501	-1.035951	-0.895333
B	-0.906604	-1.247833	0.181298	B	1.480288	0.477539	0.000000
B	0.906604	-1.247833	0.181298	B	0.445713	0.440993	-1.446013
B	-0.897901	1.235855	-1.310911	B	-0.446401	-1.085862	1.446492
H	-1.530863	2.107053	-1.802305	H	-0.768039	-1.601643	2.469077
H	1.464820	-2.016152	0.885991	H	0.736347	1.121842	-2.373628
H	0.000000	0.000000	-3.423531	H	0.080417	-3.192881	0.000000
H	1.530863	2.107053	-1.802305	H	-2.559789	-1.638464	0.000000
H	-1.464820	-2.016152	0.885991	H	2.433676	1.192590	0.000000
H	0.000000	-2.604460	-1.802305	H	2.142519	-1.512327	-1.524802
H	2.370129	0.770102	0.885991	H	-2.053206	1.049887	-1.467676
H	-2.476989	-0.804822	-1.802305	H	2.142519	-1.512327	1.524802
H	0.000000	2.492101	0.885991	H	-2.053206	1.049887	1.467676
B	1.452835	-0.472055	-1.310911	B	-0.446401	-1.085862	-1.446492
B	-1.466916	0.476630	0.181298	B	0.445713	0.440993	1.446013
H	2.476989	-0.804822	-1.802305	H	-0.768039	-1.601643	-2.469077
H	-2.370129	0.770102	0.885991	H	0.736347	1.121842	2.373628
N	0.000000	0.000000	2.333295	O	-0.109200	2.632819	0.000000
C	0.000000	0.000000	3.475667	H	0.800674	2.947075	0.000000
H	0.000000	0.000000	4.544315				

Table S6. OH_2 (**1**:**11**) and OCH_2 (**1**:**12**)

$H_{11}B_{11}C{:}OH_2 \rightarrow$ (**1**:**7**) C_s				$H_{11}B_{11}C{:}OC{=}H_2 \rightarrow$ (**1**:**12**) C_s			
Atom	X	Y	Z	Atom	X	Y	Z
C	-0.067397	1.102359	0.000000	C	0.48498200	0.75628800	0.00000000
B	0.438853	0.415640	1.447883	B	0.58240100	-0.11475900	1.45720800
B	-1.276045	0.339266	0.899306	B	-0.95428300	0.64706700	0.89642600
B	-0.435693	-1.122122	1.454295	B	-0.94427900	-1.02709200	1.45192200
B	0.077805	-2.025902	0.000000	B	-0.93855500	-2.06746800	0.00000000
B	1.273436	-1.051899	-0.899325	B	0.58240100	-1.79550400	-0.89437500
B	-0.435693	-1.122122	-1.454295	B	-0.94427900	-1.02709200	-1.45192200
B	0.438853	0.415640	-1.447883	B	0.58240100	-0.11475900	-1.45720800
B	-1.276045	0.339266	-0.899306	B	-0.95428300	0.64706700	-0.89642600
B	1.273436	-1.051899	0.899325	B	0.58240100	-1.79550400	0.89437500
H	2.163191	-1.504351	1.535075	H	1.13296900	-2.62740200	1.53154200
H	-2.068071	1.014757	-1.460560	H	-1.31345500	1.63056400	-1.46059900
H	0.128860	-3.208571	0.000000	H	-1.47358900	-3.12351400	0.00000000
H	-0.743798	-1.630787	2.477401	H	-1.45783600	-1.31191100	2.47990800
H	0.699298	1.163866	-2.335940	H	1.15314000	0.38513000	-2.36459600
H	-0.743798	-1.630787	-2.477401	H	-1.45783600	-1.31191100	-2.47990800
H	-2.068071	1.014757	1.460560	H	-1.31345500	1.63056400	1.46059900
H	2.163191	-1.504351	-1.535075	H	1.13296900	-2.62740200	-1.53154200
H	0.699298	1.163866	2.335940	H	1.15314000	0.38513000	2.36459600
B	-1.490518	-1.172934	0.000000	B	-1.89063700	-0.55291800	0.00000000
B	1.499438	0.451054	0.000000	B	1.52226600	-0.58961700	0.00000000
H	-2.540495	-1.718724	0.000000	H	-3.07358100	-0.50821900	0.00000000
H	2.403881	1.220049	0.000000	H	2.68660600	-0.38556600	0.00000000
O	-0.106595	2.631316	0.000000	O	1.19714600	2.04591400	0.00000000
H	0.362267	2.942829	0.798903	C	0.58595800	3.12344200	0.00000000
H	0.362267	2.942829	-0.798903	H	1.20357600	4.02077500	0.00000000
				H	-0.50322800	3.15096700	0.00000000

Table S7. CO_2 (**1**:**13**) and $F^{(-)}$ (**1**:**14**)

$H_{11}B_{11}C{:}O{=}C{=}O \rightarrow$ (**1**:**13**) C_{5v}				$H_{11}B_{11}C{:}F^{(-)} \rightarrow$ (**1**:**14**) C_{5v}			
Atom	X	Y	Z	Atom	X	Y	Z
C	0.000000	0.000000	0.113627	C	0.000000	0.000000	1.221333
B	-0.905896	-1.246859	-0.422993	B	0.000000	1.517621	0.446824
B	-1.465770	0.476258	-0.422993	B	1.443344	0.468971	0.446824
B	-1.462488	-0.475191	-1.943544	B	0.894706	1.231457	-1.057620
B	0.000000	0.000000	-2.823787	B	0.000000	0.000000	-1.990608
B	1.462488	-0.475191	-1.943544	B	-1.447665	-0.470375	-1.057620
B	0.903867	1.244067	-1.943544	B	0.000000	-1.522165	-1.057620
B	1.465770	0.476258	-0.422993	B	-0.892035	-1.227781	0.446824
B	0.000000	1.541202	-0.422993	B	0.892035	-1.227781	0.446824
B	0.000000	-1.537751	-1.943544	B	-0.894706	1.231457	-1.057620
H	0.000000	-2.620964	-2.418382	H	-1.527345	2.102210	-1.562653
H	0.000000	2.494459	0.272627	H	1.463293	-2.014051	1.124946
H	0.000000	0.000000	-4.012881	H	0.000000	0.000000	-3.179835
H	-2.492685	-0.809922	-2.418382	H	1.527345	2.102210	-1.562653
H	2.372371	0.770830	0.272627	H	-1.463293	-2.014051	1.124946
H	1.540564	2.120404	-2.418382	H	0.000000	-2.598475	-1.562653
H	-2.372371	0.770830	0.272627	H	2.367658	0.769299	1.124946
H	2.492685	-0.809922	-2.418382	H	-2.471296	-0.802973	-1.562653
H	-1.466206	-2.018059	0.272627	H	0.000000	2.489503	1.124946
B	-0.903867	1.244067	-1.943544	B	1.447665	-0.470375	-1.057620
B	0.905896	-1.246859	-0.422993	B	-1.443344	0.468971	0.446824
H	-1.540564	2.120404	-2.418382	H	2.471296	-0.802973	-1.562653
H	1.466206	-2.018059	0.272627	H	-2.367658	0.769299	1.124946
O	0.000000	0.000000	2.807115	F	0.000000	0.000000	2.584812
C	0.000000	0.000000	3.972225				
O	0.000000	0.000000	5.131496				

Table S8. FH (**1**:**15**) and SiH_2 (**1**:**16**)

$H_{11}B_{11}C$:FH → (**1**:**15**) C_s				$H_{11}B_{11}C$:SiH_2 → (**1**:**16**) C_s			
Atom	X	Y	Z	Atom	X	Y	Z
C	-0.091750	0.951388	0.000000	C	-0.244600	1.011357	0.000000
B	0.426912	0.397379	1.465710	B	-0.299309	0.064054	1.476265
B	-1.292821	0.290172	0.907143	B	-1.185490	-0.375716	0.000000
B	-0.420229	-1.170798	1.458879	B	-0.347745	-1.622551	0.913588
B	0.110863	-2.036478	0.000000	B	1.164309	-1.884312	0.000000
B	1.291204	-1.060644	-0.901795	B	2.110016	-0.354220	0.000000
B	-0.420229	-1.170798	-1.458879	B	1.189014	-0.843781	-1.453603
B	0.426912	0.397379	-1.465710	B	1.189014	0.866300	-0.904614
B	-1.292821	0.290172	-0.907143	B	-0.299309	0.064054	-1.476265
B	1.291204	-1.060644	0.901795	B	1.189014	-0.843781	1.453603
H	2.195462	-1.483504	1.536505	H	1.712075	-1.146057	2.470927
H	-2.104559	0.938762	-1.466238	H	-0.915201	0.524594	-2.377470
H	0.183912	-3.220317	0.000000	H	1.684623	-2.947954	0.000000
H	-0.722017	-1.673697	2.486145	H	-0.925769	-2.447558	1.532694
H	0.675557	1.121346	-2.364670	H	1.604476	1.806089	-1.486836
H	-0.722017	-1.673697	-2.486145	H	1.712075	-1.146057	-2.470927
H	-2.104559	0.938762	1.466238	H	-2.418821	-0.023192	0.000000
H	2.195462	-1.483504	-1.536505	H	3.293172	-0.335714	0.000000
H	0.675557	1.121346	2.364670	H	-0.915201	0.524594	2.377470
B	-1.478133	-1.238073	0.000000	B	-0.347745	-1.622551	-0.913588
B	1.484168	0.464405	0.000000	B	1.189014	0.866300	0.904614
H	-2.524741	-1.789284	0.000000	H	-0.925769	-2.447558	-1.532694
H	2.378141	1.242459	0.000000	H	1.604476	1.806089	1.486836
F	-0.112019	2.953908	0.000000	Si	-1.905613	1.706786	0.000000
H	0.797336	3.157472	0.000000	H	-2.558927	2.150306	-1.240450
				H	-2.558927	2.150306	1.240450

Table S9. PH_3 (**1**:**17**) and SH_2 (**1**:**18**)

$H_{11}B_{11}C$:PH_3 → (**1**:**17**) C_s				$H_{11}B_{11}C$:SH_2 → (**1**:**18**) C_s			
Atom	X	Y	Z	Atom	X	Y	Z
C	-0.000505	0.859976	0.000000	C	0.389024	0.755094	0.000000
B	-1.242057	0.084016	0.901194	B	0.476221	-0.128615	1.453955
B	-1.242057	0.084016	-0.901194	B	-1.060225	0.638194	0.898924
B	-1.528381	-1.410314	0.000000	B	-1.046923	-1.039225	1.451837
B	0.000009	-2.339153	0.000000	B	-1.043630	-2.081405	0.000000
B	1.236376	-1.410122	0.898465	B	0.476221	-1.812008	-0.897068
B	1.236376	-1.410122	-0.898465	B	-1.046923	-1.039225	-1.451837
B	1.536248	0.080369	0.000000	B	0.476221	-0.128615	-1.453955
B	0.473650	0.089844	-1.455741	B	-1.060225	0.638194	-0.898924
B	-0.471666	-1.410009	1.453190	B	0.476221	-1.812008	0.897068
H	-0.802753	-1.902487	2.477450	H	1.027290	-2.644369	1.533247
H	0.770685	0.781292	-2.373063	H	-1.427196	1.618132	-1.459528
H	0.000183	-3.523246	0.000000	H	-1.578502	-3.137859	0.000000
H	-2.604406	-1.903650	0.000000	H	-1.562950	-1.326324	2.478065
H	2.497082	0.774280	0.000000	H	1.052647	0.363081	-2.366243
H	2.104957	-1.902531	-1.534376	H	-1.562950	-1.326324	-2.478065
H	-2.020266	0.775782	-1.468326	H	-1.427196	1.618132	1.459528
H	2.104957	-1.902531	1.534376	H	1.027290	-2.644369	-1.533247
H	-2.020266	0.775782	1.468326	H	1.052647	0.363081	2.366243
B	-0.471666	-1.410009	-1.453190	B	-1.990830	-0.566375	0.000000
B	0.473650	0.089844	1.455741	B	1.418938	-0.616904	0.000000
H	-0.802753	-1.902487	-2.477450	H	-3.173930	-0.519116	0.000000
H	0.770685	0.781292	2.373063	H	2.586612	-0.421707	0.000000
H	-0.644183	3.171751	-1.115420	S	1.257892	2.332910	0.000000
H	-0.644183	3.171751	1.115420	H	0.575249	2.970238	0.983360
H	1.289165	3.169777	0.000000	H	0.575249	2.970238	-0.983360
P	0.000113	2.618905	0.000000				

Table S10. ClH (**1**:**19**)

$H_{11}B_{11}C$:ClH → (**1**:**19**) C_s			
Atom	X	Y	Z
C	-0.049130	0.770174	0.000000
B	-1.267218	0.042743	0.905923
B	-1.267218	0.042743	-0.905923
B	-1.501091	-1.466012	0.000000
B	0.056394	-2.336537	0.000000
B	1.262758	-1.378643	0.898788
B	1.262758	-1.378643	-0.898788
B	1.508117	0.128740	0.000000
B	0.449867	0.094090	-1.464855
B	-0.445369	-1.435215	1.453466
H	-0.761359	-1.934745	2.478803
H	0.724215	0.805133	-2.368502
H	0.094240	-3.520398	0.000000
H	-2.562242	-1.989920	0.000000
H	2.430297	0.878176	0.000000
H	2.151761	-1.834715	-1.533447
H	-2.060005	0.716926	-1.466318
H	2.151761	-1.834715	1.533447
H	-2.060005	0.716926	1.466318
B	-0.445369	-1.435215	-1.453466
B	0.449867	0.094090	1.464855
H	-0.761359	-1.934745	-2.478803
H	0.724215	0.805133	2.368502
Cl	-0.077128	2.751554	0.000000
H	1.216955	2.868781	0.000000

- **Atoms-in-Molecules Analysis**

Table S11. Topological analysis of the electron density in complexes {$H_{11}B_{11}C$:LB(*n*)} shown in Figures 5a-c of the main text and included in this work. The list is classified according to Scheme 1 of the main text, with *n* the label of the Lewis base (LB). *d*(C-X) is the distance between the C(ylide) and X in LB(*n*), in Å; ρ(**r**) (*e*/Å^3) and $\nabla^2\rho(\mathbf{r})$ (*e*/Å^5) are the electron density and its Laplacian respectively. G, V an H are the kinetic, potential and total (H = G + V) energy (a.u./Å^3) at the bond critical point (BCP) between C and X in C-X.

n	(1:*n*)	C-X	*d*(C-X)	ρ(**r**)	$\nabla^2\rho(\mathbf{r})$	G	V	H
2	$B_{11}H_{11}C:H^{(-)}$	C-H	1.0813	0.2878	-1.0476	0.0430	-0.3480	-0.3049
3	$B_{11}H_{11}C:CH_2$	C-C	1.3832	0.3242	-0.8949	0.1084	-0.4405	-0.3321
4	$B_{11}H_{11}C:CF_2$	C-C	1.3987	0.3116	-0.8971	0.1249	-0.4741	-0.3492
5	$B_{11}H_{11}C:C{\equiv}O$	C-C	1.3688	0.3090	-0.9643	0.1872	-0.6155	-0.4283
6	$B_{11}H_{11}C:N_2$	C-N	1.3750	0.2615	0.2796	0.4756	-0.8814	-0.4057
7	$B_{11}H_{11}C:NH_3$	C-N	1.4977	0.2344	-0.5858	0.1304	-0.4072	-0.2768
8	$B_{11}H_{11}C:NH{=}CH_2$	C-N	1.4439	0.2627	-0.7233	0.1954	-0.5717	-0.3762
9	$B_{11}H_{11}C:N{\equiv}CH$	C-N	1.3810	0.2690	0.0224	0.4338	-0.8619	-0.4282
10	$B_{11}H_{11}C:OH^-$	C-O	1.3990	0.2796	-0.7704	0.2343	-0.6612	-0.4269
11	$B_{11}H_{11}C:OH_2$	C-O	1.5295	0.1841	-0.2325	0.1539	-0.3660	-0.2121
12	$B_{11}H_{11}C:O{=}CH_2$	C-O	1.4732	0.2113	-0.2832	0.2163	-0.5033	-0.2871
13	$B_{11}H_{11}C:O{=}C{=}O$	C-O	2.6935	0.0112	0.0429	0.0089	-0.0070	0.0018
14	$B_{11}H_{11}C:F^-$	C-F	1.3635	0.2595	-0.2350	0.3455	-0.7497	-0.4042
15	$B_{11}H_{11}C:FH$	C-F	2.0026	0.0540	0.1389	0.0423	-0.0499	-0.0076
16	$B_{11}H_{11}C:SiH_2$	C-Si	1.8007	0.1336	0.2333	0.1532	-0.2481	-0.0949
17	$B_{11}H_{11}C:PH_3$	C-P	1.7589	0.1894	-0.3881	0.1091	-0.3152	-0.2061
18	$B_{11}H_{11}C:SH_2$	C-S	1.8012	0.1829	-0.2509	0.0560	-0.1748	-0.1187
19	$B_{11}H_{11}C:ClH$	C-Cl	1.9816	0.1131	-0.0067	0.0511	-0.1039	-0.0528

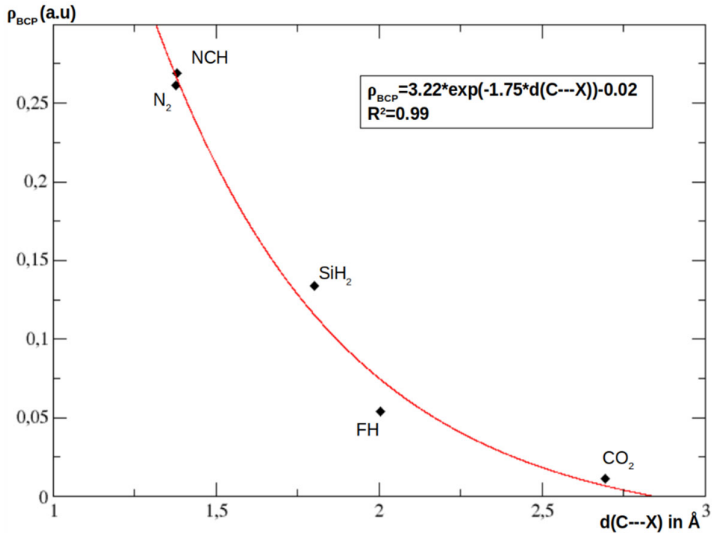
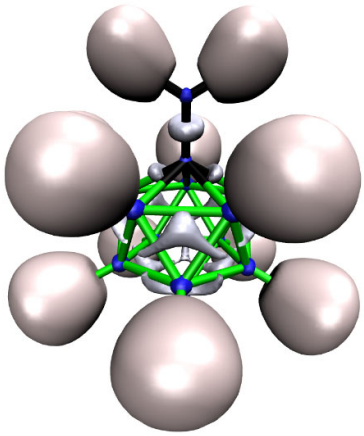


Figure S1. Fitting of ρ_{BCP} vs. *d*(C···X) for the closed-shell interaction complexes (1:6), (1:9), (1:13), (1:15) and (1:16), corresponding to Lewis bases N_2, NCH, CO_2, FH and SiH_2, respectively.

Table S12 : ELF functions of the (**1**:***n***) complexes not included in the main text.

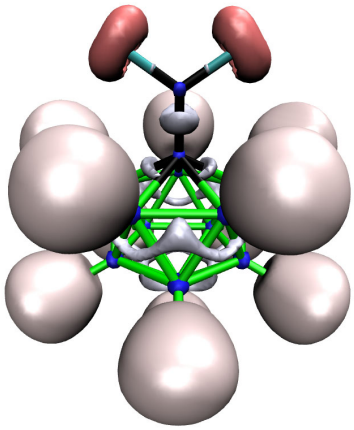
(**1:3**) **;** CH_2



11 C(B) =2.06
2 C(C) =2.09
11 V(B,H) =2.05
2 V(C,H) =2.11
1 V(C,C) =2.53
1 V(C,B,B) =2.16
1 V(C,B) =2.37
2 V(B,B,B) =1.62
3 V(B,B,B) =0.79
2 V(B,B,B) =1.12
4 V(B,B,B) =2.14
1 V(B,B,B) =2.70

No direct correlation between the population of the V(B,B,B) basins and position of the B in the compound were found. The only general trend, is that the trisynaptic basins involving boron "bonded" to the carbon have generally a higher occupancy.

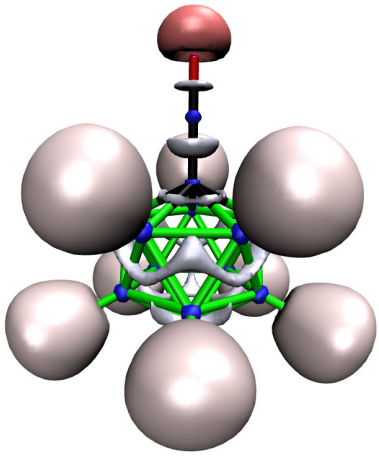
(**1:4**) ; CF_2



11 C(B) =2.06
2 C(C) =2.07
2 C(F) =2.15
11 V(B,H) =2.05
1 V(C,C) =2.71
2 V(C,F) =1.30
2 V(C,B) =2.23
1 V(C,B) =0.32
5 V(B,B,B) =2.43
3 V(B,B,B) =1,02
2 V(B,B,B) =1.85
1 V(B,B) =0.4
2 V(F) =3.18
2 V(F) =3.26

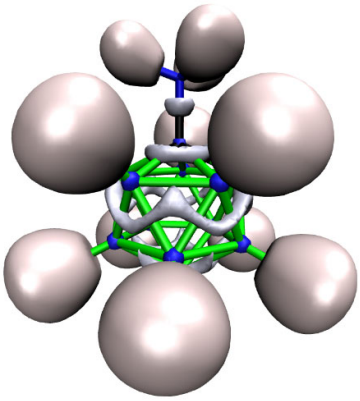
The V(B,B,B) with the highest populations involves at least two boron atoms "bonded" to the carbon.

(**1:5**) ; CO



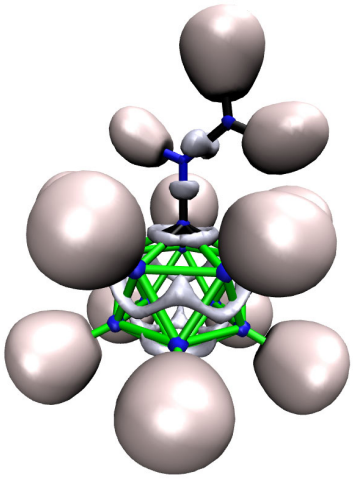
11 C(B) =2.07
2 C(C) =2.07
1 C(O) =2.12
11 V(B,H) =2.05
5 V(B,B) =0.42
5 V(B,B,B) =2.43
5 V(B,B,B) =0.99
1 V(C,O) =2.39
5 V(C,B) =0.96
1 V(C,C) =2.78
1 V(O) =5.18

(**1:7**) ; NH_3



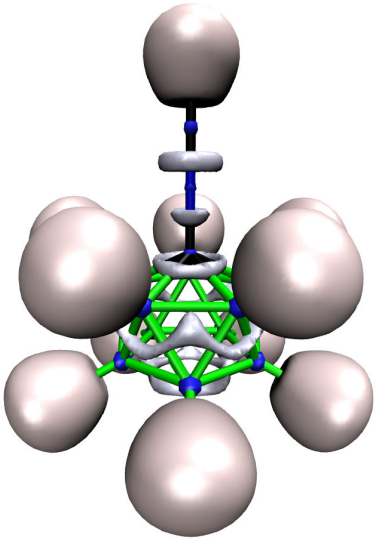
11 C(B) =2.06
1 C(C) =2.06
1 C(N) =2.12
11 V(B,H) =2.05
3 V(N,H) =2.01
5 V(C,B) =1.09
1 V(C,N) =1.76
5 V(B,B,B) =1.06
5 V(B,B,B) =0.80
15 V(B,B) =0.66

(**1:8**) ; $NH{=}CH_2$



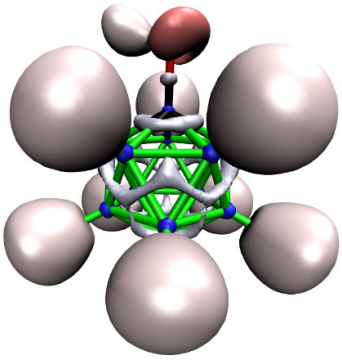
11 C(B) =2.06
2 C(C) =2.08
1 C(N) =2.08
11 V(B,H) =2.05
1 V(N,H) =2.14
2 V(C2,H) =2,15
1 V(N,C1) =2.02
2 V(N,C2) =1.71
5 V(C1,B) =1.06
5 V(B,B,B) =2.44
5 V(B,B,B) =0.89
5 V(B,B) =0.55

(**1:9**) ; N≡CH



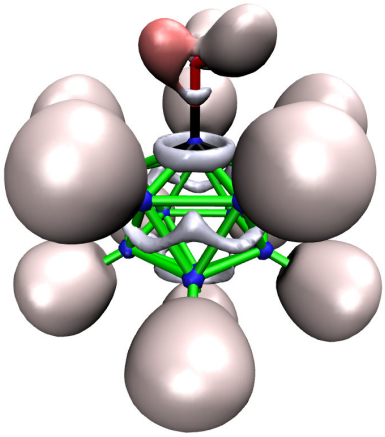
11 C(B)	=2.07
2 C(C)	=2.07
1 C(N)	=2.08
11 V(B,H)	=2.04
1 V(C2,H)	=2.45
5 V(C1,B)	=1.05
1 V(C1,N)	**=2.34**
1 V(C2,N)	=5.17
5 V(B,B,B)	=2.42
5 V(B,B,B)	=0.95
5 V(B,B)	=0.49

(**1:10**) ; $OH^{(-)}$



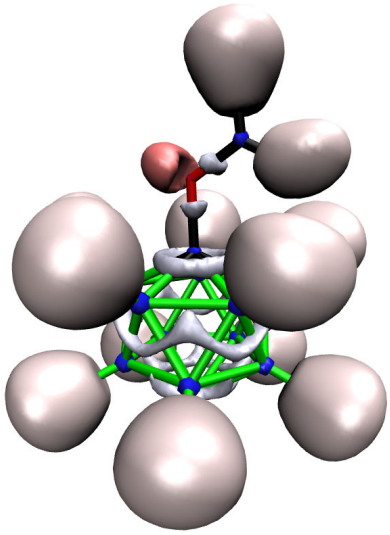
11 C(B)	=2.06
1 C(C)	=2.09
1 C(O)	=2.04
11 V(B,H)	=2.05
1 V(O,H)	=1.71
1 V(C,O)	**=1.32**
5 V(C,B)	=1.05
2 V(B,B,B)	=1.59
11 V(B,B,B)	=0.86
10 V(B,B)	=0.70
2 V(O)	=2.38

(**1:11**) ; H_2O



11 C(B)	=2.07
1 C(C)	=2.09
1 C(O)	=2.07
11 V(B,H)	=2.04
2 V(O,H)	=1.88
5 V(C,B)	=1.12
1 V(C,O)	**=1.56**
1 V(O)	=2.47
14 V(B,B,B)	=0.89
11 V(B,B)	=0.62

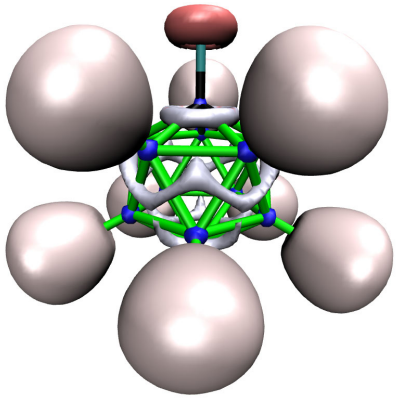
(**1:12**) ; $O{=}CH_2$



11 C(B) =2.07
2 C(C) =2.06
1 C(O) =2.08
11 V(B,H) =2.05
2 V(C2,H) =2.15
1 V(C1,O) =1.65
5 V(C,B) =1.09
1 V(O) =3.26
1 V(C2,O) =2,58
2 V(B,B,B) =2.39
2 V(B,B,B) =1.73
6 V(B,B,B) =0.94
9 V(B,B) =0.60

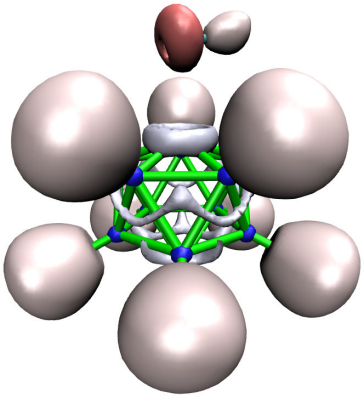
No direct correlation between the population of the V(B,B,B) basins and position of the B in the compound were found. The only general trend, is that the trisynaptic basins involving boron "bonded" to the carbon have generally a higher occupancy.

(**1:14**) ; $F^{(-)}$



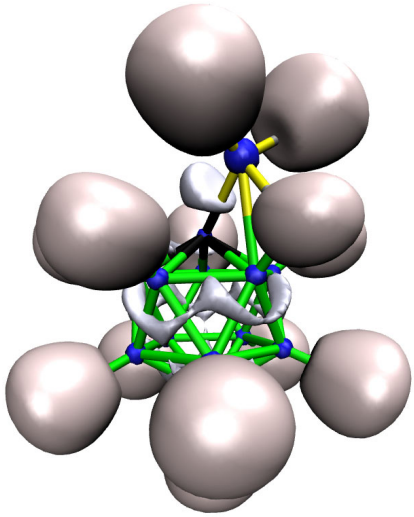
11 C(B) =2.06
1 C(C) =2.09
1 C(F) =2.06
11 V(B,H) =2.04
5 V(C,B) =1.07
4 V(F) =1.16
1 V(F) =2.16
1 V(C,F) =0.99
10 V(B,B,B) =0.88
15 V(B,B) =0.72

(**1:15**) ; FH



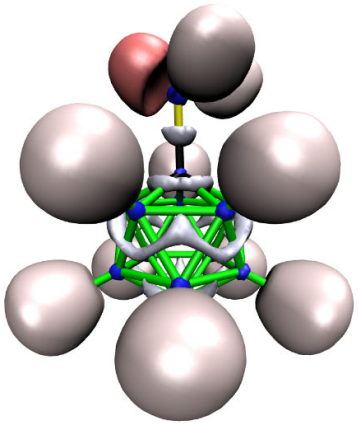
11 C(B) =2.04
1 C(C) =2.05
1 C(F) =2.12
11 V(B,H) =2.03
1 V(F,H) =1.45
5 V(C,B) =1.18
1 V(C,B,B) =1.09
2 V(F) =3.17
9 V(B,B,B) =1.02
5 V(B,B) =0.49
10 V(B,B) =0.63

(**1:16**) ; SiH_2



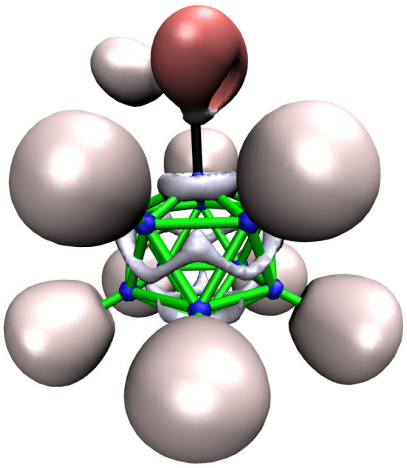
11 C(B)	=2.07
1 C(C)	=2.09
1 C(Si)	=9.95
10 V(B,H)	=2.05
1 V(B,H,Si)	=2.09
2 V(Si,H)	=2.04
2 V(C,B,B)	=1.79
1 V(C,Si)	**=2.40**
1 V(C,B)	=1.08
7 V(B,B,B)	=0.85
2 V(B,B,B)	=1.84
2 V(B,B,B)	=1.49
1 V(B,B,B)	=2.71
1 V(B,B,B)	=3.40
1 V(B,B)	=0.8

(**1:18**) ; H_2S



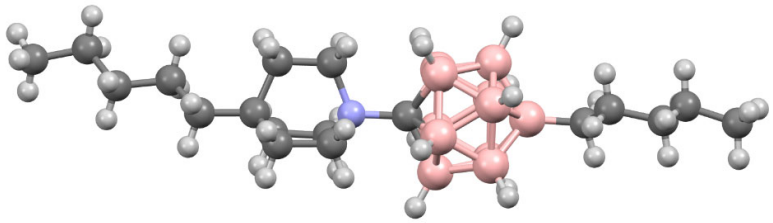
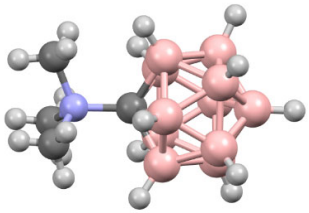
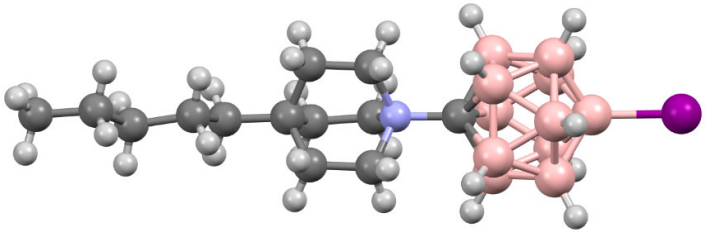
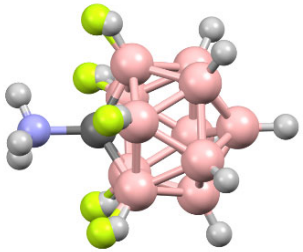
11 C(B)	=1.07
1 C(C)	=2.07
1 C(S)	=10.0
11 V(B,H)	=2.05
2 V(S,H)	=1.95
1 V(C,S)	**=1.85**
5 V(C,B)	=1.06
2 V(B,B,B)	=2.41
2 V(B,B,B)	=1.74
6 V(B,B,B)	=0.92
9 V(B,B)	=0.61
1 V(S)	=2.33

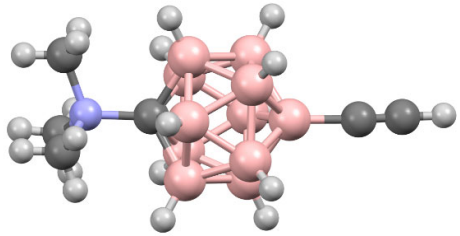
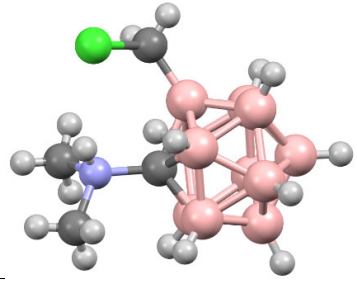
(**1:19**) ; ClH



11 C(B)	=2.07
1 C(C)	=2.08
1 C(Cl)	=10.06
11 V(B,H)	=2.04
1 V(Cl,H)	=1.78
5 V(C,B)	=1.12
1 V(C,Cl)	**=1.11**
11 V(B,B)	=0.61
7 V(B,B,B)	=0.97
2 V(B,B,B)	=1.68
1 V(B,B,B)	=2.42
2 V(Cl)	=2.46

Table S13. Complexes between derivatives of (**1**) and neutral nitrogen-bases found in the CSD.

CSD Refcode	Structure
EKEMIS	
FETWIK	
HOGFEO	
PACKIP	

QISHAD	
ZABMUK	
GORMOR