Supplementary Information

Puppeteering the Reactivity of Frustrated Lewis Pairs toward CO₂ via Coordination Dichotomy in Bridging Units

Mohmmad Faizan, and Ravinder Pawar*

Laboratory of Advanced Computation and Theory for Materials and Chemistry, Department of Chemistry, National Institute of Technology Warangal (NITW), Warangal, Telangana-506004, India.

ravinder_pawar@nitw.ac.in

S1. Computational Methodology

The geometries of the considered IFLPs i.e. BP, BP1, BP2 and BP3, transition states (TSs) reactant complexes (RCs), and adducts (ADs) were fully optimized without any geometrical or symmetrical constraints employing Def2TZVP basis set with M06-2X functional.^{1,2} The frequency calculations were conducted to depict the nature of the stationary points as first order saddle point and as local minima. The transition states were verified by the presence of single imaginary frequency in the direction of bond breaking or formation. The optimized structures were then used to study the energetics of the reaction at 1 atm pressure and 298.15 K. The energetic results were systematically compared. Further to gain insights to the frustration and catalytic behaviour of the IFLPs, natural bond orbital (NBO) and principle interacting orbital (PIO) analysis^{3,4} have been carried out. The principal interacting orbitalbased bond index (PBI) between significant interacting orbitals has been observed and plotted against the intrinsic reaction coordinates (IRC). The PBI represents the fraction of total interaction contributed by PIO pairs, serving as an indicator of the reactivity of the active site involved in the interaction. Monitoring changes in the PBI along the IRC path provides insights into the evolution of active site reactivity throughout the reaction. The slopes of the linear regression line for PBI vs. IRC curves suggest the extent of interaction changes between PIO pairs. The PBI vs. IRC plots are divided into distinct regions based on observed variations in the PBI index along the reaction coordinates, and the slopes within these regions are calculated using the following relation.

$$b = \frac{\sum (x - x')(y - y')}{\sum (x - x')^2}$$
(1)

where *b* is the slope of the curve in the selected region, *x* and *y* are the reaction coordinates and PBI values, respectively. The *x*' and *y*' represent the average of reaction coordinates and PBI in the considered region. The natural bond orbitals were plotted at 0.02 a. u. iso value. All the density functional theory (DFT) calculations were carried out using Gaussian 16 program package.⁵ The natural bond orbital analysis has been carried out using the NBO 7.0 program.⁶

The molecular electrostatic potential surface of o-carborane was analysed using Multiwfn⁷ software. The quantum theory of atoms in molecule (QTAIM) was employed to study the electron density basins of the proposed IFLPs. The Multiwfn⁷ suite is used to conduct the QTAIM calculation.

The rationale for selecting the studied sites is based on well-established studies on the expected electronic effects of specific o-carborane cage positions.^{8–10} The inductive constant (σ i) values indicate that the carbon at the 1st position is electron-withdrawing, boron at the 3rd position is virtually neutral, and boron at the 4th and 9th positions are electron-donating. These positions represent the extreme electronic effects within o-carborane, while other sites exhibit symmetric counterparts with similar properties. This symmetry is illustrated in Scheme 1 a, where similar electronic environments are marked with corresponding solid colored circles. For instance, carbons at the 1st and 2nd positions both exhibit similar electron-withdrawing effects, boron at the 3rd and 6th positions are virtually neutral, while boron at the 4th, 5th, 7th, and 11th positions display similar electron-donating effects. Notably, the electronic effects at the 1st and 9th positions enhance the acidity and basicity of boron- and phosphorus-containing functional groups. Studies have shown that attaching borane to the carbon at the 9th position creates a highly electron-rich phosphinoborane.^{12,13}

To further verify these electronic effects, the hydride ion affinity (HIA) of the $-B(CH_3)_2$ group and the proton affinity (PA) of the $-P(CH_3)_2$ group were calculated across all 12 sites of ocarborane. The HIA and PA values in Table S4 align with the σ_i values, reinforcing the observed electronic effects. Based on these values, the sites exhibiting the most pronounced electronic effects, with slight variations, are the 1st, 3rd, 4th, and 9th positions. It is also noteworthy that boron at the 8th and 10th positions is electron-donating, though to a lesser extent than at the 9th and 12th positions.

Additionally, the first Lewis acid- and base-functionalized carborane, 1-Bcat-7-PPh₂-closo-1,7-C₂B₁₀H₁₀ (where Bcat is catecholylboryl)¹⁴, cannot be classified as an FLP due to the large spatial separation between the acidic and basic sites. Based on all previous reports, in this study, we modeled the FLP by selecting sites with distinct electronic effects to comprehensively assess the impact of coordination and the dichotomous control over reactivity in the resulting IFLPs. To ensure the active sites reach their full electronic potential (i.e., acidity or basicity), their coordination sites were systematically varied, allowing for a nuanced understanding of carborane-based FLPs.

For example, in BP, where both acidic and basic sites are located on electron-withdrawing C1 and C2 atoms, the acidity of $-B(CH_3)_2$ is expected to increase, while the basicity of $-P(CH_3)_2$ may decrease. In BP3, where active sites are positioned on electron-donating B9 and B12 atoms, the opposite trend is anticipated. In BP1, $-P(CH_3)_2$ at the neutral B5 site likely retains its basicity, while $-B(CH_3)_2$ at the electron-withdrawing C1 site remains acidic. In BP2, $-B(CH_3)_2$'s acidity is expected to remain unchanged, whereas $-P(CH_3)_2$'s basicity may increase due to its placement on the B9 atom.



Figure S1. a) Optimized geometry, and b) molecular electrostatic potential surface (MESP) with V_{max} and V_{min} of the *o*-carborane.

S2. NBO analysis of o-carborane and the proposed IFLPs

The NBO analysis shows that in *o*-carborane, the carbon atoms (C1 and C2) are sp³ hybridized and form four σ bonds with neighbouring atoms. No bonding orbitals are observed between C1-B3, C1-B6, C2-B3, and C2-B6. It has been noted that B3 and B5 possess an empty sp² hybridized orbital capable of accepting electrons from neighbouring atoms and bonds. Further analysis reveals orbital charge transfers (OCTs) from the bonding orbitals of C1 and C2 to the empty sp² hybridized orbitals of B3 and B6 (see Table S1). Due to these charge transfers, an electron deficiency of approximately 1.22 e⁻ arises in the valence octet of the carbon atoms (see Table S2), causing the carbon atoms to satisfy their electronic requirements inductively, which in turn creates an electron-withdrawing effect on attached substituents. Similarly, in the proposed IFLPs, the carbon atoms exhibit an electron deficit of approximately 1.3 e⁻ in their octets (see Table S2). Consequently, the C atoms in BP, BP1, BP2, and BP3 also exert an electron-withdrawing effect on their substituents. In BP, the -B(CH₃)₂ becomes more acidic, while the basicity of -P(CH₃)₂ is significantly reduced. In BP1, the -B(CH₃)₂ is expected to exhibit high electron deficiency, and the -P(CH₃)₂ atom on B5 of the cage retains unquenched basicity.

Furthermore, the NBO analysis of the boron atoms in the cage indicates that all B atoms form three-center two-electron bonds. Total electron calculations for the boron atoms' valence shells reveal that all boron atoms, except B3 and B6, have electron excess relative to their natural occupancy (see Table S2). This electron excess renders the boron atoms electron-rich, resulting

in an electron-donating effect. Notably, B9 and B12, which are antipodal to C1 and C2, exhibit the highest electron excess, suggesting the strongest electron-donating effects at these coordination sites. Therefore, in BP2 and BP3, the $-P(CH_3)_2$ atom is expected to be the most basic, while the $-B(CH_3)_2$ atom in BP3 will be the least acidic among the proposed IFLPs. Thus, OCT analysis of natural bond orbitals and electron occupancies provides a coherent explanation for the electron-donating and electron-withdrawing effects observed in the carborane cage.

 Table S1. Orbital charge transfer (OCT) from the bonding orbitals to the empty sp² orbital of B3
 and B6. (All the values are in kcal/mol)



Schematic representation of OCT from bonding orbitals to sp² orbitals of B3 and B6

	o-carborane	BP	BP1	BP2	BP3
BD C1- C2 \rightarrow sp ² (B3)	139.65	142.46	141.36	143.61	144.32
BD C1- B4 \rightarrow sp ² (B3)	139.61	140.51	140.25	141.11	143.21
BD C1-C5 \rightarrow sp ² (B6)	139.65	142.45	141.39	143.60	144.31
BD C1- C2 \rightarrow sp ² (B6)	139.54	140.41	140.15	141.09	143.21

Table S2. Natural Bonding orbitals with electron occ	upancies of the atoms present in cage of o-
carbornae and proposed IFLPs.	

	o-carborane	BP	BP1	BP2	BP3
C1					
BD (1) C 1- B	1.96924	1.90593	1.8961	1.96738	1.96954
BD (1) C 1- B4	1.55615	1.536	1.5421	1.56399	1.56134
BD (1) C 1- B 5	1.55596	1.53598	1.5288	1.53073	1.56133
BD (1) C 1- C2	1.68909	1.66623	1.67148	1.68937	1.68104
Total e-	6.77044	6.64414	6.63848	6.75147	6.77325
e- Deficit	1.22956	1.35586	1.36152	1.24853	1.22675
C2					
BD (1) C 2-P	1.96925	1.96206	1.96948	1.96969	1.96892
BD (1) C 2- C 1	1.68909	1.66623	1.67148	1.68937	1.68104
BD (1) C 2- B 11	1.55593	1.56264	1.55672	1.5621	1.5551
BD (1) C 2- B 7	1.55621	1.56266	1.53937	1.54766	1.55504
Total e-	6.77048	6.75359	6.73705	6.76882	6.7601

e- Deficit	1.22952	1.24641	1.26295	1.23118	1.2399
B3					
BD (1) B 3- H	1.9805	1.976	1.97679	1.97847	1.98049
3C (1) B 3- B 11- B 10	1.78545	1.78513	1.7833	1.78249	1.78474
3C (1) B 3- B 5- B 10	1.78542	1.77569	1.77673	1.74663	1.78175
LV(1)B 3	0.48047	0.48477	0.48664	0.47947	0.48417
Total e-	6.03184	6.02159	6.02346	5.98706	6.03115
e- excess	0.03184	0.02159	0.02346	-0.01294	0.03115
B6					
BD (1) B 6- H	1.9805	1.976	1.97654	1.97989	1.98049
3C (1) B 6- B 8- B 4	1.78543	1.77566	1.79654	1.79471	1.78472
3C (1) B 7- B 6- B 8	1.78544	1.78512	1.79743	1.78421	1.78175
LV (1) B 6	0.48042	0.48477	0.48646	0.48126	0.48419
Total e-	6.03179	6.02155	6.05697	6.04007	6.03115
e- excess	0.03179	0.02155	0.05697	0.04007	0.03115
B4					
BD (1) C 1- B 4	1.55615	1.536	1.5288	1.53073	1.56134
BD (1) B 4- H	1.97135	1.96373	1.9622	1.91183	1.97292
3C (1) B 6- B 8- B 4	1.78545	1.77566	1.77673	1.74663	1.78474
3C (1) B 5- B 4- B 9	1.84033	1.84239	1.83979	1.81983	1.84735
Total e-	7.15328	7.11778	7.10752	7.00902	7.16635
e- excess	1.15328	1.11778	1.10752	1.00902	1.16635
B5					
BD (1) C 1- B 5	1.55596	1.53598	1.5421	1.56399	1.56133
BD (1) B 5- H	1.97135	1.96372	1.95313	1.9658	1.97292
3C (1) B 3- B 5- B 10	1.78543	1.77569	1.79743	1.79471	1.78472
3C (1) B 5- B 4- B 9	1.84033	1.84239	1.83979	1.81983	1.84735
Total e-	7.15307	7.11778	7.13245	7.14433	7.16632
e- excess	1.15307	1.11778	1.13245	1.14433	1.16632
B7					
BD (1) C 2- B 7	1.55593	1.56266	1.55672	1.5621	1.5551
BD (1) B 7- H	1.97136	1.97028	1.97145	1.97222	1.97236
3C (1) B 11- B 7- B 12	1.8403	1.84602	1.84066	1.83184	1.83302
3C (1) B 7- B 6- B 8	1.78542	1.78512	1.7833	1.78249	1.78175
Total e-	7.15301	7.16408	7.15213	7.14865	7.14223
e- excess	1.15301	1.16408	1.15213	1.14865	1.14223
B11					
BD (1) C 2- B 11	1.55621	1.56264	1.53937	1.54766	1.55504
BD (1) B 11- H	1.97135	1.97028	1.96985	1.97069	1.97236

3C (1) B 3- B 11- B 10	1.78544	1.78513	1.79654	1.78421	1.78175
3C (1) B 11- B 7- B 12	1.8403	1.84602	1.84066	1.83184	1.83302
Total e-	7.1533	7.16407	7.14642	7.1344	7.14217
e- excess	1.1533	1.16407	1.14642	1.1344	1.14217
B9					
BD (1) B 9- H	1.97854	1.97874	1.97898	1.95442	1.95782
3C (1) B 5- B 4- B 9	1.84033	1.84239	1.83979	1.81983	1.84735
3C (1) B 10- B 12- B 9	1.80571	1.81189	1.80057	1.81665	1.80541
3C (1) B 12- B 8- B 9	1.80564	1.81189	1.80934	1.80705	1.80542
Total e-	7.43022	7.44491	7.42868	7.39795	7.416
e- excess	1.43022	1.44491	1.42868	1.39795	1.416
B8					
BD (1) B 8- H	1.97674	1.97602	1.97708	1.97486	1.97512
3C (1) B 7- B 6- B 8	1.78545	1.78512	1.7833	1.78249	1.78474
3C (1) B 6- B 8- B 4	1.78542	1.77566	1.77673	1.74663	1.78175
3C (1) B 12- B 8- B 9	1.80571	1.81189	1.80057	1.80705	1.80541
Total e-	7.35332	7.34869	7.33768	7.31103	7.34702
e- excess	1.35332	1.34869	1.33768	1.31103	1.34702
B10					
BD (1) B 10- H	1.97673	1.97602	1.97665	1.977	1.97513
3C (1) B 3- B 11- B 10	1.78543	1.78513	1.79654	1.79471	1.78472
3C (1) B 3- B 5- B 10	1.78544	1.77569	1.79743	1.78421	1.78175
3C (1) B 10- B 12- B 9	1.80564	1.81189	1.80934	1.81665	1.80542
Total e-	7.35324	7.34873	7.37996	7.37257	7.34702
e- excess	1.35324	1.34873	1.37996	1.37257	1.34702
B12					
BD (1) B 12- H	1.97855	1.97817	1.9782	1.97933	1.92779
3C (1) B 11- B 7- B 12	1.8403	1.84602	1.84066	1.83184	1.83302
3C (1) B 10- B 12- B 9	1.80571	1.81189	1.80934	1.81665	1.80541
3C (1) B 12- B 8- B 9	1.80564	1.81189	1.80057	1.80705	1.80542
Total e-	7.4302	7.44797	7.42877	7.43487	7.37164
e- excess	1.4302	1.44797	1.42877	1.43487	1.37164



Figure S2. Optimized geometries of the reactant complexes obtained in the reaction of CO_2 with proposed IFLPs. (The distances are in Å and the angles are in degrees, relative energies are in kcal/mol)

Table S3. Important orbital charge transfer observed in the reactant complexes (RCs) and strain energy released in the formation of RC during the reaction of CO_2 with the proposed IFLPs. (All the values are in kcal/mol)

		$lp(P) \rightarrow \pi^*(C=O)$	$lp(\mathbf{O}) \rightarrow p_z(\mathbf{B})$	Energy
				released
<i>lp</i> (P)	BP	3.30	3.54	2.1
P ₂ (B)	BP1	5.22	7.22	1.1
	BP2	4.16	6.85	2.9
	BP3	4.30	6.00	4.8

Table S4. The hydride ion affinity (HIA) and proton affinity (PA) of $-B(CH_3)_2$ and $-P(CH_3)_2$ groups, respectively, placed all coordinating sites of the o-carborane. (All the values are in kcal/mol, PA and FIA values are estimated from the energy change of the reactions, $[P]+H^+ \rightarrow [PH]^+$ and $[B]+H^- \rightarrow [BF]^-$)

	HIA	РА
C1, C2	-99.9428	-187.52
B3, B6	-91.4947	-201.931
B4, B5, B7 and B11	-82.1171	-209.827
B8, B10	-74.4032	-218.964
B9, B12	-71.8862	-221.63

References

- 1 J.-D. Chai and M. Head-Gordon, Phys. Chem. Chem. Phys., 2008, 10, 6615.
- 2 S. Grimme, S. Ehrlich and L. Goerigk, J. Comput. Chem., 2011, 32, 1456-1465.
- 3 J.-X. Zhang, F. K. Sheong and Z. Lin, Chem. Eur. J., 2018, 24, 9639–9650.
- 4 J. Zhang, F. K. Sheong and Z. Lin, WIREs Comput Mol Sci, DOI:10.1002/wcms.1469.
- 5 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, Williams, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, Gaussian 16 Rev. C.01 2016.
- 6E. D. Glendening, C. R. Landis and F. Weinhold, J Comput Chem, 2019, 40, 2234–2241.
- 7 T. Lu and F. Chen, Journal of Computational Chemistry, 2012, 33, 580–592.
- 8 A. M. Spokoyny, C. W. Machan, D. J. Clingerman, M. S. Rosen, M. J. Wiester, R. D. Kennedy, C. L. Stern, A. A. Sarjeant and C. A. Mirkin, *Nature Chem*, 2011, 3, 590–596.
- 9 V. N. Kalinin and V. A. Ol'shevskaya, Russ Chem Bull, 2008, 57, 815-836.
- 10 A. Weller, *Nature Chem*, 2011, **3**, 577–578.
- 11 M. O. Akram, C. D. Martin and J. L. Dutton, *Inorg. Chem.*, 2023, **62**, 13495–13504.
- 12 A. M. Spokoyny, C. D. Lewis, G. Teverovskiy and S. L. Buchwald, *Organometallics*, 2012, **31**, 8478–8481.
- 13 J. Schulz, R. Clauss, A. Kazimir, S. Holzknecht and E. Hey-Hawkins, *Angew Chem Int Ed*, 2023, **62**, e202218648.
- 14 A. Benton, J. D. Watson, S. M. Mansell, G. M. Rosair and A. J. Welch, *Journal of Organometallic Chemistry*, 2020, **907**, 121057.