Electronic Supplementary Material (ESI) for Dalton Transactions

Supporting Information for

Fixation of carbon dioxide and related small molecules by a bifunctional frustrated pyrazolylborane Lewis pair

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1. Computational Details:

All computations were performed using the hybrid density functional method M06-2X implemented in the Gaussian09 program.[1] For all main-group elements (C, H, N, B, F) the all-electron triple-ζ basis set (6-311++G**) was used.[2]

[1] Gaussian 09, Revision A.1, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

[2] R. Krishnan, J. S. Binkley, R. Seeger, J. A. Pople, *J. Chem. Phys.*, 1980, **72**, 650.

2. Energies of all optimized structures:

Compound	E(0 K)[a] [Ha]	H(298 K)[b] [Ha]	G(298 K)[b] [Ha]
pyrazolylborane **1**	-2020.477314	-2020.048934	-2020.152469
CO_2 adduct **3**	-2209.099688	-2208.652493	-2208.755688
CO_2	-188.5748808	-188.559323	-188.583543
Transition state (**TS**)	-2209.051971	-2208.607065	-2208.712996
van der Waals complex (**vdW**)	-2209.063577	-2208.617514	-2208.729232

[a]DFT energy excl. ZPE.
[b]standard conditions T = 298.15 K and p = 1 atm.

3. Figure S1

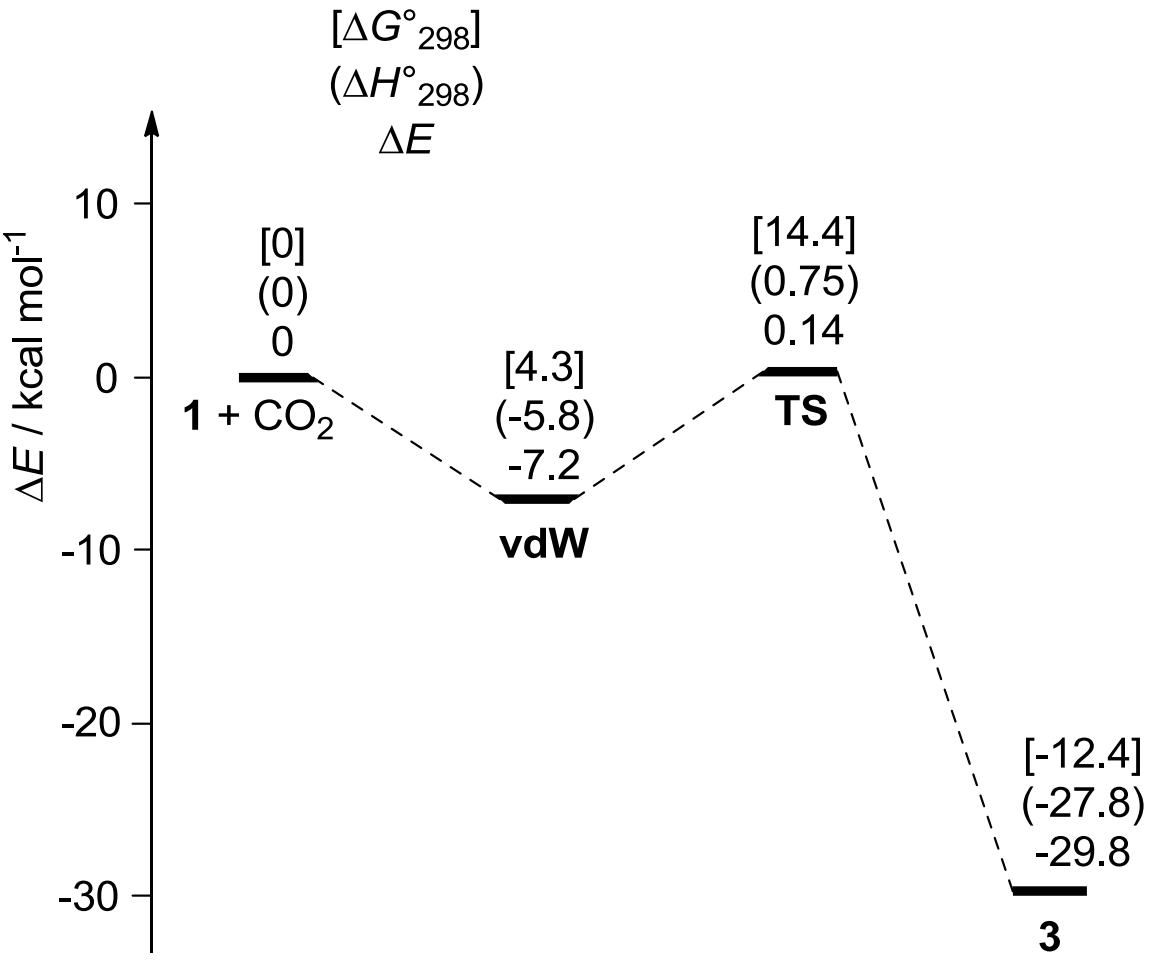
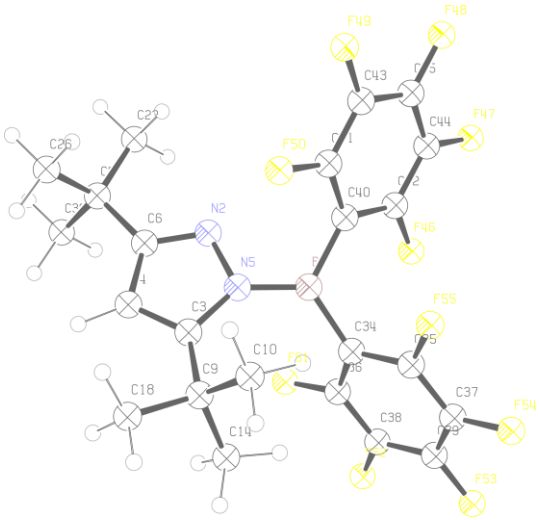


Fig. S1 Relative energies (kcal mol^{-1}) for stationary points on the **1** + CO_2 hypersurface. Values correspond to ΔE = zero-point uncorrected M06-2X/6-311++G(d,p) electronic energies, $\Delta H°_{298}$ = enthalpies at 298 K (in round brackets), $\Delta G°_{298}$ = Gibbs free energies at 298 K [in square brackets].

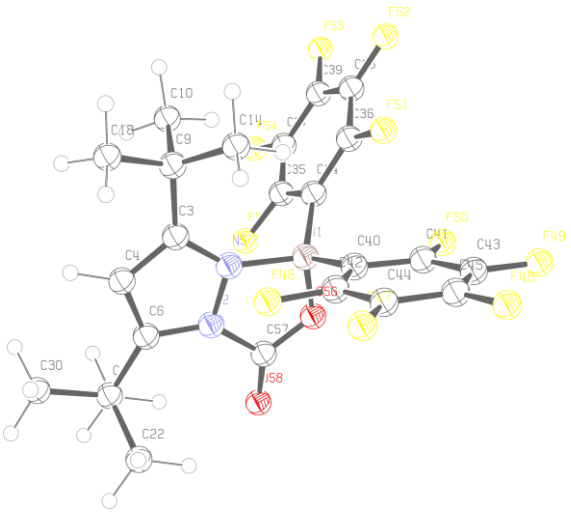
Calculated structure of the pyrazolylborane 1



B	0.117000	0.009200	0.089500
N	-2.068500	-0.637200	-0.509600
N	-0.894500	-1.004200	0.124800
F	1.222100	2.127900	-1.568800
F	0.438900	4.682900	-1.517300
F	-1.538800	5.466700	0.162300
F	-2.727900	3.670900	1.799000
F	-1.956000	1.114900	1.778600
F	1.285500	-1.663500	-1.929100
F	3.922300	-1.925700	-2.377100
F	5.700800	-0.721700	-0.730700
F	4.838500	0.771400	1.356900
F	2.196800	1.076100	1.788200
C	-0.978100	-2.322800	0.577700
C	-2.201100	-2.776300	0.176800
C	-2.834900	-1.690900	-0.507900
C	-4.207800	-1.687400	-1.133200
C	-0.013000	-3.010200	1.531300
C	0.347300	-2.060800	2.685900
C	1.263500	-3.531300	0.846900
C	-0.733400	-4.229300	2.131200
C	-4.520900	-0.313300	-1.727400
C	-5.240100	-2.027900	-0.047000
C	-4.250300	-2.756100	-2.235500
C	1.652700	-0.289700	-0.049700
C	2.599100	0.328600	0.756900
C	2.135900	-1.046400	-1.110100
C	3.960500	0.185700	0.554100
C	3.490300	-1.195200	-1.357800
C	4.403900	-0.578600	-0.515900
C	-0.346700	1.507900	0.088700
C	-1.362000	1.953600	0.933000
C	0.249600	2.470500	-0.718800
C	-1.768600	3.275800	0.970700
C	-0.142800	3.798500	-0.716700
C	-1.157000	4.200300	0.137300
H	-2.631000	-3.741600	0.386900
H	-0.554000	-1.712500	3.196300
H	0.973000	-2.588800	3.410200
H	0.906700	-1.186200	2.349200
H	1.027200	-4.049500	-0.085200
H	1.973700	-2.734700	0.636500
H	1.761600	-4.238800	1.514700
H	-1.666100	-3.941300	2.620200
H	-0.953000	-4.976300	1.364500
H	-0.084900	-4.697000	2.875000

H	-4.481800	0.461700	-0.959200
H	-3.800900	-0.049800	-2.504200
H	-5.522400	-0.323600	-2.164800
H	-6.244700	-2.034700	-0.478400
H	-5.053100	-3.013000	0.388300
H	-5.213800	-1.288000	0.756400
H	-4.039500	-3.750000	-1.831900
H	-5.242200	-2.780100	-2.694700
H	-3.514200	-2.540800	-3.013600

Calculated structure of the CO_2 adduct 3



B	0.22960300	-0.05826300	-0.56860700
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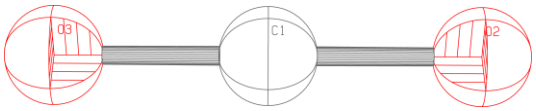
C	-1.65809000	0.07597800	1.47315900
C	-3.04449600	-0.14842000	1.36257600
N	-1.13306400	-0.08610900	0.26110900
C	-3.33020900	-0.43246500	0.03869200
H	-3.75911100	-0.10876100	2.16516600
C	-4.66807100	-0.73114800	-0.59835100
C	-0.90060400	0.49817900	2.71434200
C	-0.73623100	2.03015400	2.68582000
H	-1.70241100	2.52562500	2.56308800
H	-0.29780300	2.35977900	3.63118000
H	-0.07716300	2.34803800	1.87650900
C	0.47314100	-0.17325600	2.81559600
H	0.37602900	-1.25588400	2.91307600
H	1.10888000	0.04360200	1.95802100
H	0.98415300	0.20589900	3.70371900
C	-1.72688100	0.11471700	3.95025500
H	-2.67070000	0.66295800	3.99124200
H	-1.93898200	-0.95691400	3.96804900
H	-1.16032500	0.36636500	4.84903200
C	-4.63260500	-2.10337400	-1.29066800
H	-3.92887600	-2.11553700	-2.12145900
H	-4.36346000	-2.88799800	-0.57902500
H	-5.62782600	-2.32640500	-1.68293500
C	-5.03514200	0.38051700	-1.59673800
H	-6.03537100	0.18409700	-1.99087600
H	-5.05022600	1.35377300	-1.09986500
H	-4.34020100	0.41795800	-2.43366100
C	-5.72980500	-0.76397900	0.50851300
H	-5.81132600	0.20034900	1.01630300
H	-6.69956000	-0.98639500	0.05949200
H	-5.51579100	-1.53833500	1.24943800

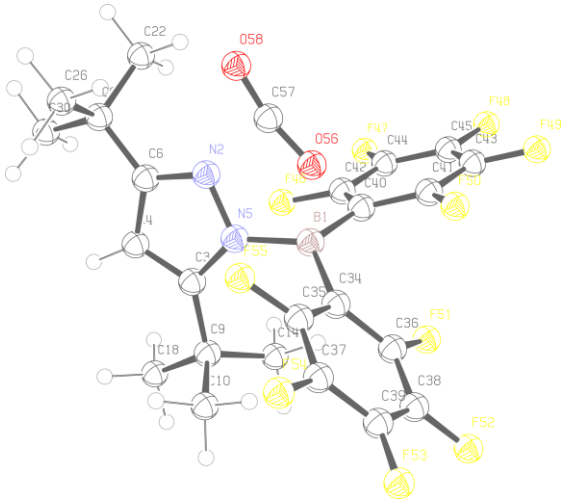
C	0.89860700	1.40970300	-0.41760700
C	0.15459600	2.50885100	-0.83626800
C	2.13625900	1.70938000	0.13586600
C	0.59678000	3.81663200	-0.73773400
C	2.61646300	3.00561500	0.25883500
C	1.84350800	4.06497900	-0.18531000
C	1.16144700	-1.36166500	-0.32754000
C	2.37731400	-1.44723800	-0.99716600
C	0.79965000	-2.49380900	0.38902400
C	3.21313400	-2.54756000	-0.92192600
C	1.60721800	-3.61732200	0.49214300
C	2.82468200	-3.64158600	-0.16420800
F	-0.38367100	-2.56339500	1.02414000
F	1.21445900	-4.66964400	1.20424900
F	3.60826400	-4.70713700	-0.07940000
F	4.37389500	-2.57048200	-1.56555200
F	2.78417600	-0.42953200	-1.76104900
F	2.92567300	0.74303400	0.61933400
F	3.80390300	3.24011200	0.80457200
F	2.28645900	5.30816800	-0.07101200
F	-0.16010400	4.82790000	-1.14769500
F	-1.08239800	2.33017300	-1.32386300
O	-0.36470300	-0.20922000	-1.94086100
C	-1.64355400	-0.43177800	-1.97356700
O	-2.34856600	-0.63788100	-2.90863000

Calculated structure of carbon dioxide, CO_2



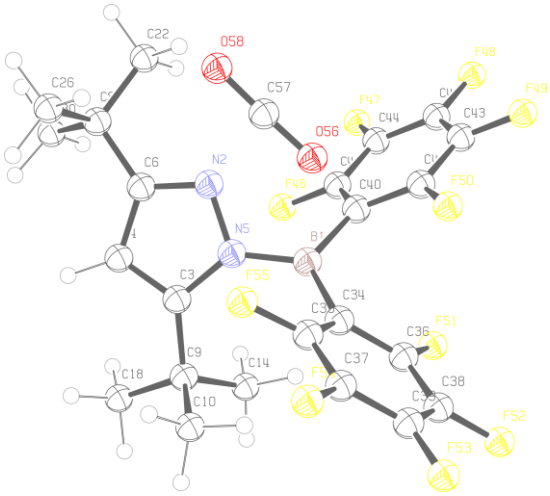
C	0.00000000	0.00000000	0.00000000
O	0.00000000	0.00000000	1.15490700
O	0.00000000	0.00000000	-1.15490700

Calculated structure of the transition state (TS) associated with the CO_2 fixation by 1



B	-0.21227400	0.06567500	-0.24377600
N	1.94200200	-0.95019300	-0.62277900
C	1.08586400	-1.58941600	1.34760200
C	2.36753300	-2.09668800	1.24380200
N	0.84689100	-0.91100400	0.18277000
C	2.86012000	-1.67717100	-0.00763200
H	2.88973800	-2.67748800	1.98374700
C	4.19671100	-1.97015500	-0.65067300
C	0.15993000	-1.68323600	2.54832600
C	-1.03822000	-2.60874100	2.27404800
H	-0.70228200	-3.56392000	1.86344100
H	-1.56476100	-2.80418600	3.21199300
H	-1.75279400	-2.16651400	1.58232000
C	-0.32067800	-0.28974900	2.98109000
H	0.52776500	0.34181300	3.25299400
H	-0.89261900	0.22453100	2.20698400
H	-0.97460800	-0.38381700	3.85220700
C	0.94910700	-2.28808200	3.71960800
H	1.25722700	-3.31387100	3.50402000
H	1.83689000	-1.69552500	3.95078100
H	0.31215100	-2.30987800	4.60660300
C	4.76433300	-0.68176900	-1.26089300
H	4.10056700	-0.29151500	-2.03334600
H	4.88981500	0.08650200	-0.49361700
H	5.73901100	-0.88252000	-1.71386400
C	4.00404900	-3.02574500	-1.75113700
H	4.96707900	-3.26370700	-2.21149900
H	3.58341700	-3.94577500	-1.33748000
H	3.33281300	-2.65705000	-2.52841100
C	5.16950200	-2.50808400	0.40332600
H	4.81956300	-3.45562700	0.82133000
H	6.14570900	-2.68549300	-0.05436800
H	5.30051200	-1.79436100	1.22083800
C	-1.71473800	-0.44539200	-0.27280300
C	-2.02414700	-1.65173400	-0.89743100
C	-2.78285000	0.22505700	0.31143500
C	-3.30789300	-2.16716700	-0.94318600
C	-4.07815200	-0.26702300	0.30042800
C	-4.34042600	-1.47014800	-0.33444600
C	0.13302100	1.60830400	-0.09375800
C	-0.61230400	2.57625700	-0.76431600
C	1.18704500	2.08536700	0.68086500
C	-0.35253400	3.93068600	-0.67353400
C	1.47202600	3.43830400	0.80131400
C	0.69855100	4.36305300	0.12197900
F	1.97665400	1.25626000	1.36420200
F	2.47980400	3.85226800	1.56067200
F	0.96286400	5.65521200	0.22695300
F	-1.09128500	4.81543300	-1.33125800
F	-1.62796000	2.20419200	-1.54649300
F	-2.58868100	1.38103300	0.95238000
F	-5.06385500	0.40115100	0.88486200
F	-5.57060900	-1.95543700	-0.35707700
F	-3.55800100	-3.32249700	-1.54602300
F	-1.06401600	-2.38163100	-1.46722400
O	0.10486100	-0.04138500	-2.16938100
C	1.11838800	-0.40141600	-2.66090400
O	1.95317100	-0.66452900	-3.40478300

Calculated structure of the van der Waals complex (vdW)



B	0.25230000	0.06230000	-0.27370000
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C	-0.83460000	-2.19080000	-1.04160000
C	-2.05620000	-2.71440000	-0.71320000
N	-0.74160000	-0.98740000	-0.36090000
C	-2.67410000	-1.77770000	0.16590000
H	-2.49000000	-3.62140000	-1.09820000
C	-4.03640000	-1.88830000	0.80980000
C	0.12150000	-2.68550000	-2.11580000
C	1.40510000	-3.31600000	-1.54680000
H	1.17570000	-4.00810000	-0.73380000
H	1.91120000	-3.87310000	-2.33940000
H	2.10520000	-2.56640000	-1.18350000
C	0.47030000	-1.53560000	-3.07550000
H	-0.43640000	-1.08340000	-3.48450000
H	1.05600000	-0.75060000	-2.59100000
H	1.07120000	-1.91900000	-3.90430000
C	-0.60140000	-3.77290000	-2.92760000
H	-0.82310000	-4.64690000	-2.31050000
H	-1.53490000	-3.39770000	-3.35240000
H	0.04350000	-4.09790000	-3.74680000
C	-4.51290000	-0.51650000	1.29480000
H	-3.83630000	-0.10780000	2.04470000
H	-4.57090000	0.18990000	0.46310000
H	-5.50660000	-0.61250000	1.74020000
C	-3.94410000	-2.86200000	1.99560000
H	-4.92830000	-2.98240000	2.45710000
H	-3.59690000	-3.84550000	1.66780000
H	-3.25200000	-2.48400000	2.75040000
C	-5.03280000	-2.43590000	-0.22270000
H	-4.75960000	-3.44200000	-0.54970000
H	-6.03040000	-2.48940000	0.22060000
H	-5.08070000	-1.78870000	-1.10200000
C	1.77310000	-0.25410000	-0.06240000
C	2.18170000	-1.22540000	0.84800000
C	2.78190000	0.49930000	-0.65370000
C	3.51470000	-1.43590000	1.16090000
C	4.12350000	0.30100000	-0.38430000
C	4.48760000	-0.67050000	0.53710000
C	-0.26940000	1.53870000	-0.32650000
C	0.33750000	2.58170000	0.37120000
C	-1.39070000	1.88030000	-1.08520000
C	-0.15290000	3.87570000	0.36180000
C	-1.89740000	3.16810000	-1.12710000
C	-1.27850000	4.16730000	-0.39290000
F	-2.00530000	0.97510000	-1.84260000
F	-2.96190000	3.45730000	-1.86600000
F	-1.75760000	5.39950000	-0.41830000

F	0.44040000	4.83500000	1.06140000
F	1.42870000	2.36140000	1.10340000
F	2.46630000	1.45200000	-1.53310000
F	5.05730000	1.03000000	-0.98060000
F	5.76420000	-0.86960000	0.81590000
F	3.86940000	-2.36890000	2.03500000
F	1.29050000	-2.01330000	1.44610000
O	0.02010000	0.30890000	2.52000000
C	-0.95050000	-0.07180000	3.02340000
O	-1.90180000	-0.42870000	3.56980000