Supplementary Information

Ability of Carbenes to Act as Lewis Base within a Halogen Bond

Steve Scheiner

Department of Chemistry and Biochemistry
Utah State University
Logan, Utah 84322-0300
USA

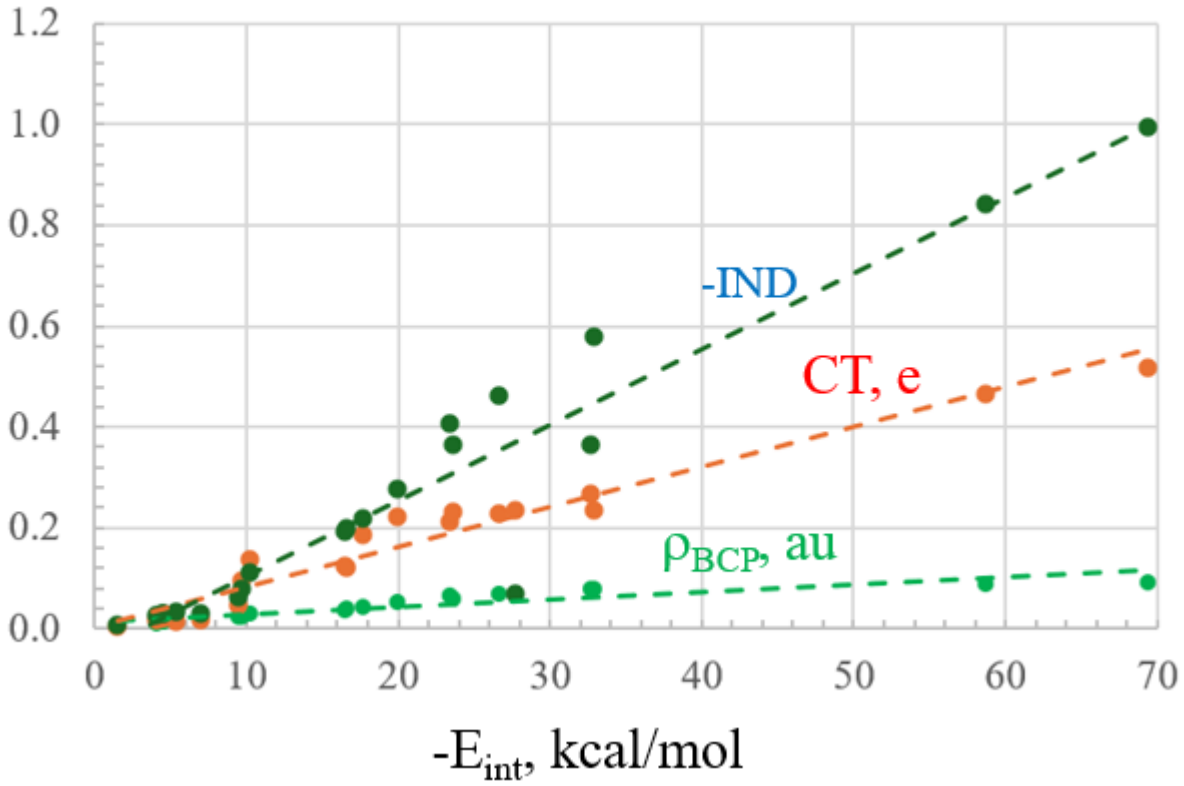

Fig S1. Correlations of the interaction energy with various properties. Induction energy IND in units of 100 kcal/mol so as to fit onto the same plot as charge transfer and bond critical point electron density.

Table S1. SAPT0 components (kcal/mol) of triplet complexes with ICN, including the percentage contribution of each to the total attractive energy (ES+IND+DISP).

	ES	IND	DISP	EX	%ES	%IND	%DISP
$C(NH_2)_2$	-12.75	-7.81	-6.69	20.23	46.8	28.7	24.5
$C(C_2H_5)_2$	-6.30	-2.91	-6.32	11.02	40.5	18.7	40.7
$C(C_6H_{11})_2$	-5.22	-3.10	-7.63	9.48	32.7	19.4	47.8
$C(CH=CH_2)_2$	-4.86	-2.76	-5.78	8.87	36.3	20.6	43.1
ring-$C(C(CH_2)_2)_2$	-4.99	-3.11	-5.86	8.87	35.7	22.3	42.0
$C(CH=CH=CH=CH_2)_2$	-4.67	-2.64	-6.59	8.34	33.6	19.0	47.4
$C(C_6H_5)_2$	-8.77	-4.93	-7.95	14.29	40.5	22.8	36.7
$C(NH_3)_2$	-38.12	-22.58	-11.91	51.64	52.5	31.1	16.4

Table S2. Interaction energy (kcal/mol) of Lewis base with ICN calculated at M06-2X and CCSD(T) levels.

	M06-2X	CCSD(T)
$C(NH_2)_2$	19.99	17.51
NHC	17.64	15.85
$C(C_2H_5)_2$	23.36	19.39
$C(CH=CH_2)_2$	23.59	19.01
ring-$C(C(CH_2)_2)_2$	27.67	23.99
$C(CH=CH=CH=CH_2)_2$	32.70	28.41
$C(C_6H_5)_2$	26.62	23.68
$C(NH_3)_2$	69.40	64.36
$C(PH_3)_2$	16.48	14.20

Table S3. SAPT0 components (kcal/mol) of complexes with ICN, including the percentage contribution of each to the total attractive energy (ES+IND+DISP).

	ES	IND	DISP	EX	%ES	%IND	%DISP
prototype XB							
OH_2	-10.95	-1.65	-2.32	7.78	73.4	11.1	15.5
NH_3	-18.40	-2.61	-3.40	14.40	75.4	10.7	13.9
CH_4	-1.73	-0.66	-2.10	3.42	38.6	14.7	46.7
$H_2C=CH_2$	-8.09	-1.37	-3.91	8.71	60.5	10.2	29.3
HC≡CH	-6.91	-1.22	-3.34	7.39	60.2	10.7	29.1
saturated R							
$C(OH)_2$ t	-20.73	-3.26	-4.65	17.70	72.4	11.4	16.2
$C(OH)_2$ c	-27.28	-3.69	-5.59	26.13	74.6	10.1	15.3
$C(NH_2)_2$	-62.06	-9.18	-10.06	58.51	76.3	11.3	12.4
NHC	-49.87	-7.59	-9.03	46.36	75.0	11.4	13.6
$C(C_2H_5)_2$	-85.22	-13.97	-15.36	87.88	74.4	12.2	13.4
$C(C_6H_{11})_2$	-114.24	-21.06	-19.63	115.69	73.7	13.6	12.7
unsaturated R							
$C(CH=CH_2)_2$	-76.16	-12.79	-14.18	76.21	73.9	12.4	13.7
ring-$C(C(CH_2)_2)_2$	-94.70	-17.06	-16.39	95.40	73.9	13.3	12.8

$C(CH=CH=CH=CH_2)_2$	-108.24	-22.55	-18.28	108.91	72.6	15.1	12.3
$C(C_6H_5)_2$	-89.78	-18.19	-18.03	93.39	71.3	14.4	14.3
$C(CH_2)_2$	-7.23	-1.61	-4.48	8.64	54.3	12.1	33.6
$C(CH=CH=CH_2)_2$	-7.07	-2.09	-4.48	9.56	51.8	15.3	32.8
dative C(0)							
$C(OH_2)_2$	-173.16	-27.08	-17.07	153.78	79.7	12.5	7.9
$C(NH_3)_2$	-192.76	-36.29	-20.29	165.33	77.3	14.6	8.1
$C(SeH_2)_2$	-43.12	-8.81	-10.78	40.14	68.8	14.1	17.2
$C(PH_3)_2$	-41.10	-8.63	-10.75	39.25	68.0	14.3	17.8

Cartesian coordinates of complexes with ICN

OH_2

8	2.910525000	0.000083000	-0.016919000
1	3.470832000	0.770070000	0.111418000
1	3.470557000	-0.770112000	0.111415000
6	-1.945992000	-0.000029000	0.006558000
7	-3.094741000	0.000104000	0.013382000
53	0.058746000	-0.000022000	-0.004160000

NH_3

7	2.929367000	0.000121000	0.000335000
1	3.294392000	-0.536516000	0.778578000
1	3.299327000	-0.405494000	-0.851476000
1	3.297725000	0.941025000	0.076992000
6	-1.961678000	0.000460000	0.000051000
7	-3.110669000	-0.000235000	0.000694000
53	0.059391000	-0.000018000	-0.000219000

CH_4

6	-1.992028000	0.007832000	-0.000209000
7	-3.140320000	0.015573000	-0.000619000
53	0.000946000	-0.005374000	0.000195000
6	3.385213000	0.012984000	-0.000480000
1	3.015197000	-1.009662000	-0.062732000
1	3.044235000	0.587508000	-0.860571000
1	4.472558000	-0.007253000	0.000348000
1	3.041028000	0.480341000	0.921069000

$H_2C=CH_2$

6	2.221900000	0.000081000	0.000422000
7	3.370444000	-0.000112000	0.001005000
53	0.216460000	0.000008000	-0.000328000

6	-3.023297000	-0.663003000	0.000485000
6	-3.023220000	0.662982000	0.000485000
1	-3.029317000	-1.230373000	-0.922334000
1	-3.029943000	-1.230221000	0.923399000
1	-3.028552000	1.230297000	-0.922386000
1	-3.030000000	1.230324000	0.923319000

HC≡CH

6	2.145025000	0.000299000	-0.000680000
7	3.293543000	0.000710000	-0.001447000
53	0.142658000	-0.000453000	0.000501000
6	-3.101929000	0.599328000	-0.000884000
6	-3.106278000	-0.596881000	-0.000870000
1	-3.124668000	-1.661887000	-0.000931000
1	-3.111932000	1.664450000	-0.000880000

$C(OH)_2$ t

6	-2.360326000	-0.000323000	0.000039000
8	-3.060740000	-1.098015000	0.000264000
1	-4.033651000	-0.980236000	0.000508000
8	-3.057050000	1.099743000	0.000176000
1	-4.030352000	0.985252000	0.000445000
6	2.586301000	0.000490000	-0.000078000
7	3.735505000	0.001155000	-0.000078000
53	0.556640000	-0.000527000	-0.000070000

$C(OH)_2$ c

6	2.305513000	-0.000044000	0.000061000
8	3.082666000	-1.047690000	0.000143000
1	2.530652000	-1.839137000	0.000106000
8	3.079767000	1.049749000	0.000147000
1	2.525566000	1.839677000	0.000085000
6	-2.556276000	0.000420000	0.000006000
7	-3.705446000	0.000947000	0.000440000
53	-0.507792000	-0.000489000	-0.000113000

$C(NH_2)_2$

6	-1.981629000	0.000016000	-0.466044000
7	-2.306719000	1.188531000	0.442824000
1	-3.299774000	1.312553000	0.653751000

1	-1.756910000	1.238721000	1.323904000
1	-2.019155000	1.998773000	-0.106895000
7	-2.306527000	-1.188659000	0.442773000
1	-2.019100000	-1.998729000	-0.107253000
1	-1.756576000	-1.238929000	1.323718000
1	-3.299552000	-1.312688000	0.653799000
6	2.622180000	0.000215000	0.295020000
7	3.722673000	-0.000147000	0.646390000
53	0.312109000	0.000016000	-0.253562000

NHC

7	2.449607000	-1.049942000	-0.000110000
6	1.605440000	-0.000201000	-0.000044000
6	3.779635000	-0.673705000	-0.000030000
6	3.779301000	0.674362000	-0.000198000
7	2.449101000	1.049951000	0.000007000
1	2.122279000	-2.001563000	-0.000199000
1	2.121273000	2.001403000	-0.000129000
1	4.590796000	1.378855000	-0.000168000
1	4.591471000	-1.377806000	0.000063000
6	-3.115859000	0.000170000	0.000149000
7	-4.266169000	0.000493000	-0.000583000
53	-1.021598000	-0.000154000	0.000113000

$C(C_2H_5)_2$

6	2.492477000	1.216406000	0.217633000
1	3.515096000	1.139684000	-0.175437000
6	1.835466000	2.552695000	-0.100857000
1	1.630572000	2.630879000	-1.168205000
1	0.891822000	2.661280000	0.430182000
1	2.613203000	1.115862000	1.317803000
1	2.492448000	3.373961000	0.181462000
6	1.836175000	-2.552569000	0.100399000
1	1.630941000	-2.631401000	1.167635000
1	0.892717000	-2.660991000	-0.431008000
6	2.492983000	-1.215974000	-0.217069000
1	3.515315000	-1.139006000	0.176715000
1	2.614552000	-1.114862000	-1.317125000
1	2.493366000	-3.373580000	-0.182169000
6	1.712217000	0.000056000	0.000120000

6	-2.906403000	-0.000148000	0.000089000
7	-4.057893000	-0.000130000	0.000218000
53	-0.729477000	-0.000070000	-0.000062000

$C(C_6H_{11})_2$

6	0.296802000	4.288609000	0.022861000
6	0.480950000	3.588754000	1.366753000
6	0.040778000	2.130645000	1.288429000
6	0.828117000	1.388525000	0.201653000
6	0.591207000	2.086486000	-1.180594000
6	1.031019000	3.547395000	-1.090490000
1	0.648232000	5.319991000	0.079203000
1	-0.770372000	4.328152000	-0.217274000
1	-0.087029000	4.102865000	2.143312000
1	1.534888000	3.637642000	1.661127000
1	0.184947000	1.629491000	2.247904000
1	-1.025270000	2.073544000	1.056021000
1	1.902122000	1.466025000	0.413738000
1	1.138185000	1.570596000	-1.970823000
1	-0.473053000	2.027161000	-1.419597000
1	0.847847000	4.027497000	-2.053541000
1	2.109936000	3.589237000	-0.912108000
6	1.396684000	-1.020438000	-0.319915000
6	1.736349000	-1.469303000	1.151180000
6	2.698717000	-2.655689000	1.106810000
6	3.966628000	-2.329219000	0.325924000
6	3.634160000	-1.869738000	-1.090087000
6	2.685656000	-0.673391000	-1.074531000
1	0.915769000	-1.882762000	-0.793075000
1	0.823234000	-1.736305000	1.683495000
1	2.202884000	-0.631652000	1.678101000
1	2.942006000	-2.942501000	2.131566000
1	2.191059000	-3.508427000	0.647741000
1	4.622225000	-3.200780000	0.297367000
1	4.515726000	-1.535752000	0.844029000
1	4.545204000	-1.608985000	-1.630741000
1	3.165538000	-2.693239000	-1.638144000
1	2.438329000	-0.379864000	-2.096127000
1	3.187022000	0.176740000	-0.604248000
6	0.402216000	0.012526000	-0.043974000

6	-3.957696000	-1.386091000	-0.155897000
7	-5.048680000	-1.755023000	-0.206018000
53	-1.834117000	-0.667508000	-0.059519000

$C(CH=CH_2)_2$

1	-2.578929000	-3.327921000	0.000643000
6	-2.005958000	-2.408239000	0.000541000
1	-3.695370000	-1.156854000	-0.000870000
1	-0.925711000	-2.486627000	0.001107000
6	-2.606002000	-1.206262000	-0.000298000
6	-1.828644000	0.000072000	-0.000221000
6	-2.605323000	1.206869000	-0.000385000
1	-3.694725000	1.157997000	-0.000978000
6	-2.004877000	2.408633000	0.000550000
1	-0.924620000	2.486795000	0.001131000
1	-2.577651000	3.328436000	0.000813000
6	2.834510000	-0.000095000	-0.000009000
7	3.985789000	-0.000031000	0.000051000
53	0.675363000	-0.000141000	-0.000062000

ring-$C(C(CH_2)_2)_2$

1	-2.238226000	-3.263138000	-0.099086000
1	-4.202547000	-1.354386000	-0.397407000
6	-1.590360000	-2.394078000	-0.073506000
6	-3.532667000	-0.741510000	0.203370000
1	-0.523555000	-2.552974000	-0.172398000
1	-3.832653000	-0.851140000	1.247700000
6	-2.077497000	-1.149712000	0.056091000
6	-1.206356000	-0.000168000	0.000012000
6	-2.077016000	1.149771000	-0.056096000
6	-3.532383000	0.742118000	-0.203215000
6	-1.589608000	2.394045000	0.073187000
1	-3.832439000	0.851815000	-1.247521000
1	-0.522783000	2.552862000	0.171964000
1	-4.201968000	1.355282000	0.397597000
1	-2.237374000	3.263189000	0.098521000
6	3.393165000	0.000048000	-0.000033000
7	4.545246000	0.000080000	-0.000050000
53	1.189644000	-0.000097000	0.000040000

$C(CH=CH=CH=CH_2)_2$

6	-1.792734000	-0.957244000	0.357387000
6	-3.104944000	-0.842186000	0.033135000
1	-1.406856000	-1.945680000	0.593271000
1	-3.504739000	0.121852000	-0.267745000
6	-4.018358000	-1.958161000	-0.009791000
6	-5.294730000	-1.821057000	-0.373700000
1	-3.629512000	-2.929260000	0.276958000
1	-5.691387000	-0.857056000	-0.670183000
1	-5.975636000	-2.661199000	-0.385144000
6	-1.265866000	1.447052000	0.291904000
6	-0.405428000	2.460317000	0.011410000
1	-2.278987000	1.704058000	0.602845000
1	0.613140000	2.210168000	-0.270896000
6	-0.752836000	3.856553000	0.062460000
6	0.137554000	4.807504000	-0.230525000
1	-1.765542000	4.117444000	0.350165000
1	1.150727000	4.551885000	-0.517697000
1	-0.117665000	5.857946000	-0.190674000
6	-0.846151000	0.095899000	0.208643000
6	3.502266000	-1.346950000	-0.090211000
7	4.595307000	-1.711185000	-0.131445000
53	1.386541000	-0.615891000	-0.003114000

$C(C_6H_5)_2$

6	-2.555862000	3.701274000	-0.145804000
6	-1.337053000	3.598082000	0.517627000
6	-3.121089000	2.589776000	-0.761691000
1	-0.901220000	4.468380000	0.989354000
1	-4.056987000	2.683377000	-1.296201000
6	-0.669868000	2.390002000	0.548679000
6	-2.486882000	1.364885000	-0.686320000
1	0.289644000	2.304017000	1.040318000
1	-2.914452000	0.500325000	-1.176800000
6	-1.244423000	1.238954000	-0.027882000
6	-0.526379000	-0.000032000	-0.000037000
1	-3.061988000	4.657038000	-0.194143000
6	-1.244762000	-1.238840000	0.028068000
6	-2.486769000	-1.364867000	0.687223000
6	-0.670544000	-2.389618000	-0.549334000

1	-2.913942000	-0.500460000	1.178313000
1	0.288887000	-2.303394000	-1.041111000
6	-3.121071000	-2.589748000	0.762313000
6	-1.337872000	-3.597628000	-0.518598000
1	-4.056609000	-2.683593000	1.297409000
1	-0.902451000	-4.467771000	-0.990986000
6	-2.556347000	-3.700946000	0.145450000
1	-3.062587000	-4.656664000	0.193564000
6	4.088266000	-0.000064000	0.000183000
7	5.240305000	-0.000779000	0.000112000
53	1.891198000	-0.000060000	0.000004000

$C(CH_2)_2$

6	-3.042757000	1.414265000	0.000016000
1	-4.043290000	1.828516000	0.000591000
6	-2.856675000	0.129343000	0.000180000
1	-2.205192000	2.101369000	-0.000566000
6	-2.668000000	-1.160661000	0.000368000
1	-2.601874000	-1.713941000	0.929755000
1	-2.602603000	-1.714396000	-0.928798000
6	2.408698000	0.261449000	0.000224000
7	3.532829000	0.496932000	0.000534000
53	0.446709000	-0.148046000	-0.000178000

$C(CH{=}CH{=}CH_2)_2$

6	-1.468409000	-2.293505000	0.187453000
6	-1.421612000	-2.342644000	-1.138779000
1	-1.379494000	-3.208008000	0.762216000
1	-1.307056000	-3.283309000	-1.658866000
1	-1.496462000	-1.443324000	-1.740341000
6	-1.627884000	-1.060976000	0.983278000
1	-1.528255000	-1.149416000	2.061831000
6	-3.583626000	1.760658000	-0.235438000
6	-4.649569000	0.973750000	-0.311310000
1	-3.694667000	2.832673000	-0.351471000
1	-5.637745000	1.384576000	-0.465170000
1	-4.561229000	-0.103318000	-0.225724000
6	-2.205740000	1.285711000	-0.014387000
1	-1.395507000	1.959691000	-0.280899000
6	-1.899217000	0.119725000	0.485291000
6	3.246486000	0.559023000	-0.316581000

7	4.324690000	0.848350000	-0.586993000
53	1.365755000	0.057765000	0.154155000

$C(OH_2)_2$

6	-1.995162000	-0.000348000	-0.530737000
8	-2.320384000	-1.193016000	0.535082000
1	-1.488941000	-1.625561000	0.823978000
1	-2.900714000	-1.824609000	0.088654000
8	-2.321043000	1.194214000	0.533788000
1	-2.898978000	1.826596000	0.085408000
1	-1.489835000	1.625714000	0.824703000
6	2.572036000	0.000452000	0.295880000
7	3.678078000	0.001086000	0.624882000
53	0.315134000	-0.000376000	-0.251674000

$C(NH_3)_2$

6	-1.981629000	0.000016000	-0.466044000
7	-2.306719000	1.188531000	0.442824000
1	-3.299774000	1.312553000	0.653751000
1	-1.756910000	1.238721000	1.323904000
1	-2.019155000	1.998773000	-0.106895000
7	-2.306527000	-1.188659000	0.442773000
1	-2.019100000	-1.998729000	-0.107253000
1	-1.756576000	-1.238929000	1.323718000
1	-3.299552000	-1.312688000	0.653799000
6	2.622180000	0.000215000	0.295020000
7	3.722673000	-0.000147000	0.646390000
53	0.312109000	0.000016000	-0.253562000

$C(SeH_2)_2$

6	0.954199000	-0.000028000	-0.251180000
34	1.911432000	1.538786000	0.019062000
1	2.707663000	1.414815000	1.299370000
1	3.215847000	1.413720000	-0.728003000
34	1.911528000	-1.538762000	0.019061000
1	3.215990000	-1.413605000	-0.727939000
1	2.707771000	-1.414707000	1.299350000
6	-3.777386000	-0.000027000	0.089628000
7	-4.924752000	-0.000062000	0.171749000
53	-1.705953000	-0.000006000	-0.050413000

$C(PH_3)_2$

6	-1.716966000	0.000031000	-0.033281000
15	-2.422286000	-1.484365000	0.000514000
1	-3.047981000	-1.958827000	1.175542000
1	-3.426753000	-1.814798000	-0.936327000
1	-1.494918000	-2.509606000	-0.224289000
15	-2.422731000	1.484182000	0.000527000
1	-1.494546000	2.509963000	-0.218383000
1	-3.423017000	1.816208000	-0.940238000
1	-3.053859000	1.956534000	1.173539000
6	3.041123000	0.000115000	-0.006742000
7	4.191279000	0.000057000	-0.012960000
53	0.968536000	0.000038000	0.005385000