Supporting Information

Effect of Substituents at the Hetreoatom on the Structure and Ligating Properties of N-Heterocyclic Carbene, Silylene, Germylene and Abnormal Carbene: A Theoretical study

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Cartesian coordinates of the optimized geometries of the systems 1 – 6 along with the total energies including zero point vibrational energies (in a. u) of the respective molecules.

1.   **1** (R = H), T. E. = -226.11260

6   0.000000 -1.279186 -0.000054

7   -1.052041 -0.403598 -0.000211

6   -0.679203   0.939260   0.000024

6   0.679203   0.939260   0.000027

7   1.052041 -0.403598 -0.000212

1   -2.008034 -0.727390   0.001433

1   -1.386940   1.754574   0.000053

1   1.386940   1.754575   0.000057

1   2.008034 -0.727390   0.001430

2.   **1** (R = F), T. E. = -424.45331

6   0.000010 -1.038098   0.000214

7   -1.003969 -0.151932   0.000078

6   -0.683975   1.192066 -0.000061

6   0.683998   1.192051 -0.000008

7   1.003957 -0.151940   0.000466

1   -1.414032   1.985993 -0.000518

1   1.414034   1.985998   0.000447

9   2.321784 -0.551168 -0.000359

9   -2.321796 -0.551166 -0.000153

3.   **1** (R = Cl), T. E. = -1145.22636

6   -0.000077 -0.854006   0.000000

7   -0.000021   0.028543   1.034787

6   -0.000021   1.377544   0.678995

6   -0.000021   1.377544   -0.678995

7   -0.000021   0.028543   -1.034787

17   0.000021   -0.475548   2.678554

1   0.000148   2.181264   1.398644

1   0.000148   2.181264   -1.398644

17   0.000021   -0.475548   -2.678554

4.   **1** (R = OH), T. E. = -376.43231

6   -0.000033   -0.988366   0.000026

7   -1.030907   -0.115015   0.000013

6   -0.685566   1.217120   0.000025

6   0.685692   1.217041   0.000053

7   1.030879   -0.115081   -0.000062

1   -1.409278   2.016648   -0.000044

1   1.409471   2.016524   -0.000040

8   -2.363696   -0.508095   -0.000115

1   -2.299635   -1.483640   0.000744

8   2.363657   -0.508147   0.000041

1   2.299392   -1.483681   -0.000352

5.   **1** (R = NH$_2$), T. E. = -336.71582

6   -0.036867   -1.008626   0.000035

7   -1.060399   -0.104858   -0.000025

6   -0.654541   1.223633   -0.000041

6   0.702870   1.185721   0.000091

7   1.041576   -0.172802   -0.000004

```
1   -1.358301    2.041939   -0.000235

1    1.440024    1.975504    0.000006

7   -2.432823   -0.441860   -0.000011

1   -2.594603   -1.030320   -0.816790

1   -2.594693   -1.029977    0.817018

7    2.359710   -0.667806   -0.000014

1    2.841146   -0.325188   -0.829615

1    2.841213   -0.325037    0.829485
```

6.   **1** (R = PH$_2$), T. E. = -909.98383

```
6   -0.000345   -0.790836    0.000000

7   -0.000045    0.073695    1.071416

6    0.000339    1.422080    0.676244

6    0.000339    1.422080   -0.676244

7   -0.000045    0.073695   -1.071416

1    0.000633    2.237823    1.384031

1    0.000633    2.237823   -1.384031

15   -0.000045   -0.410376    2.773071

15   -0.000045   -0.410376   -2.773071

1    1.034262   -1.379316   -2.683532

1   -1.034912   -1.378714   -2.683630

1   -1.034912   -1.378714    2.683630

1    1.034262   -1.379316    2.683532
```

7.   **1** (R = CH$_3$), T. E. = -304.68218

```
6   -0.001160   -0.983199    0.000000

7   -0.000301   -0.122356    1.065346
```

4

6   0.001057   1.214495   0.679600

6   0.001057   1.214495   -0.679600

7   -0.000301   -0.122356   -1.065346

1   0.001947   2.033770   1.384435

1   0.001947   2.033770   -1.384435

6   -0.000301   -0.571485   -2.449283

1   -0.891962   -0.210251   -2.974391

1   0.893241   -0.213363   -2.973348

1   -0.002180   -1.662126   -2.442093

6   -0.000301   -0.571485   2.449283

1   -0.002180   -1.662126   2.442093

1   0.893241   -0.213363   2.973348

1   -0.891962   -0.210251   2.974391

8.   **1** (R = Ph), T. E. = -688.06701

6   0.351847   -0.078836   0.000000

7   -0.472556   0.172474   1.068423

6   -1.756346   0.566829   0.676819

6   -1.756346   0.566829   -0.676819

7   -0.472556   0.172474   -1.068423

1   -2.527817   0.852612   1.374846

1   -2.527817   0.852612   -1.374846

6   -0.056469   0.022805   2.425853

6   1.282831   0.242670   2.768845

6   1.688165   0.096911   4.095481

6   0.767817   -0.258083   5.087322

6   -0.566289   -0.478395   4.738289

6	-0.980221	-0.346197	3.410315
1	1.986640	0.516032	1.990863
1	2.729499	0.268998	4.355363
1	1.088665	-0.365196	6.120012
1	-1.289736	-0.767869	5.496064
1	-2.011822	-0.554618	3.142671
6	-0.056469	0.022805	-2.425853
6	-0.980221	-0.346197	-3.410315
6	-0.566289	-0.478395	-4.738289
6	0.767817	-0.258083	-5.087322
6	1.688165	0.096911	-4.095481
6	1.282831	0.242670	-2.768845
1	-2.011822	-0.554618	-3.142671
1	-1.289736	-0.767869	-5.496064
1	1.088665	-0.365196	-6.120012
1	2.729499	0.268998	-4.355363
1	1.986640	0.516032	-1.990863

9.   **1** (R = ^{t}Bu), T. E. = -540.40593

6	0.560586	-0.000265	0.000000
7	-0.288745	-0.000249	1.071894
6	-1.625942	-0.000090	0.679390
6	-1.625942	-0.000090	-0.679390
7	-0.288745	-0.000249	-1.071894
1	-2.459373	-0.000056	1.363090
1	-2.459373	-0.000056	-1.363090
6	0.221850	0.000010	2.476121

6   0.221850   0.000010   -2.476121

6   -0.950377   -0.000874   3.468213

1   -0.551085   -0.000914   4.487753

1   -1.579292   0.890307   3.359540

1   -1.578324   -0.892680   3.359064

6   1.076984   -1.263180   2.684255

1   1.486290   -1.278674   3.701664

1   0.474177   -2.167807   2.540575

1   1.903343   -1.284254   1.968712

6   1.075227   1.264374   2.684397

1   0.471237   2.168185   2.540544

1   1.484323   1.280493   3.701882

1   1.901713   1.286492   1.969021

6   1.075227   1.264374   -2.684397

1   1.484323   1.280493   -3.701882

1   0.471237   2.168185   -2.540544

1   1.901713   1.286492   -1.969021

6   1.076984   -1.263180   -2.684255

1   1.903343   -1.284254   -1.968712

1   0.474177   -2.167807   -2.540575

1   1.486290   -1.278674   -3.701664

6   -0.950377   -0.000874   -3.468213

1   -1.578324   -0.892680   -3.359064

1   -1.579292   0.890307   -3.359540

1   -0.551085   -0.000914   -4.487753

10.   **2** (R = H), T. E. = -242.15972

7

```
7   1.090569   -0.107662   -0.000110

6   0.327041   -1.219552    0.000000

7  -0.915807   -0.626636    0.000152

6  -0.815804    0.748696   -0.000082

7   0.434051    1.112028   -0.000074

1   2.100214   -0.096026    0.000731

1  -1.776714   -1.154799   -0.000624

1  -1.652607    1.431839    0.000611
```

11.   **2** (R = F), T. E. = -440.49348

```
7   0.988381   -0.144415   -0.000658

6   0.010789   -1.052950    0.000108

7  -0.996911   -0.150933    0.000302

6  -0.604220    1.160435    0.000034

7   0.707905    1.178535    0.000000

1  -1.257713    2.019038    0.000333

9   2.308572   -0.470265    0.000246

9  -2.317163   -0.512653   -0.000100
```

12.   **2** (R = Cl), T. E. = -1161.26923

```
7   -1.019326    0.006686   -0.000089

6   -0.006830   -0.885645    0.000401

7    1.028127    0.015942    0.000221

6    0.593753    1.326473   -0.000118

7   -0.707789    1.351817    0.000152

1    1.238448    2.192553    0.000014

17  -2.673594   -0.416575   -0.000098
```

17   2.681413   -0.433933   -0.000120

13.   **2** (R = OH), T. E. = -392.47481

7   -1.010526   -0.146504   -0.004822

6   0.017621   -1.019468   -0.004839

7   1.027024   -0.113230   0.004519

6   0.592761   1.182352   0.002283

7   -0.718404   1.188876   -0.008342

1   1.231650   2.052272   0.006726

8   -2.330658   -0.509628   -0.101263

8   2.372495   -0.441520   0.012966

1   -2.672107   -0.506003   0.812561

1   2.356806   -1.418380   -0.037058

14.   **2** (R = NH$_2$), T. E. = -352.76817

7   -1.024287   -0.182938   0.000077

6   0.028251   -1.026724   0.000028

7   1.049946   -0.107475   -0.000060

6   0.572606   1.181650   -0.000042

7   -0.729259   1.180092   0.000046

1   1.205123   2.057544   -0.000153

7   -2.359855   -0.592591   -0.000031

7   2.430330   -0.391666   -0.000030

1   -2.808623   -0.193540   0.823647

1   2.619421   -0.968619   0.818927

1   -2.808470   -0.193600   -0.823825

1   2.619277   -0.969291   -0.818525

15.   **2** (R = PH$_2$), T. E. = -926.03191

7 -1.050097   0.005035 -0.000099

6   0.000318 -0.853261 -0.000068

7   1.065575   0.031328   0.000030

6   0.586788   1.335770   0.000083

7 -0.708094   1.367768 -0.000021

1   1.217491   2.214235   0.000008

15 -2.734956 -0.534433   0.000004

15 2.737529 -0.549894 -0.000088

1 -3.171045   0.345695   1.030609

1   3.206032   0.318218 -1.030331

1 -3.171364   0.346163 -1.030048

1   3.205970   0.316635   1.031557

16.   **2** (R = CH$_3$), T. E. = -320.73193

7 -1.041748 -0.136517   0.000015

6 -0.003491 -1.000956 -0.000030

7   1.057195 -0.120903 -0.000068

6   0.594940   1.174921   0.000043

7 -0.707746   1.207247   0.000020

1   1.225992   2.053102 -0.000229

6 -2.450473 -0.492073 -0.000004

6   2.457689 -0.522164   0.000035

1 -2.938831 -0.088256   0.891978

1   2.967728 -0.146125   0.893112

1 -2.939113 -0.086830 -0.891161

1   2.486035 -1.612163   0.000307

1 -2.515443 -1.580292 -0.000809

1 2.967731 -0.146589 -0.893237

17. **2** (R = Ph), T. E. = -704.11644

6 0.001770 0.448151 0.075016

7 -1.048248 -0.397352 -0.058996

7 -0.716419 -1.729757 -0.279657

6 0.581300 -1.707807 -0.278379

7 1.057301 -0.426235 -0.066556

1 1.202489 -2.574616 -0.448304

6 -2.429132 -0.031295 0.007944

6 -2.776471 1.304398 0.242686

6 -4.123720 1.659984 0.305131

6 -5.124246 0.697377 0.136295

6 -4.763897 -0.631853 -0.096190

6 -3.419054 -1.004226 -0.161577

1 -1.993211 2.042086 0.373506

1 -4.390132 2.697819 0.487959

1 -6.172122 0.981098 0.186103

1 -5.530845 -1.390596 -0.228903

1 -3.135237 -2.034043 -0.341991

6 2.434722 -0.050438 -0.012279

6 3.385693 -0.941691 0.495661

6 4.732488 -0.571414 0.526909

6 5.128756 0.687547 0.069918

6 4.168225 1.577625 -0.421190

6 2.822377 1.213209 -0.469622

```
1    3.079802   -1.907693    0.887060

1    5.467836   -1.266204    0.923729

1    6.176174    0.974951    0.100555

1    4.466686    2.560469   -0.776101

1    2.067251    1.892734   -0.849093
```

18.   **2** (R = ^{t}Bu), T. E. = -556.45940

```
6   -0.015183    0.665204    0.000131

7    1.043693   -0.168705   -0.000085

7    0.731196   -1.520503   -0.000098

6   -0.571212   -1.515134    0.000112

7   -1.064886   -0.229675    0.000309

1   -1.167797   -2.414078    0.000240

6    2.485170    0.201134   -0.000026

6   -2.495054    0.197547   -0.000006

6    3.135198   -0.388004    1.265447

1    4.202713   -0.140636    1.284861

1    2.669661    0.026235    2.167215

1    3.029527   -1.476599    1.288845

6    2.613380    1.729130   -0.000201

1    2.141890    2.170421    0.882386

1    3.678177    1.990365    0.000189

1    2.142581    2.170173   -0.883251

6    3.135614   -0.388315   -1.265152

1    4.203053   -0.140632   -1.284235

1    3.030271   -1.476951   -1.288171

1    2.670267    0.025545   -2.167183
```

6   -2.749233   1.037408   1.264406

1   -3.787648   1.388979   1.278868

1   -2.573650   0.442751   2.168633

1   -2.082317   1.903621   1.287527

6   -3.409164   -1.036518   -0.000591

1   -3.259066   -1.656411   -0.892183

1   -3.260323   -1.656372   0.891243

1   -4.452191   -0.704256   -0.001298

6   -2.748532   1.037978   -1.264189

1   -2.081786   1.904344   -1.286518

1   -2.572271   0.443773   -2.168568

1   -3.787012   1.389323   -1.279062

19.   **3** (R = H), T. E. = -815.30367

15 -1.307243   -0.348290   -0.121370

6   0.036573   -1.427412   0.007692

15   1.339179   -0.317339   0.104504

6   0.537280   1.346985   -0.052776

7   -0.741953   1.319269   0.061555

1   1.085974   2.288882   -0.060647

1   -2.242215   -0.524167   0.920174

1   2.427761   -0.532598   -0.766927

20.   **3** (R = F), T. E. = -1013.84805

15   1.248923   -0.239032   0.477694

6   -0.027988   -1.331003   0.061186

15 -1.205672   -0.217295   -0.334526

6   -0.500723   1.530161   -0.040447

7   0.756477   1.504961   0.066512

1   -1.098066   2.431463   -0.164149

9   2.538063   -0.428795   -0.478319

9   -2.724038   -0.384119   0.192387

21.   **3** (R = Cl), T. E. = -1734.55182

15   1.225928   -0.099245   0.654429

6   -0.006842   -1.213282   0.163663

15   -1.161939   -0.133182   -0.416617

6   -0.476250   1.613710   -0.129023

7   0.758366   1.610817   0.146004

1   -1.051867   2.509245   -0.358246

17   3.016161   -0.399428   -0.331874

17   -3.152513   -0.347696   0.070768

22.   **3** (R = OH), T. E. = -965.77003

15   1.266103   -0.233626   0.479319

6   -0.043622   -1.292687   0.068197

15   -1.221223   -0.181492   -0.327087

6   -0.502402   1.542267   -0.037196

7   0.756917   1.504946   0.084422

1   -1.085996   2.453443   -0.158012

8   2.542637   -0.510944   -0.536309

8   -2.798367   -0.352185   0.108904

1   3.383046   -0.215910   -0.148162

1   -2.946702   -1.137823   0.664978

23.   **3** (R = NH$_2$), T. E. = -926.00474

15 -1.277754 -0.198912 -0.463027

6 0.019793 -1.267410 -0.054467

15 1.252932 -0.177277 0.348095

6 0.519007 1.518750 0.062028

7 -0.748309 1.509140 -0.072815

1 1.095641 2.436446 0.182334

7 -2.704175 -0.564011 0.368436

7 2.850834 -0.373763 -0.204137

1 -2.682073 -0.599629 1.382918

1 3.523143 -0.659567 0.500676

1 -3.545725 -0.116587 0.022952

1 2.960089 -0.925447 -1.050658

24.   **3** (R = PH$_2$), T. E. = -1499.20992

15 -1.235715 -0.048041 -0.644064

6 -0.008311 -1.155134 -0.140128

15 1.195067 -0.097587 0.479233

6 0.486862 1.592806 0.176624

7 -0.745666 1.605312 -0.181393

1 1.017130 2.514049 0.422030

15 -3.195961 -0.551972 0.261745

15 3.328748 -0.273230 -0.111560

1 -2.952303 0.060189 1.524400

1 3.636768 -1.318364 0.800725

1 -3.849879 0.594740 -0.269658

1 3.114575 -1.151373 -1.207034

25.   **3** (R = CH$_3$), T. E. = -893.90011

15 -1.257425 -0.200463 -0.487363

6   0.022502 -1.275793 -0.061444

15 1.246867 -0.174839   0.371848

6   0.503265   1.488559   0.091727

7   -0.766410   1.459391 -0.127762

1   1.026805   2.431551   0.253788

6   -2.849851 -0.461801   0.403501

6   2.988751 -0.420532 -0.182270

1   -2.726677 -0.322695   1.481239

1   3.645754   0.289298   0.329407

1   -3.592477   0.246484   0.026017

1   3.287207 -1.437438   0.087443

1   -3.188058 -1.482259   0.204486

1   3.082686 -0.293753 -1.264409

26.   **3** (R = Ph), T. E. = -1277.27486

6   -0.008831 -0.908659   0.178106

15 1.155515   0.069889 -0.587735

7   0.717937   1.765143 -0.492393

6   -0.509149   1.842207 -0.096393

15 -1.179668   0.271145   0.606329

1   -1.019218   2.803933 -0.041812

6   2.910546 -0.120724 -0.181108

6   3.380751 -1.350881   0.307892

6   4.743693 -1.523302   0.554338

6   5.642307 -0.478304   0.316812

6   5.173457   0.744832   -0.171419

6   3.812821   0.927548   -0.427340

1   2.680706   -2.157536   0.504783

1   5.101934   -2.474255   0.940197

1   6.702349   -0.616132   0.513521

1   5.866870   1.561864   -0.353618

1   3.450580   1.880128   -0.801829

6   -2.933235   -0.056474   0.246102

6   -3.917980   0.826336   0.720579

6   -5.266582   0.577707   0.458943

6   -5.643606   -0.563879   -0.254974

6   -4.666934   -1.454097   -0.711250

6   -3.314630   -1.203662   -0.468846

1   -3.636053   1.703130   1.299233

1   -6.022103   1.269209   0.822850

1   -6.694435   -0.760545   -0.450821

1   -4.955977   -2.343817   -1.264797

1   -2.553682   -1.889367   -0.828517

27.   **3** (R = ^{t}Bu), T. E. = -1129.61603

6   0.002364   1.038188   -0.095962

15   -1.230832   -0.041715   -0.612688

7   -0.765125   -1.692781   -0.198457

6   0.482849   -1.712880   0.130466

15   1.202066   -0.045051   0.458829

1   0.984497   -2.655809   0.351029

6   -2.963929   0.239727   0.070160

6   3.006626   0.223666   -0.020500

6   -3.905179   -0.796685   -0.574357

1   -4.924060   -0.643095   -0.193953

1   -3.935062   -0.693839   -1.665187

1   -3.602690   -1.821080   -0.334882

6   -3.385774   1.668465   -0.321956

1   -3.407300   1.802355   -1.409644

1   -4.397154   1.860160   0.060891

1   -2.710008   2.418640   0.100550

6   -2.962366   0.082668   1.602751

1   -3.980819   0.242301   1.984828

1   -2.642497   -0.920394   1.904373

1   -2.301985   0.815657   2.077766

6   3.158762   0.146967   -1.552037

1   4.211693   0.309183   -1.823463

1   2.858868   -0.832162   -1.942349

1   2.555026   0.912658   -2.049292

6   3.856672   -0.866195   0.660752

1   3.756225   -0.840483   1.751803

1   3.591137   -1.871584   0.313328

1   4.915162   -0.704465   0.417731

6   3.414885   1.619772   0.487418

1   2.781899   2.402581   0.057741

1   3.349936   1.688920   1.579128

1   4.455032   1.819268   0.196290

28.   **4** (R = H), T. E. = -477.58064

18

```
14   1.340051    0.000000   -0.000002

7   0.027154    1.200933   -0.000057

6  -1.262468    0.679820    0.000019

6  -1.262468   -0.679821    0.000017

7   0.027155   -1.200932   -0.000056

1   0.138104    2.207450    0.000358

1  -2.133734    1.322858   -0.000054

1  -2.133734   -1.322858   -0.000058

1   0.138104   -2.207450    0.000361
```

29.   **4** (R = F), T. E. = -675.92213

```
14   0.000000   -1.356777   -0.000447

7  -1.140705    0.036712   -0.000543

6  -0.682741    1.334476   -0.000256

6   0.682741    1.334476   -0.000256

7   1.140705    0.036712   -0.000543

9  -2.530242   -0.104718    0.000997

1  -1.360369    2.176059   -0.000512

1   1.360369    2.176059   -0.000513

9   2.530242   -0.104718    0.000997
```

30.   **4** (R = Cl), T. E. = -1396.70045

```
14   0.008808   -1.277344    0.000000

7   0.000108    0.079815    1.184239

6  -0.008440    1.375287    0.679489

6  -0.008440    1.375287   -0.679489

7   0.000108    0.079815   -1.184239
```

17   0.000108   -0.123884   2.903998

1   -0.013610   2.237015   1.332518

1   -0.013610   2.237015   -1.332518

17   0.000108   -0.123884   -2.903998

31.   **4** (R = OH), T. E. = -627.88948

14   0.000014   -1.320232   -0.000013

7   1.174805   0.033325   -0.002231

6   0.681241   1.326130   -0.008548

6   -0.681248   1.326142   0.008558

7   -1.174847   0.033345   0.002010

8   2.573170   -0.116026   -0.108678

1   1.351102   2.175047   -0.033771

1   -1.351190   2.174999   0.033730

8   -2.573121   -0.116049   0.108860

1   -2.893663   -0.195297   -0.807534

1   2.893502   -0.195223   0.807787

32.   **4** (R = NH$_2$), T. E. = -588.17647

14   0.015430   -1.289619   0.000086

7   1.203353   0.057174   -0.000002

6   0.658710   1.331640   -0.000041

6   -0.701517   1.310351   0.000000

7   -1.199592   0.008945   0.000000

7   2.630035   -0.014014   -0.000226

1   1.310510   2.195828   -0.000019

1   -1.370190   2.163342   0.000086

7   -2.594613   -0.255474   -0.000039

1   -3.015409   0.170400   0.826008

1   2.928685   -0.535486   0.822338

1   -3.015384   0.170244   -0.826175

1   2.928326   -0.538023   -0.821323

33.   4 (R = PH$_2$), T. E. = -1161.45344

14   -0.004894   -1.211970   -0.000004

7   -1.232634   0.096882   -0.000035

6   -0.663064   1.377622   -0.000031

6   0.691532   1.369401   0.000002

7   1.234456   0.077791   0.000012

15   -2.989455   -0.029448   -0.000064

1   -1.291659   2.261230   -0.000061

1   1.332743   2.242852   0.000005

15   2.950556   -0.270606   0.000017

1   3.353939   0.626790   -1.035359

1   -3.140133   -0.997829   -1.033488

1   3.353941   0.626894   1.035298

1   -3.140386   -0.996388   1.034690

34.   4 (R = CH$_3$), T. E. = -556.14156

14   0.000000   -1.265963   -0.000002

7   -1.222354   0.030839   -0.000058

6   -0.680708   1.307776   0.000030

6   0.680708   1.307776   0.000078

7   1.222354   0.030839   -0.000051

6   -2.671090   -0.136512   0.000032

1   -1.318797   2.184770   -0.000214

1   1.318797   2.184770   -0.000134

6   2.671090   -0.136512   0.000019

1   3.122713   0.318716   -0.891076

1   -2.914618   -1.203117   -0.000397

1   3.122643   0.317920   0.891576

1   -3.122634   0.317941   0.891583

1   -3.122722   0.318695   -0.891069

1   2.914618   -1.203117   -0.000437

35.   **4** (R = Ph), T. E. = -939.53203

14   -0.000157   -0.970366   -0.430865

7   -1.229053   0.175880   0.205877

6   -0.677940   1.314332   0.792440

6   0.678091   1.314347   0.792175

7   1.229015   0.175780   0.205476

1   -1.313009   2.066264   1.243805

1   1.313338   2.066355   1.243289

6   -2.638021   0.044827   0.057989

6   -3.253594   -1.195970   0.284112

6   -4.632103   -1.339423   0.115760

6   -5.418337   -0.246511   -0.259213

6   -4.809015   0.992803   -0.476109

6   -3.428671   1.139141   -0.328348

1   -2.650984   -2.039181   0.609707

1   -5.093036   -2.307429   0.295159

```
1   -6.492466   -0.358431   -0.379402

1   -5.407181    1.849662   -0.776335

1   -2.957381    2.095883   -0.534879

6    2.638054    0.044772    0.057831

6    3.428627    1.139051   -0.328563

6    4.808970    0.992828   -0.476156

6    5.418378   -0.246437   -0.259014

6    4.632236   -1.339380    0.115928

6    3.253660   -1.196049    0.284011

1    2.957220    2.095787   -0.535128

1    5.407041    1.849565   -0.776482

1    6.492562   -0.358274   -0.378898

1    5.093242   -2.307351    0.295252

1    2.651102   -2.039345    0.609505
```

36.   **4** (R = ^{t}Bu), T. E. = -791.86384

```
14   0.000000    1.181696   -0.000275

7    1.238715   -0.112238   -0.000209

6    0.679152   -1.384378   -0.000100

6   -0.679152   -1.384378   -0.000101

7   -1.238715   -0.112239   -0.000209

1    1.292508   -2.276786   -0.000110

1   -1.292508   -2.276786   -0.000111

6    2.719299    0.039693    0.000046

6   -2.719299    0.039693    0.000046

6    3.310085   -0.616453    1.266140

1    4.398888   -0.487974    1.287910
```

1	2.889529	-0.156877	2.167530
1	3.100683	-1.690839	1.304150
6	3.087420	1.532839	0.000258
1	2.698163	2.044948	0.887325
1	4.178213	1.638754	0.000504
1	2.698536	2.045163	-0.886857
6	3.310445	-0.616279	-1.265991
1	4.399284	-0.488018	-1.287515
1	3.100844	-1.690629	-1.304259
1	2.890191	-0.156485	-2.167412
6	-3.087419	1.532839	0.000259
1	-4.178213	1.638754	0.000505
1	-2.698163	2.044948	0.887325
1	-2.698536	2.045164	-0.886857
6	-3.310085	-0.616453	1.266140
1	-3.100683	-1.690840	1.304149
1	-2.889529	-0.156877	2.167530
1	-4.398888	-0.487974	1.287910
6	-3.310445	-0.616279	-1.265992
1	-2.890191	-0.156485	-2.167412
1	-3.100844	-1.690629	-1.304259
1	-4.399284	-0.488018	-1.287515

37.   **5** (R = H), T. E. = -2263.10861

32	0.990593	0.000000	-0.000003
7	-0.409850	-1.230642	0.000027
6	-1.679846	-0.681068	-0.000037

6   -1.679846   0.681068   -0.000037

7   -0.409850   1.230642   0.000027

1   -0.337313   -2.240606   -0.000028

1   -2.564146   -1.307563   0.000101

1   -2.564146   1.307563   0.000101

1   -0.337313   2.240606   -0.000028

38.   **5** (R = F), T. E. = -2461.45987

32   0.000000   -1.101336   0.000255

7   1.180185   0.368201   -0.000455

6   0.683538   1.645733   0.000446

6   -0.683538   1.645733   0.000445

7   -1.180185   0.368201   -0.000455

9   2.574981   0.296465   -0.000515

1   1.344202   2.501386   0.001059

1   -1.344202   2.501387   0.001058

9   -2.574981   0.296464   -0.000515

39.   **5** (R = Cl), T. E. = -3182.23625

32   -0.001697   -1.106688   0.000000

7   0.000387   0.329115   1.217637

6   0.002392   1.605093   0.680724

6   0.002392   1.605093   -0.680724

7   0.000387   0.329115   -1.217637

17   0.000387   0.193673   2.943144

1   0.003517   2.480211   1.316886

1   0.003517   2.480211   -1.316886

17   0.000387   0.193673   -2.943144

40.   **5** (R = OH), T. E. = -2413.42711

32 -0.000504 -1.070245   0.000002

7 -1.211884   0.357042 -0.015494

6 -0.681525   1.629129 -0.012728

6   0.682594   1.628554   0.012451

7   1.212385   0.356227   0.015211

8 -2.614541   0.273485 -0.102674

1 -1.334603   2.491781 -0.038665

1   1.336272   2.490761   0.038418

8   2.615035   0.272989   0.103047

1   2.925897   0.174995 -0.814771

1 -2.925309   0.179540   0.815608

41.   **5** (R = NH$_2$), T. E. = -2373.71086

32   0.000195 -1.057751 -0.000047

7 -1.231841   0.342637 -0.000065

6 -0.681304   1.614365 -0.000070

6   0.680803   1.614634 -0.000046

7   1.231646   0.343071 -0.000090

7 -2.636259   0.161691   0.000155

1 -1.320230   2.491736 -0.000150

1   1.319340   2.492286 -0.000259

7   2.636158   0.162007   0.000209

1   3.036186   0.606182 -0.826523

1 -3.036013   0.605586   0.827132

1   3.035867   0.606414   0.826971

1   -3.036321   0.606007   -0.826447

42.   **5** (R = PH₂), T. E. = -2946.98793

32   -0.000018   -1.047431   -0.000014

7   -1.266253   0.330391   -0.009715

6   -0.678099   1.596273   -0.008221

6   0.678098   1.596266   0.008104

7   1.266260   0.330383   0.009653

15   -3.019972   0.247404   -0.037975

1   -1.294990   2.488547   -0.022245

1   1.295020   2.488517   0.021993

15   3.019991   0.247523   0.037749

1   3.258752   -0.328583   -1.247426

1   -3.259087   -0.324718   1.248951

1   3.141138   -1.004154   0.703857

1   -3.140591   -1.006389   -0.700167

43.   **5** (R = CH₃), T. E. = -2341.67582

32   0.000000   -1.029803   -0.000031

7   -1.250337   0.349270   -0.000041

6   -0.682085   1.606619   0.000006

6   0.682085   1.606619   -0.000001

7   1.250337   0.349270   -0.000042

6   -2.700610   0.224052   0.000116

1   -1.305984   2.494990   -0.000306

1   1.305984   2.494990   -0.000317

6   2.700610   0.224052   0.000118

1   3.140546   0.693325   -0.890198

1   -3.140545   0.693328   -0.890199

1   3.140333   0.693597   0.890368

1   -2.979130   -0.833970   0.000213

1   2.979130   -0.833970   0.000219

1   -3.140334   0.693594   0.890367

44.   **5** (R = Ph), T. E. = -2725.07690

32   0.002060   -0.983973   0.000000

7   -0.000429   0.421140   1.247171

6   -0.002687   1.684415   0.681581

6   -0.002687   1.684415   -0.681581

7   -0.000429   0.421140   -1.247171

1   -0.004264   2.566748   1.311496

1   -0.004264   2.566748   -1.311496

6   -0.000368   0.237588   2.659647

6   1.209975   0.120765   3.355317

6   1.208467   -0.092952   4.735793

6   -0.000118   -0.207390   5.428730

6   -1.208829   -0.096227   4.735488

6   -1.210565   0.117498   3.355010

1   2.143620   0.202081   2.805343

1   2.152630   -0.182220   5.267225

1   -0.000018   -0.381423   6.501547

1   -2.152884   -0.188049   5.266677

1   -2.144291   0.196275   2.804805

6	-0.000368	0.237588	-2.659647
6	-1.210565	0.117498	-3.355010
6	-1.208829	-0.096227	-4.735488
6	-0.000118	-0.207390	-5.428730
6	1.208467	-0.092952	-4.735793
6	1.209975	0.120765	-3.355317
1	-2.144291	0.196275	-2.804805
1	-2.152884	-0.188049	-5.266677
1	-0.000018	-0.381423	-6.501547
1	2.152630	-0.182220	-5.267225
1	2.143620	0.202081	-2.805343

45.   **5** (R = ^{t}Bu), T. E. = -2577.40846

32	1.088339	-0.000187	0.000000
7	-0.285097	-0.000082	1.267553
6	-1.536502	-0.000253	0.680777
6	-1.536502	-0.000253	-0.680777
7	-0.285097	-0.000082	-1.267553
1	-2.441529	-0.000331	1.277041
1	-2.441529	-0.000331	-1.277041
6	-0.161589	0.000082	2.744305
6	-0.161589	0.000082	-2.744305
6	-0.825931	-1.268346	3.318820
1	-0.726060	-1.291928	4.410682
1	-1.893618	-1.312362	3.079358
1	-0.349199	-2.165035	2.907281
6	-0.825720	1.268819	3.318386

1	-0.725897	1.292606	4.410236
1	-0.348770	2.165275	2.906607
1	-1.893370	1.312902	3.078793
6	1.325921	0.000070	3.130553
1	1.839914	0.887847	2.744811
1	1.423943	0.000347	4.221954
1	1.839763	-0.887994	2.745248
6	-0.825931	-1.268346	-3.318820
1	-0.349199	-2.165035	-2.907281
1	-1.893618	-1.312362	-3.079358
1	-0.726060	-1.291928	-4.410682
6	-0.825720	1.268819	-3.318386
1	-1.893370	1.312902	-3.078793
1	-0.348770	2.165275	-2.906607
1	-0.725897	1.292606	-4.410236
6	1.325921	0.000070	-3.130553
1	1.423943	0.000347	-4.221954
1	1.839914	0.887847	-2.744811
1	1.839763	-0.887994	-2.745248

46.   **6** (R = H), T. E. = -226.08239

6	-0.647616	0.907017	-0.000113
7	-1.061806	-0.373332	0.000017
6	-0.023675	-1.329078	-0.000432
6	1.082523	-0.490605	0.000287
7	0.689624	0.853917	-0.000085
1	2.135673	-0.732548	0.000737

1   1.288806   1.670514   -0.000292

1   -2.039551   -0.631661   0.001338

1   -1.247042   1.805600   0.000240

47.   **6** (R = F), T. E. = -424.42664

6   -0.041200   -0.892692   0.000331

7   -1.042295   -0.002740   0.000023

6   -0.740025   1.302848   0.000088

6   0.652286   1.257713   0.000031

7   1.021554   -0.071383   -0.000012

1   1.395182   2.040223   0.000004

1   -0.044448   -1.970124   0.000432

9   -2.360755   -0.482736   -0.000191

9   2.312765   -0.579314   -0.000165

48.   **6** (R = Cl), T. E. = -1145.20268

6   -0.024820   -0.680643   0.000061

7   -1.067939   0.163734   0.000023

6   -0.746562   1.498505   -0.000007

6   0.635023   1.462380   0.000001

7   1.048017   0.130282   0.000011

1   1.366621   2.255949   0.000029

1   -0.013988   -1.758888   0.000069

17   2.681849   -0.499266   -0.000019

17   -2.705086   -0.455830   -0.000020

49.   **6** (R = OH), T. E. = -376.40586

6 -0.015218 -0.899244 -0.005819

7 -1.059839 -0.065866   0.003673

6 -0.774553   1.279152   0.006898

6   0.614678   1.250983 -0.009372

7   1.046162 -0.068301 -0.002080

1   1.338461   2.052300 -0.030865

1   0.007527 -1.976379 -0.025696

8 -2.358310 -0.560633   0.008998

8   2.352942 -0.530154 -0.098432

1 -2.872977   0.275110   0.005222

1   2.716235 -0.470923   0.805410

50. **6** (R = NH$_2$), T. E. = -336.69541

6 0.029956 -0.875806 -0.000037

7 1.081092 -0.042775   0.000019

6 0.749529   1.321074   0.000056

6 -0.632818   1.245907 -0.000010

7 -1.055246 -0.092912 -0.000072

1 -1.377362   2.031060   0.000061

1 0.033286 -1.954025 -0.000318

7 2.396064 -0.571477   0.000031

1 2.858336 -0.161311 -0.812725

1 2.858396 -0.161004   0.812595

7 -2.359536 -0.627953 -0.000085

1 -2.844274 -0.278927   0.825878

1 -2.845007 -0.277026 -0.824800

51. **6** (R = PH$_2$), T. E. = -909.95635

6   0.011831   -0.693259   -0.004050

7   1.092086   0.105868   -0.021299

6   0.757751   1.490983   -0.018513

6 -0.619941   1.431940   0.005673

7 -1.078157   0.096175   0.007514

1 -1.348935   2.230375   0.015601

1 -0.012011   -1.773726   0.004308

15 2.805305   -0.347466   -0.078843

1   3.037300   -0.286515   1.326252

1   2.568121   -1.757988   -0.050517

15 -2.724311   -0.568223   0.005618

1 -3.228927   0.271044   1.036694

1 -3.225796   0.259859   -1.036133

52.   **6** (R = CH$_3$), T. E. = -304.65316

6 -0.030109   -0.843115   -0.000106

7 -1.095592   -0.021456   -0.000467

6 -0.746162   1.345691   -0.000115

6   0.636585   1.258323   0.000043

7   1.066501   -0.074254   0.000240

1   1.378564   2.045825   0.000508

1 -0.032545   -1.923923   -0.000017

6 -2.477823   -0.485175   0.000208

1 -2.507954   -1.579317   -0.001532

1 -2.986637   -0.104718   0.889472

1 -2.988477   -0.101736   -0.886674

6   2.443348   -0.550335   -0.000026

1   2.963778   -0.189559   -0.892585

1   2.965108   -0.186240   0.890389

1   2.456769   -1.642688   0.001998

53.   **6** (R = Ph), T. E. = -688.03888

6   0.014080   -0.237287   0.013323

7   1.093172   0.572245   -0.010128

6   0.751445   1.951077   -0.081193

6   -0.626265   1.879492   -0.075662

7   -1.074541   0.544081   -0.022702

1   -1.360658   2.669750   -0.136760

1   -0.002904   -1.315204   0.052649

6   2.439675   0.091413   0.034419

6   2.754764   -1.107609   0.683936

6   4.075633   -1.562830   0.696542

6   5.083429   -0.819569   0.077552

6   4.761830   0.387524   -0.552066

6   3.445048   0.847401   -0.576869

1   1.985943   -1.671559   1.204628

1   4.315365   -2.492013   1.206996

1   6.111203   -1.172364   0.094157

1   5.540492   0.976955   -1.029252

1   3.173424   1.786190   -1.046418

6   -2.424686   0.082041   -0.027859

6   -3.363420   0.704100   0.802565

6   -4.689484   0.267781   0.790034

6   -5.078380   -0.790138   -0.036941

6	-4.134742	-1.406816	-0.863475
6	-2.809399	-0.967617	-0.870185
1	-3.049446	1.509430	1.459642
1	-5.416796	0.750706	1.436990
1	-6.110674	-1.128986	-0.040410
1	-4.431283	-2.222032	-1.517959
1	-2.082239	-1.418923	-1.539190

54.   **6** (R = ^{t}Bu), T. E. = -540.38017

6	-0.016090	0.521601	-0.000012
7	-1.096336	-0.282418	-0.000009
6	-0.753694	-1.653852	-0.000008
6	0.625814	-1.582689	0.000021
7	1.079066	-0.253596	0.000049
1	1.344350	-2.389647	0.000019
1	-0.009298	1.597242	-0.000096
6	-2.516512	0.183138	0.000009
6	2.500406	0.194939	-0.000001
6	-3.194682	-0.375450	-1.263072
1	-4.257127	-0.104414	-1.270095
1	-2.727095	0.030603	-2.168298
1	-3.098950	-1.464094	-1.285254
6	-2.589531	1.717150	-0.000115
1	-2.122639	2.151154	0.892504
1	-2.122324	2.151003	-0.892641
1	-3.641127	2.022172	-0.000313
6	-3.194627	-0.375261	1.263194

1   -4.257050   -0.104127   1.270287

1   -3.098994   -1.463909   1.285534

1   -2.726919   0.030853   2.168328

6   2.580720   1.728901   0.000082

1   2.113612   2.161448   0.891979

1   3.633896   2.029122   -0.000178

1   2.113171   2.161578   -0.891521

6   3.182035   -0.355442   -1.267400

1   3.153286   -1.448789   -1.294711

1   2.685351   0.019843   -2.168857

1   4.231830   -0.041821   -1.293126

6   3.182151   -0.355537   1.267281

1   3.153522   -1.448888   1.294530

1   4.231928   -0.041843   1.292939

1   2.685519   0.019621   2.168818

Cartesian coordinates of the IrCl(CO)$_2$ complexes of **1** and **6** along with the total energies

including zero point vibrational energies (in a. u) of the respective molecules.

1.   IrCl(CO)$_2$-**1** (R = H), T. E. = -1017.81613

6   -1.535954   0.000031   -0.050904

7   -2.399126   1.060894   -0.012584

6   -3.72924   0.673352   -0.109604

6   -3.722433   -0.680198   -0.207643

7   -2.388578   -1.064455   -0.165045

1   -2.085783   2.016620   0.079559

1   -4.543555   1.380908   -0.097066

1   -4.529609   -1.390150   -0.298924

1	-2.064094	-2.018909	-0.226807
77	0.454292	-0.000331	-0.055974
6	0.568185	1.870148	0.311685
8	0.656312	2.962955	0.671126
6	0.564516	-1.861078	0.366025
8	0.653428	-2.942654	0.75649
17	2.847534	-0.006708	-0.422447

2. $IrCl(CO)_2$-**1** (R = F), T. E. = -1216.13667

6	-1.337236	0.000188	-0.000976
7	-2.246482	0.995707	0.251415
6	-3.581527	0.657939	0.171029
6	-3.580943	-0.658751	-0.176237
7	-2.245618	-0.995720	-0.255034
1	-4.375131	1.362005	0.362308
1	-4.373905	-1.363113	-0.369083
77	0.630505	-0.000065	-0.001059
6	0.778984	1.903141	-0.307524
8	0.947452	3.020655	-0.497135
6	0.777307	-1.900986	0.320845
8	0.944199	-3.016182	0.524898
17	3.044668	-0.002127	-0.008119
9	-1.867049	2.242410	0.642166
9	-1.864861	-2.242698	-0.643642

3. $IrCl(CO)_2$-**1** (R = Cl), T. E. = -1936.91107

6	-1.205730	-0.038922	-0.041845

7	-2.141114	0.913611	0.290996
6	-3.457467	0.491088	0.128197
6	-3.385259	-0.783048	-0.327374
7	-2.028622	-1.075676	-0.419636
1	-4.299446	1.127300	0.349289
1	-4.149968	-1.494882	-0.594200
77	0.778418	-0.001428	-0.024650
6	0.887224	1.623136	-1.044394
8	0.998639	2.638113	-1.573010
6	0.872698	-1.252054	1.439749
8	0.961506	-1.909667	2.378096
17	3.184595	-0.139088	-0.184224
17	-1.753606	2.449147	0.922937
17	-1.445729	-2.572222	-0.993021

4. $IrCl(CO)_2$-**1** (R = OH), T. E. = -1168.13003

6	-1.369543	-0.000053	0.000059
7	-2.223905	-0.000284	-1.051443
6	-3.547672	-0.000143	-0.685870
6	-3.547601	-0.000137	0.686208
7	-2.223791	0.000028	1.051645
1	-4.348987	-0.000214	-1.406910
1	-4.348832	-0.000186	1.407339
77	0.636919	0.000041	-0.000032
6	0.697664	1.932281	-0.000422
8	0.750873	3.077190	-0.000674
6	0.698039	-1.932196	-0.000093

8   0.751770   -3.077079   -0.000055

17   3.044669   0.000133   0.000334

8   -1.808324   -0.000559   -2.364275

8   -1.808099   0.000267   2.364446

1   -0.822865   -0.000369   -2.279475

1   -0.822650   0.000106   2.279603

5.   IrCl(CO)$_2$-**1** (R = NH$_2$), T. E. = -1128.41647

6   1.360643   -0.018803   -0.044441

7   2.166762   -0.992750   -0.579239

6   3.514835   -0.695677   -0.453721

6   3.585534   0.491829   0.196424

7   2.268903   0.893948   0.426104

1   4.272190   -1.353690   -0.849439

1   4.429165   1.088601   0.507449

77 -0.633743   -0.007593   -0.032493

6   -0.726661   -1.680784   0.887882

8   -0.803728   -2.623057   1.548902

6   -0.733302   1.888846   -0.362769

8   -0.863769   3.024959   -0.475018

17 -3.042132   -0.079480   -0.284455

7   1.738022   -2.135516   -1.274185

1   1.372604   -2.809445   -0.601536

1   0.963392   -1.854085   -1.875860

7   1.877370   2.074868   1.066360

1   2.047703   1.996742   2.067643

1   2.405705   2.856176   0.684805

6. $IrCl(CO)_2$-**1** (R = PH_2), T. E. = -1701.68111

6	-1.243849	0.112574	-0.006516
7	-2.225492	-0.824949	0.197483
6	-3.488250	-0.238055	0.053327
6	-3.294534	1.067165	-0.250798
7	-1.913948	1.273290	-0.278458
1	-4.397614	-0.804106	0.188096
1	-4.000951	1.860031	-0.441857
77	0.757609	-0.026730	-0.001780
6	0.868334	0.412797	1.869424
8	0.946807	0.558027	3.007989
6	0.778430	-1.053057	-1.619631
8	0.812318	-1.763150	-2.526146
17	3.177804	0.079781	-0.116519
15	-2.039595	-2.545805	0.625588
1	-1.339594	-2.949064	-0.542507
1	-0.852828	-2.375404	1.380719
15	-0.989307	2.772228	-0.588951
1	-0.991035	2.679733	-2.010203

7. $IrCl(CO)_2$-**1** (R = CH_3), T. E. = -1096.38473

6	-1.377098	-0.001578	0.070805
7	-2.168094	-0.041769	1.184207
6	-3.512265	-0.029912	0.840999
6	-3.569586	0.018149	-0.514399
7	-2.259030	0.035137	-0.971429
1	-4.296102	-0.057174	1.582735

```
1   -4.413821    0.041320   -1.186710

77   0.643547   -0.000604    0.040747

6    0.705211   -1.867977   -0.382094

8    0.754841   -2.952633   -0.769400

6    0.705529    1.888833   -0.270613

8    0.754596    2.994483   -0.593232

17   3.046469   -0.012218    0.345521

6   -1.675320   -0.090706    2.558627

1   -2.042144   -0.993730    3.056083

1   -0.584071   -0.109443    2.528270

1   -2.009561    0.793701    3.109809

6   -1.892611    0.083856   -2.385084

1   -0.804154    0.082644   -2.450746

1   -2.293800   -0.791289   -2.905650

1   -2.288251    0.995799   -2.842996
```

8.   IrCl(CO)$_2$-**1** (R = Ph), T. E. = -1479.75694

```
6   -0.069299    0.998262   -0.057560

7    0.973002    1.890292   -0.160404

6    0.512089    3.204663   -0.187381

6   -0.837132    3.148292   -0.104857

7   -1.184299    1.799898   -0.021040

1    1.185043    4.041901   -0.284951

1   -1.581497    3.928269   -0.077682

77   0.114308   -0.999657   -0.015596

6    1.006602   -0.959572    1.684966

8    1.409562   -0.978186    2.764463
```

6 -1.321780 -1.302722 -1.240724

8 -2.244982 -1.551451 -1.884341

17 0.622262 -3.370172 -0.168545

6 2.364119 1.545364 -0.240353

6 2.814585 0.653596 -1.218721

6 4.173804 0.338733 -1.282132

6 5.077273 0.921997 -0.388801

6 4.618974 1.820551 0.579074

6 3.259376 2.131382 0.660045

1 2.109733 0.211270 -1.914742

1 4.523082 -0.364046 -2.033031

1 6.133513 0.673480 -0.443664

1 5.314372 2.269151 1.283034

1 2.891572 2.804316 1.429802

6 -2.547816 1.369360 0.122837

6 -2.928934 0.582374 1.213224

6 -4.266069 0.203494 1.346692

6 -5.216170 0.617481 0.407759

6 -4.826789 1.411622 -0.674190

6 -3.489407 1.787520 -0.822102

1 -2.184562 0.262324 1.933340

1 -4.563360 -0.416458 2.187743

1 -6.254809 0.317739 0.516575

1 -5.557964 1.728027 -1.412812

1 -3.173444 2.381959 -1.674996

9.   IrCl(CO)$_2$-**1** (R = ^{t}Bu), T. E. = -1332.08792

6   0.950407   0.384297   -0.019515

7   1.262766   1.728553   -0.003837

6   2.639412   1.896537   -0.036725

6   3.196783   0.667014   -0.073655

7   2.165610   -0.264908   -0.070178

1   3.121203   2.857490   -0.037782

1   4.237107   0.400180   -0.109375

77   -0.960047   -0.339498   -0.004975

6   -0.962438   -0.646879   -1.896534

8   -0.961575   -0.963384   -3.005472

6   -0.947538   -0.788277   1.853219

8   -0.958215   -1.183020   2.937711

17   -3.345490   -0.838272   -0.005687

6   0.299966   2.897605   0.047297

6   2.456562   -1.754427   -0.002376

6   2.255580   -2.232651   1.446105

1   1.213150   -2.151640   1.754500

1   2.549135   -3.285428   1.528449

1   2.873244   -1.651268   2.140493

6   1.569619   -2.547407   -0.973707

1   0.517068   -2.502419   -0.690307

1   1.676675   -2.177272   -1.999378

1   1.885360   -3.596431   -0.956727

6   3.925337   -1.999672   -0.406261

1   4.640064   -1.598813   0.320242

1   4.087692   -3.080561   -0.447421

1   4.151974   -1.592438   -1.397886

6   -0.525372   2.830972   1.343776

1   -1.157006   3.723043   1.419074

1   -1.181127   1.956425   1.356841

1   0.128644   2.796665   2.222660

6   1.096322   4.216326   0.049110

1   0.379141   5.041377   0.089209

1   1.749219   4.309863   0.923927

1   1.691462   4.346523   -0.861512

6   -0.604536   2.884162   -1.196992

1   -1.232150   3.782229   -1.199266

1   -0.006791   2.879387   -2.115700

1   -1.268068   2.015206   -1.202555

10. $IrCl(CO)_2 - 6$ (R = H), T. E. = -1017.79336

6   3.687187   -0.685898   -0.187611

7   2.393715   -1.031034   -0.104619

6   1.531972   0.083951   -0.055659

6   2.426940   1.146489   -0.106151

7   3.719105   0.649449   -0.190442

1   2.244655   2.208815   -0.086929

1   4.564858   1.202258   -0.242995

1   2.068624   -1.989320   -0.082881

1   4.536378   -1.348868   -0.240986

77   -0.474319   0.000709   -0.060535

17   -2.861743   -0.050153   -0.499838

6   -0.522720   -1.839539   0.396664

8   -0.556853   -2.911200   0.835493

44

6   -0.609856   1.851452   0.390354

8   -0.707300   2.918384   0.821014

11.   IrCl(CO)$_2$ – **6** (R = F), T. E. = -1216.11251

6   -3.373741   0.807653   -0.275494

7   -2.046488   1.036760   -0.325299

6   -1.215763   -0.033729   -0.014819

6   -2.173182   -1.030193   0.248086

7   -3.413520   -0.477156   0.079783

1   -2.052049   -2.054058   0.561751

1   -4.190132   1.475249   -0.492928

77   0.781599   -0.074927   -0.029938

17   3.175967   -0.124837   -0.344113

6   0.978378   1.745127   0.555840

8   1.149978   2.779172   1.030072

6   0.804455   -1.985288   0.054911

8   0.842645   -3.123130   0.234518

9   -1.606135   2.284540   -0.648190

9   -4.591000   -1.141939   0.234528

12.   IrCl(CO)$_2$ – **6** (R = Cl), T. E. = -1936.89132

6   -3.027459   0.849776   -0.426056

7   -1.695834   1.032217   -0.528848

6   -0.938450   -0.036204   -0.000665

6   -1.932031   -0.900095   0.441515

7   -3.170788   -0.339943   0.169938

1   -1.848937   -1.849367   0.945129

1   -3.811041   1.508343   -0.762464

77   1.064709   -0.160148   0.035844

17   3.469111   -0.155716   -0.207263

6   1.206099   1.268086   1.307206

8   1.300445   2.023382   2.172622

6   1.015464   -1.970763   -0.578051

8   0.988678   -3.099430   -0.812268

17   -1.039407   2.450139   -1.233400

17   -4.695055   -1.049123   0.512613

13.   IrCl(CO)$_2$ – **6** (R = OH), T. E. = -1168.10923

6   3.283769   -0.004661   0.891163

7   1.959853   -0.008261   1.052518

6   1.241146   -0.008938   -0.143390

6   2.242916   -0.014440   -1.099893

7   3.459658   0.007138   -0.443715

1   2.190648   -0.038283   -2.176657

1   4.050177   -0.018058   1.648202

77   -0.786624   -0.000095   -0.104086

17   -3.206110   0.020960   -0.058894

6   -0.812414   1.926708   -0.107532

8   -0.825324   3.074905   -0.121141

6   -0.841682   -1.928785   -0.112788

8   -0.878343   -3.076018   -0.130128

8   1.361066   -0.005847   2.283334

8   4.703126   -0.104659   -1.028802

1   0.388807   -0.006488   2.016712

1   4.941136   0.795351   -1.325526

14.   IrCl(CO)$_2$ – **6** (R = NH$_2$), T. E. = -1128.39898

6   3.303760   -0.684192   -0.610428

7   1.984108   -0.885724   -0.739387

6   1.224082   0.039202   0.008566

6   2.200123   0.813735   0.609542

7   3.451383   0.356514   0.221986

1   2.121165   1.646940   1.289127

1   4.083209   -1.247290   -1.098950

77   -0.798503   0.059767   0.005643

17   -3.193987   -0.000974   -0.353386

6   -0.877096   -1.595723   0.944067

8   -0.925368   -2.513796   1.645380

6   -0.809799   1.967299   -0.137504

8   -0.820358   3.118783   -0.069053

7   1.500172   -1.904622   -1.582368

7   4.651254   0.935412   0.666460

1   1.070268   -2.615742   -0.989253

1   5.200766   0.240020   1.166663

1   0.741239   -1.489205   -2.126376

1   5.176812   1.286920   -0.131104

15.   IrCl(CO)$_2$ – **6** (R = PH$_2$), T. E. = -1701.66171

6   -2.983981   0.861806   -0.486957

7   -1.656551   1.054601   -0.584938

6   -0.949675   -0.024398   0.019841

6   -1.958547   -0.842430   0.477704

7   -3.206404   -0.290243   0.160903

1   -1.893462   -1.779571   1.008914

1   -3.746782   1.521993   -0.872541

77   1.070079   -0.155412   0.058799

17   3.483010   -0.060459   -0.176844

6   1.151282   0.899302   1.648574

8   1.189275   1.394053   2.691989

6   1.012552   -1.810220   -0.888142

8   0.967874   -2.881991   -1.316330

15   -0.971528   2.487829   -1.416122

1   -0.268947   2.994026   -0.291696

1   0.156804   1.788107   -1.917558

15   -4.759615   -1.065486   0.581675

1   -5.377549   0.102750   1.105530

1   -5.356504   -0.919265   -0.700253

16.   IrCl(CO)$_2$ – **6** (R = CH$_3$), T. E. = -1096.36474

6   3.297816   -0.696668   -0.589194

7   1.983785   -0.920286   -0.751730

6   1.220291   0.012689   -0.017486

6   2.183391   0.798501   0.587860

7   3.446838   0.352431   0.225586

1   2.064612   1.638433   1.254644

1   4.100810   -1.259454   -1.040604

77   -0.804142   0.059669   -0.001581

17   -3.206593   0.006779   -0.344735

6   -0.889272   -1.538460   1.032638

8   -0.941364   -2.406073   1.795678

6   -0.789046   1.956039   -0.199058

8   -0.777318   3.110629   -0.152632

6   4.716978   0.927257   0.658553

1   4.797058   0.870619   1.747594

1   5.539102   0.367497   0.208236

1   4.777239   1.972357   0.342858

6   1.429630   -1.991508   -1.579121

1   0.998516   -2.770719   -0.945429

1   0.645283   -1.578528   -2.216190

1   2.224754   -2.418470   -2.195362

17.   IrCl(CO)$_2$ – **6** (R = Ph), T. E. = -1479.74070

6   -2.011090   1.335374   -0.225209

7   -0.674715   1.174224   -0.210556

6   -0.332080   -0.187211   0.012006

6   -1.563825   -0.801580   0.123734

7   -2.580227   0.140449   -0.020673

1   -1.798602   -1.827901   0.355699

1   -2.535150   2.250293   -0.451324

77   1.551750   -0.911918   0.110952

17   3.886163   -1.563677   -0.075911

6   1.944258   0.122125   1.669912

8   2.132075   0.604315   2.702868

6   1.012368   -2.518257   -0.750122

8   0.654449   -3.554980   -1.118314

6   -3.989099   -0.112511   0.014435

6   -4.829517   0.734761   0.743252

6   -6.203453   0.484783   0.761233

6   -6.729057   -0.612484   0.072889

6   -5.876815   -1.460770   -0.640857

6   -4.503448   -1.212427   -0.678978

1   -4.411560   1.562645   1.308900

1   -6.858825   1.139884   1.328114

1   -7.797214   -0.808465   0.096262

1   -6.279982   -2.313715   -1.179215

1   -3.839312   -1.852946   -1.251382

6   0.236159   2.267274   -0.409724

6   0.085565   3.431029   0.350200

6   0.957935   4.502565   0.143095

6   1.979431   4.401741   -0.805438

6   2.127148   3.228022   -1.551225

6   1.253030   2.155940   -1.362367

1   -0.683165   3.485231   1.116332

1   0.849578   5.404966   0.738163

1   2.664997   5.230997   -0.955880

1   2.926565   3.140337   -2.281117

1   1.360459   1.241225   -1.936186

18.   IrCl(CO)$_2$ – **6** (R = ^{t}Bu), T. E. = -1332.08569

6   2.544170   0.970820   -0.000002

7   1.218242   1.206406   -0.000072

6   0.516142   -0.024595   -0.000013

6	1.518271	-0.968402	0.000061
7	2.761245	-0.348603	0.000251
1	1.422979	-2.041588	0.000205
1	3.313623	1.719863	0.000097
77	-1.503895	-0.337738	-0.000051
17	-3.935812	-0.349528	-0.000172
6	-1.448029	-0.835982	-1.835180
8	-1.375588	-1.313136	-2.887253
6	-1.448787	-0.835533	1.835260
8	-1.377210	-1.312456	2.887487
6	4.082701	-1.052561	0.000189
6	0.615579	2.589238	-0.000088
6	4.161990	-1.920447	-1.269447
1	4.081823	-1.303690	-2.171200
1	5.121653	-2.447553	-1.295408
1	3.365284	-2.669970	-1.296344
6	5.223667	-0.025087	0.001418
1	6.177701	-0.561001	0.001244
1	5.204587	0.610979	-0.890874
1	5.203895	0.609525	0.894726
6	4.161148	-1.922383	1.268553
1	5.120971	-2.449201	1.294517
1	4.080013	-1.307010	2.171155
1	3.364747	-2.672280	1.293628
6	-0.235505	2.755673	-1.270237
1	0.373357	2.617219	-2.171288
1	-1.060786	2.037980	-1.291919

1	-0.661880	3.764509	-1.293220
6	-0.235297	2.755720	1.270209
1	-1.060345	2.037771	1.292229
1	0.373801	2.617641	2.171167
1	-0.661972	3.764422	1.293055
6	1.731552	3.647871	-0.000248
1	2.363078	3.588756	-0.894558
1	1.263339	4.636630	-0.000311
1	2.363184	3.588955	0.893995

Table S1: Location of the σ Symmetric Lone Pair Orbital at the 'ene' Centre for the Molecules 1

- 6 and Their Respective Energies (eV) Calculated at B3LYP/6-31+G* Level of Theory.

Str. No.	R	Location of σ symmetric lone pair at 'ene' centre	Energy (eV)
1	H	HOMO	-6.0
	F	HOMO	-7.6
	Cl	HOMO	-6.9
	OH	HOMO-2	-7.2
	NH$_2$	HOMO	-6.1
	PH$_2$	HOMO	-6.1
	CH$_3$	HOMO	-5.8
	Ph	HOMO	-6.1
	^{t}Bu	HOMO	-5.6
2	H	HOMO	-6.6
	F	HOMO	-8.0
	Cl	HOMO	-7.4
	OH	HOMO	-7.3
	NH$_2$	HOMO	-6.6
	PH$_2$	HOMO	-6.5
	CH$_3$	HOMO	-6.3

	Ph	HOMO-1	-6.6
	^tBu	HOMO	-6.0
3	H	HOMO	-7.0
	F	HOMO	-7.9
	Cl	HOMO-1	-7.8
	OH	HOMO-1	-7.2
	NH_2	HOMO	-6.6
	PH_2	HOMO	-6.7
	CH_3	HOMO	-6.5
	Ph	HOMO-1	-6.6
	^tBu	HOMO	-6.3
4	H	HOMO-1	-6.7
	F	HOMO-1	-7.9
	Cl	HOMO-2	-7.6
	OH	HOMO-1	-7.2
	NH_2	HOMO-1	-6.7
	PH_2	HOMO-1	-6.9
	CH_3	HOMO-1	-6.6
	Ph	HOMO-2	-6.8

	tBu	HOMO-1	-6.2
5	H	HOMO-1	-7.0
	F	HOMO-2	-8.2
	Cl	HOMO-2	-7.9
	OH	HOMO-1	-7.3
	NH₂	HOMO-1	-6.8
	PH₂	HOMO-1	-7.1
	CH₃	HOMO-1	-6.8
	Ph	HOMO-1	-6.8
	tBu	HOMO-1	-6.4
6	H	HOMO	-5.2
	F	HOMO	-6.8
	Cl	HOMO	-6.3
	OH	HOMO	-6.1
	NH₂	HOMO	-5.4
	PH₂	HOMO	-5.4
	CH₃	HOMO	-5.0
	Ph	HOMO	-5.3
	tBu	HOMO	-4.8