Supporting Information

NMR Shifts, Orbitals, and M···H–X Bonding in d^8 Square Planar Metal Complexes

Yong Zhang,[†] Jared C. Lewis,[‡] Robert G. Bergman,[‡] Jonathan A. Ellman,[‡] and Eric Oldfield*[,†]

[†]Department of Chemistry, University of Illinois at Urbana-Champaign,

600 South Mathews Avenue, Urbana, IL 61801

[‡] Department of Chemistry, University of California, Berkeley, California 94702

Table S1. Coordinates of fully optimized complex 1 (minus the counterion PF_6^-) in PDB format

```
HEADER    PROTEIN
COMPND    C:\babel\t.ent
AUTHOR    GENERATED BY BABEL 1.6
ATOM      1 RH   UNK     1       0.154   1.493  -0.191  1.00  0.00
ATOM      2 Fe   UNK     1      -2.087  -1.926  -0.754  1.00  0.00
ATOM      3  P   UNK     1       0.984  -0.762   0.228  1.00  0.00
ATOM      4  C   UNK     1      -2.928  -0.082  -0.539  1.00  0.00
ATOM      5  C   UNK     1      -3.963  -1.074  -0.762  1.00  0.00
ATOM      6  C   UNK     1      -3.732  -1.690  -2.031  1.00  0.00
ATOM      7  C   UNK     1      -2.565  -1.089  -2.613  1.00  0.00
ATOM      8  C   UNK     1      -2.071  -0.101  -1.704  1.00  0.00
ATOM      9  C   UNK     1      -0.253  -2.131   0.128  1.00  0.00
ATOM     10  C   UNK     1      -1.302  -2.352   1.096  1.00  0.00
ATOM     11  C   UNK     1      -2.090  -3.464   0.654  1.00  0.00
ATOM     12  C   UNK     1      -1.539  -3.936  -0.585  1.00  0.00
ATOM     13  C   UNK     1      -0.403  -3.125  -0.908  1.00  0.00
ATOM     14  N   UNK     1      -1.535   1.178   1.068  1.00  0.00
ATOM     15  C   UNK     1      -2.756   0.664   0.714  1.00  0.00
ATOM     16  C   UNK     1      -3.852   0.793   1.593  1.00  0.00
ATOM     17  C   UNK     1      -3.695   1.368   2.852  1.00  0.00
ATOM     18  C   UNK     1      -2.422   1.818   3.232  1.00  0.00
ATOM     19  C   UNK     1      -1.385   1.718   2.311  1.00  0.00
ATOM     20  C   UNK     1       1.667  -0.937   1.949  1.00  0.00
ATOM     21  C   UNK     1       1.785  -2.198   2.560  1.00  0.00
ATOM     22  C   UNK     1       2.325  -2.303   3.848  1.00  0.00
ATOM     23  C   UNK     1       2.752  -1.153   4.531  1.00  0.00
ATOM     24  C   UNK     1       2.636   0.105   3.923  1.00  0.00
ATOM     25  C   UNK     1       2.092   0.213   2.636  1.00  0.00
ATOM     26  C   UNK     1       2.360  -1.356  -0.887  1.00  0.00
ATOM     27  C   UNK     1       3.632  -1.664  -0.377  1.00  0.00
ATOM     28  C   UNK     1       4.650  -2.099  -1.239  1.00  0.00
ATOM     29  C   UNK     1       4.405  -2.234  -2.612  1.00  0.00
ATOM     30  C   UNK     1       3.135  -1.927  -3.126  1.00  0.00
ATOM     31  C   UNK     1       2.120  -1.485  -2.269  1.00  0.00
ATOM     32  C   UNK     1       2.164   2.146  -0.639  1.00  0.00
ATOM     33  C   UNK     1       1.487   1.902  -1.856  1.00  0.00
ATOM     34  C   UNK     1       0.971   2.985  -2.796  1.00  0.00
ATOM     35  C   UNK     1      -0.506   3.351  -2.525  1.00  0.00
ATOM     36  C   UNK     1      -0.887   3.216  -1.065  1.00  0.00
ATOM     37  C   UNK     1      -0.120   3.675   0.020  1.00  0.00
ATOM     38  C   UNK     1       1.187   4.443  -0.106  1.00  0.00
```

```
ATOM      39  C   UNK     1       2.417   3.512  -0.032  1.00  0.00
ATOM      40  H   UNK     1      -4.754  -1.340  -0.077  1.00  0.00
ATOM      41  H   UNK     1      -4.324  -2.481  -2.466  1.00  0.00
ATOM      42  H   UNK     1      -2.132  -1.342  -3.568  1.00  0.00
ATOM      43  H   UNK     1      -1.197   0.523  -1.850  1.00  0.00
ATOM      44  H   UNK     1      -1.461  -1.775   1.994  1.00  0.00
ATOM      45  H   UNK     1      -2.955  -3.865   1.160  1.00  0.00
ATOM      46  H   UNK     1      -1.913  -4.759  -1.175  1.00  0.00
ATOM      47  H   UNK     1       0.228  -3.246  -1.774  1.00  0.00
ATOM      48  H   UNK     1      -4.823   0.439   1.273  1.00  0.00
ATOM      49  H   UNK     1      -4.541   1.461   3.523  1.00  0.00
ATOM      50  H   UNK     1      -2.236   2.250   4.207  1.00  0.00
ATOM      51  H   UNK     1      -0.394   2.070   2.558  1.00  0.00
ATOM      52  H   UNK     1       1.459  -3.091   2.037  1.00  0.00
ATOM      53  H   UNK     1       2.415  -3.278   4.316  1.00  0.00
ATOM      54  H   UNK     1       3.172  -1.239   5.527  1.00  0.00
ATOM      55  H   UNK     1       2.968   0.995   4.447  1.00  0.00
ATOM      56  H   UNK     1       1.998   1.185   2.161  1.00  0.00
ATOM      57  H   UNK     1       3.835  -1.574   0.684  1.00  0.00
ATOM      58  H   UNK     1       5.629  -2.333  -0.836  1.00  0.00
ATOM      59  H   UNK     1       5.192  -2.574  -3.275  1.00  0.00
ATOM      60  H   UNK     1       2.938  -2.028  -4.187  1.00  0.00
ATOM      61  H   UNK     1       1.144  -1.245  -2.682  1.00  0.00
ATOM      62  H   UNK     1       2.852   1.372  -0.299  1.00  0.00
ATOM      63  H   UNK     1       1.686   0.944  -2.328  1.00  0.00
ATOM      64  H   UNK     1       1.606   3.872  -2.723  1.00  0.00
ATOM      65  H   UNK     1       1.065   2.631  -3.828  1.00  0.00
ATOM      66  H   UNK     1      -0.716   4.372  -2.873  1.00  0.00
ATOM      67  H   UNK     1      -1.158   2.693  -3.109  1.00  0.00
ATOM      68  H   UNK     1      -1.944   3.024  -0.882  1.00  0.00
ATOM      69  H   UNK     1      -0.640   3.797   0.968  1.00  0.00
ATOM      70  H   UNK     1       1.193   5.015  -1.038  1.00  0.00
ATOM      71  H   UNK     1       1.247   5.179   0.701  1.00  0.00
ATOM      72  H   UNK     1       3.283   3.982  -0.522  1.00  0.00
ATOM      73  H   UNK     1       2.703   3.373   1.016  1.00  0.00
CONECT     1    3   14   32   33   36   37
CONECT     2    4    5    6    7    8    9   10   11   12   13
CONECT     3    1    9   20   26
CONECT     4    2    5    8   15
CONECT     5    2    4    6   40
CONECT     6    2    5    7   41
CONECT     7    2    6    8   42
CONECT     8    2    4    7   43
CONECT     9    2    3   10   13
```

```
CONECT   10    2    9   11   44
CONECT   11    2   10   12   45
CONECT   12    2   11   13   46
CONECT   13    2    9   12   47
CONECT   14    1   15   19
CONECT   15    4   14   16
CONECT   16   15   17   48
CONECT   17   16   18   49
CONECT   18   17   19   50
CONECT   19   14   18   51
CONECT   20    3   21   25
CONECT   21   20   22   52
CONECT   22   21   23   53
CONECT   23   22   24   54
CONECT   24   23   25   55
CONECT   25   20   24   56
CONECT   26    3   27   31
CONECT   27   26   28   57
CONECT   28   27   29   58
CONECT   29   28   30   59
CONECT   30   29   31   60
CONECT   31   26   30   61
CONECT   32    1   33   39   62
CONECT   33    1   32   34   63
CONECT   34   33   35   64   65
CONECT   35   34   36   66   67
CONECT   36    1   35   37   68
CONECT   37    1   36   38   69
CONECT   38   37   39   70   71
CONECT   39   32   38   72   73
CONECT   40    5
CONECT   41    6
CONECT   42    7
CONECT   43    8
CONECT   44   10
CONECT   45   11
CONECT   46   12
CONECT   47   13
CONECT   48   16
CONECT   49   17
CONECT   50   18
CONECT   51   19
CONECT   52   21
CONECT   53   22
```

```
CONECT   54   23
CONECT   55   24
CONECT   56   25
CONECT   57   27
CONECT   58   28
CONECT   59   29
CONECT   60   30
CONECT   61   31
CONECT   62   32
CONECT   63   33
CONECT   64   34
CONECT   65   34
CONECT   66   35
CONECT   67   35
CONECT   68   36
CONECT   69   37
CONECT   70   38
CONECT   71   38
CONECT   72   39
CONECT   73   39
MASTER        0    0    0    0    0    0    0    0   73    0   73    0
END
```

Table S2. Coordinates of fully optimized complex 2 in PDB format

```
HEADER    PROTEIN
COMPND    C:\babel\t.ent
AUTHOR    GENERATED BY BABEL 1.6
ATOM      1 Pt   UNK     1       0.307  -0.343  -0.068  1.00  0.00
ATOM      2  P   UNK     1       2.532   0.218   0.312  1.00  0.00
ATOM      3 Cl   UNK     1      -0.167   0.366   2.171  1.00  0.00
ATOM      4 Cl   UNK     1       0.737  -1.180  -2.267  1.00  0.00
ATOM      5  N   UNK     1      -1.690  -0.907  -0.268  1.00  0.00
ATOM      6  C   UNK     1      -1.911  -2.227  -0.255  1.00  0.00
ATOM      7  C   UNK     1      -3.191  -2.786  -0.057  1.00  0.00
ATOM      8  C   UNK     1      -4.258  -1.938   0.169  1.00  0.00
ATOM      9  C   UNK     1      -5.130   0.378   0.363  1.00  0.00
ATOM     10  C   UNK     1      -4.915   1.742   0.310  1.00  0.00
ATOM     11  C   UNK     1      -3.639   2.236  -0.051  1.00  0.00
ATOM     12  C   UNK     1      -2.573   1.384  -0.317  1.00  0.00
ATOM     13  C   UNK     1      -2.752  -0.026  -0.166  1.00  0.00
ATOM     14  C   UNK     1      -4.062  -0.531   0.122  1.00  0.00
ATOM     15  C   UNK     1      -1.343   1.994  -0.894  1.00  0.00
```

```
ATOM     16  O   UNK     1      -1.046   3.192  -0.723  1.00  0.00
ATOM     17  C   UNK     1       3.237  -0.776   1.737  1.00  0.00
ATOM     18  C   UNK     1       3.241  -2.287   1.479  1.00  0.00
ATOM     19  C   UNK     1       3.686  -0.055  -1.139  1.00  0.00
ATOM     20  C   UNK     1       5.158   0.273  -0.861  1.00  0.00
ATOM     21  C   UNK     1       2.774   1.997   0.855  1.00  0.00
ATOM     22  C   UNK     1       2.509   3.027  -0.249  1.00  0.00
ATOM     23  H   UNK     1      -0.755   1.364  -1.576  1.00  0.00
ATOM     24  H   UNK     1      -1.041  -2.856  -0.387  1.00  0.00
ATOM     25  H   UNK     1      -3.304  -3.862  -0.052  1.00  0.00
ATOM     26  H   UNK     1      -5.248  -2.329   0.380  1.00  0.00
ATOM     27  H   UNK     1      -6.113  -0.021   0.594  1.00  0.00
ATOM     28  H   UNK     1      -5.723   2.435   0.511  1.00  0.00
ATOM     29  H   UNK     1      -3.469   3.302  -0.158  1.00  0.00
ATOM     30  H   UNK     1       2.604  -0.534   2.596  1.00  0.00
ATOM     31  H   UNK     1       4.247  -0.404   1.944  1.00  0.00
ATOM     32  H   UNK     1       3.876  -2.557   0.628  1.00  0.00
ATOM     33  H   UNK     1       2.229  -2.648   1.276  1.00  0.00
ATOM     34  H   UNK     1       3.620  -2.817   2.359  1.00  0.00
ATOM     35  H   UNK     1       3.292   0.543  -1.964  1.00  0.00
ATOM     36  H   UNK     1       3.556  -1.097  -1.444  1.00  0.00
ATOM     37  H   UNK     1       5.572  -0.346  -0.058  1.00  0.00
ATOM     38  H   UNK     1       5.302   1.324  -0.591  1.00  0.00
ATOM     39  H   UNK     1       5.752   0.081  -1.760  1.00  0.00
ATOM     40  H   UNK     1       3.797   2.084   1.241  1.00  0.00
ATOM     41  H   UNK     1       2.084   2.140   1.691  1.00  0.00
ATOM     42  H   UNK     1       1.476   2.979  -0.602  1.00  0.00
ATOM     43  H   UNK     1       3.178   2.892  -1.106  1.00  0.00
ATOM     44  H   UNK     1       2.672   4.036   0.142  1.00  0.00
CONECT    1    2    3    4    5
CONECT    2    1   17   19   21
CONECT    3    1
CONECT    4    1
CONECT    5    1    6   13
CONECT    6    5    7   24
CONECT    7    6    8   25
CONECT    8    7   14   26
CONECT    9   10   14   27
CONECT   10    9   11   28
CONECT   11   10   12   29
CONECT   12   11   13   15
CONECT   13    5   12   14
CONECT   14    8    9   13
CONECT   15   12   16   23
```

```
CONECT   16   15
CONECT   17    2   18   30   31
CONECT   18   17   32   33   34
CONECT   19    2   20   35   36
CONECT   20   19   37   38   39
CONECT   21    2   22   40   41
CONECT   22   21   42   43   44
CONECT   23   15
CONECT   24    6
CONECT   25    7
CONECT   26    8
CONECT   27    9
CONECT   28   10
CONECT   29   11
CONECT   30   17
CONECT   31   17
CONECT   32   18
CONECT   33   18
CONECT   34   18
CONECT   35   19
CONECT   36   19
CONECT   37   20
CONECT   38   20
CONECT   39   20
CONECT   40   21
CONECT   41   21
CONECT   42   22
CONECT   43   22
CONECT   44   22
MASTER        0    0    0    0    0    0    0    0   44    0   44    0
END
```

Table S3. Coordinates of fully optimized complex 3 (modeled by $[RhCl(PMe_3)(Me_2POXy)]_2$) in PDB format

```
HEADER    PROTEIN
COMPND    C:\babel\t.ent
AUTHOR    GENERATED BY BABEL 1.6
HETATM    1 RH   UNK     1       1.646  -0.209  -0.278
HETATM    2 RH   UNK     1      -1.649   0.237  -0.270
HETATM    3 CL   UNK     1      -0.224  -1.646   0.467
HETATM    4 CL   UNK     1       0.218   1.619   0.581
HETATM    5  P   UNK     1       3.245   1.232  -0.890
HETATM    6  P   UNK     1       2.739  -2.110  -0.961
```

HETATM	7	P	UNK	1	-3.250	-1.153	-0.986
HETATM	8	P	UNK	1	-2.735	2.184	-0.822
HETATM	9	O	UNK	1	4.947	0.841	-0.549
HETATM	10	O	UNK	1	-4.950	-0.789	-0.612
HETATM	11	C	UNK	1	3.566	1.582	-2.687
HETATM	12	C	UNK	1	3.210	2.945	-0.155
HETATM	13	C	UNK	1	5.455	0.488	0.703
HETATM	14	C	UNK	1	4.641	0.212	1.811
HETATM	15	C	UNK	1	5.247	-0.142	3.022
HETATM	16	C	UNK	1	6.641	-0.219	3.118
HETATM	17	C	UNK	1	7.460	0.058	2.006
HETATM	18	C	UNK	1	6.865	0.421	0.777
HETATM	19	C	UNK	1	8.963	-0.036	2.152
HETATM	20	C	UNK	1	7.666	0.740	-0.461
HETATM	21	C	UNK	1	4.333	-2.073	-1.940
HETATM	22	C	UNK	1	1.693	-3.240	-2.028
HETATM	23	C	UNK	1	3.186	-3.216	0.479
HETATM	24	C	UNK	1	-3.211	-2.917	-0.383
HETATM	25	C	UNK	1	-3.579	-1.366	-2.804
HETATM	26	C	UNK	1	-5.455	-0.538	0.666
HETATM	27	C	UNK	1	-4.636	-0.335	1.786
HETATM	28	C	UNK	1	-5.238	-0.086	3.025
HETATM	29	C	UNK	1	-6.632	-0.040	3.136
HETATM	30	C	UNK	1	-7.455	-0.241	2.011
HETATM	31	C	UNK	1	-6.865	-0.496	0.753
HETATM	32	C	UNK	1	-8.958	-0.186	2.175
HETATM	33	C	UNK	1	-7.670	-0.736	-0.500
HETATM	34	C	UNK	1	-4.346	2.223	-1.772
HETATM	35	C	UNK	1	-3.154	3.205	0.689
HETATM	36	C	UNK	1	-1.691	3.366	-1.833
HETATM	37	H	UNK	1	3.730	0.645	-3.219
HETATM	38	H	UNK	1	2.297	3.454	-0.468
HETATM	39	H	UNK	1	3.558	0.247	1.723
HETATM	40	H	UNK	1	4.627	-0.359	3.886
HETATM	41	H	UNK	1	7.103	-0.494	4.061
HETATM	42	H	UNK	1	9.232	-0.314	3.175
HETATM	43	H	UNK	1	9.390	-0.789	1.480
HETATM	44	H	UNK	1	9.454	0.917	1.928
HETATM	45	H	UNK	1	7.452	0.024	-1.263
HETATM	46	H	UNK	1	7.393	1.726	-0.853
HETATM	47	H	UNK	1	8.740	0.728	-0.271
HETATM	48	H	UNK	1	-2.284	-3.389	-0.712
HETATM	49	H	UNK	1	-3.784	-0.395	-3.253
HETATM	50	H	UNK	1	-3.554	-0.346	1.686

```
HETATM   51  H   UNK     1      -4.614   0.072   3.899
HETATM   52  H   UNK     1      -7.091   0.152   4.101
HETATM   53  H   UNK     1      -9.406   0.604   1.560
HETATM   54  H   UNK     1      -9.434  -1.130   1.887
HETATM   55  H   UNK     1      -9.224   0.015   3.216
HETATM   56  H   UNK     1      -8.744  -0.662  -0.319
HETATM   57  H   UNK     1      -7.401  -0.018  -1.282
HETATM   58  H   UNK     1      -7.458  -1.729  -0.912
HETATM   59  H   UNK     1       4.749  -3.082  -2.008
HETATM   60  H   UNK     1       4.133  -1.705  -2.949
HETATM   61  H   UNK     1       5.047  -1.405  -1.457
HETATM   62  H   UNK     1       2.234  -4.165  -2.251
HETATM   63  H   UNK     1       0.770  -3.465  -1.492
HETATM   64  H   UNK     1       1.442  -2.726  -2.958
HETATM   65  H   UNK     1       3.580  -4.175   0.126
HETATM   66  H   UNK     1       3.935  -2.714   1.095
HETATM   67  H   UNK     1       2.290  -3.380   1.080
HETATM   68  H   UNK     1      -4.749   3.241  -1.771
HETATM   69  H   UNK     1      -4.171   1.914  -2.805
HETATM   70  H   UNK     1      -5.060   1.538  -1.314
HETATM   71  H   UNK     1      -3.546   4.185   0.399
HETATM   72  H   UNK     1      -3.899   2.671   1.282
HETATM   73  H   UNK     1      -2.250   3.328   1.288
HETATM   74  H   UNK     1      -2.220   4.313  -1.982
HETATM   75  H   UNK     1      -0.754   3.538  -1.302
HETATM   76  H   UNK     1      -1.470   2.911  -2.800
HETATM   77  H   UNK     1      -3.233  -2.927   0.707
HETATM   78  H   UNK     1      -4.079  -3.449  -0.779
HETATM   79  H   UNK     1      -2.686  -1.792  -3.268
HETATM   80  H   UNK     1      -4.436  -2.026  -2.950
HETATM   81  H   UNK     1       2.686   2.078  -3.104
HETATM   82  H   UNK     1       4.446   2.222  -2.787
HETATM   83  H   UNK     1       3.204   2.872   0.933
HETATM   84  H   UNK     1       4.094   3.494  -0.489
CONECT    1    3    4    5    6
CONECT    2    3    4    7    8
CONECT    3    1    2    4
CONECT    4    1    2    3
CONECT    5    1    9   11   12
CONECT    6    1   21   22   23
CONECT    7    2   10   24   25
CONECT    8    2   34   35   36
CONECT    9    5   13
CONECT   10    7   26
```

```
CONECT   11    5   37   81   82
CONECT   12    5   38   83   84
CONECT   13    9   14   18
CONECT   14   13   15   39
CONECT   15   14   16   40
CONECT   16   15   17   41
CONECT   17   16   18   19
CONECT   18   13   17   20
CONECT   19   17   42   43   44
CONECT   20   18   45   46   47
CONECT   21    6   59   60   61
CONECT   22    6   62   63   64
CONECT   23    6   65   66   67
CONECT   24    7   48   77   78
CONECT   25    7   49   79   80
CONECT   26   10   27   31
CONECT   27   26   28   50
CONECT   28   27   29   51
CONECT   29   28   30   52
CONECT   30   29   31   32
CONECT   31   26   30   33
CONECT   32   30   53   54   55
CONECT   33   31   56   57   58
CONECT   34    8   68   69   70
CONECT   35    8   71   72   73
CONECT   36    8   74   75   76
CONECT   37   11
CONECT   38   12
CONECT   39   14
CONECT   40   15
CONECT   41   16
CONECT   42   19
CONECT   43   19
CONECT   44   19
CONECT   45   20
CONECT   46   20
CONECT   47   20
CONECT   48   24
CONECT   49   25
CONECT   50   27
CONECT   51   28
CONECT   52   29
CONECT   53   32
CONECT   54   32
```

```
CONECT   55   32
CONECT   56   33
CONECT   57   33
CONECT   58   33
CONECT   59   21
CONECT   60   21
CONECT   61   21
CONECT   62   22
CONECT   63   22
CONECT   64   22
CONECT   65   23
CONECT   66   23
CONECT   67   23
CONECT   68   34
CONECT   69   34
CONECT   70   34
CONECT   71   35
CONECT   72   35
CONECT   73   35
CONECT   74   36
CONECT   75   36
CONECT   76   36
CONECT   77   24
CONECT   78   24
CONECT   79   25
CONECT   80   25
CONECT   81   11
CONECT   82   11
CONECT   83   12
CONECT   84   12
END
```

Table S4. Coordinates of fully optimized complex 4 in PDB format

```
HEADER    PROTEIN
COMPND    C:\babel\t.ent
AUTHOR    GENERATED BY BABEL 1.6
ATOM      1 Pt   UNK     1      -0.005  -0.282  -0.948  1.00  0.00
ATOM      2  P   UNK     1       1.209   1.645  -0.191  1.00  0.00
ATOM      3  P   UNK     1      -2.004  -0.028   0.268  1.00  0.00
ATOM      4  N   UNK     1       1.686  -0.605  -2.070  1.00  0.00
ATOM      5  N   UNK     1      -0.339  -2.294   1.708  1.00  0.00
ATOM      6  O   UNK     1       2.697  -2.257  -3.419  1.00  0.00
```

ATOM	7	O	UNK	1	0.311	-3.197	3.744	1.00	0.00
ATOM	8	C	UNK	1	1.716	-1.807	-2.763	1.00	0.00
ATOM	9	C	UNK	1	0.440	-2.559	-2.664	1.00	0.00
ATOM	10	C	UNK	1	-0.594	-2.016	-1.866	1.00	0.00
ATOM	11	C	UNK	1	-1.809	-2.727	-1.831	1.00	0.00
ATOM	12	C	UNK	1	-1.973	-3.926	-2.544	1.00	0.00
ATOM	13	C	UNK	1	-0.924	-4.452	-3.314	1.00	0.00
ATOM	14	C	UNK	1	0.290	-3.758	-3.373	1.00	0.00
ATOM	15	C	UNK	1	0.610	-2.770	2.602	1.00	0.00
ATOM	16	C	UNK	1	2.698	1.461	-1.268	1.00	0.00
ATOM	17	C	UNK	1	3.713	2.427	-1.270	1.00	0.00
ATOM	18	C	UNK	1	4.828	2.285	-2.098	1.00	0.00
ATOM	19	C	UNK	1	4.904	1.153	-2.926	1.00	0.00
ATOM	20	C	UNK	1	3.901	0.182	-2.933	1.00	0.00
ATOM	21	C	UNK	1	2.757	0.316	-2.099	1.00	0.00
ATOM	22	C	UNK	1	1.219	2.421	2.559	1.00	0.00
ATOM	23	C	UNK	1	1.742	2.436	3.858	1.00	0.00
ATOM	24	C	UNK	1	2.934	1.757	4.148	1.00	0.00
ATOM	25	C	UNK	1	3.600	1.059	3.131	1.00	0.00
ATOM	26	C	UNK	1	3.084	1.046	1.829	1.00	0.00
ATOM	27	C	UNK	1	1.895	1.736	1.535	1.00	0.00
ATOM	28	C	UNK	1	-0.383	3.442	-1.638	1.00	0.00
ATOM	29	C	UNK	1	-0.851	4.697	-2.048	1.00	0.00
ATOM	30	C	UNK	1	-0.380	5.861	-1.422	1.00	0.00
ATOM	31	C	UNK	1	0.564	5.763	-0.389	1.00	0.00
ATOM	32	C	UNK	1	1.038	4.508	0.018	1.00	0.00
ATOM	33	C	UNK	1	0.562	3.342	-0.601	1.00	0.00
ATOM	34	C	UNK	1	-1.976	0.833	2.992	1.00	0.00
ATOM	35	C	UNK	1	-2.084	1.782	4.019	1.00	0.00
ATOM	36	C	UNK	1	-2.296	3.133	3.713	1.00	0.00
ATOM	37	C	UNK	1	-2.386	3.536	2.372	1.00	0.00
ATOM	38	C	UNK	1	-2.274	2.590	1.344	1.00	0.00
ATOM	39	C	UNK	1	-2.082	1.231	1.650	1.00	0.00
ATOM	40	C	UNK	1	-4.574	1.096	-0.330	1.00	0.00
ATOM	41	C	UNK	1	-5.597	1.509	-1.193	1.00	0.00
ATOM	42	C	UNK	1	-5.452	1.356	-2.581	1.00	0.00
ATOM	43	C	UNK	1	-4.277	0.795	-3.100	1.00	0.00
ATOM	44	C	UNK	1	-3.250	0.383	-2.239	1.00	0.00
ATOM	45	C	UNK	1	-3.395	0.527	-0.849	1.00	0.00
ATOM	46	C	UNK	1	2.377	-2.762	0.767	1.00	0.00
ATOM	47	C	UNK	1	3.726	-2.773	0.386	1.00	0.00
ATOM	48	C	UNK	1	4.730	-2.776	1.365	1.00	0.00
ATOM	49	C	UNK	1	4.384	-2.779	2.727	1.00	0.00
ATOM	50	C	UNK	1	3.038	-2.765	3.107	1.00	0.00

ATOM	51	C	UNK	1	2.027	-2.744	2.129	1.00	0.00
ATOM	52	C	UNK	1	-2.622	-1.569	1.146	1.00	0.00
ATOM	53	C	UNK	1	-4.004	-1.817	1.191	1.00	0.00
ATOM	54	C	UNK	1	-4.527	-2.900	1.903	1.00	0.00
ATOM	55	C	UNK	1	-3.652	-3.754	2.588	1.00	0.00
ATOM	56	C	UNK	1	-2.275	-3.539	2.540	1.00	0.00
ATOM	57	C	UNK	1	-1.736	-2.457	1.811	1.00	0.00
ATOM	58	H	UNK	1	-0.001	-1.799	0.879	1.00	0.00
ATOM	59	H	UNK	1	-2.651	-2.370	-1.250	1.00	0.00
ATOM	60	H	UNK	1	-2.924	-4.449	-2.492	1.00	0.00
ATOM	61	H	UNK	1	-1.054	-5.381	-3.858	1.00	0.00
ATOM	62	H	UNK	1	1.130	-4.115	-3.959	1.00	0.00
ATOM	63	H	UNK	1	3.631	3.292	-0.619	1.00	0.00
ATOM	64	H	UNK	1	5.613	3.033	-2.101	1.00	0.00
ATOM	65	H	UNK	1	5.760	1.019	-3.581	1.00	0.00
ATOM	66	H	UNK	1	3.981	-0.687	-3.567	1.00	0.00
ATOM	67	H	UNK	1	0.292	2.943	2.354	1.00	0.00
ATOM	68	H	UNK	1	1.212	2.970	4.640	1.00	0.00
ATOM	69	H	UNK	1	3.337	1.767	5.156	1.00	0.00
ATOM	70	H	UNK	1	4.515	0.519	3.345	1.00	0.00
ATOM	71	H	UNK	1	3.608	0.503	1.050	1.00	0.00
ATOM	72	H	UNK	1	-0.746	2.541	-2.123	1.00	0.00
ATOM	73	H	UNK	1	-1.576	4.764	-2.851	1.00	0.00
ATOM	74	H	UNK	1	-0.741	6.834	-1.739	1.00	0.00
ATOM	75	H	UNK	1	0.936	6.661	0.094	1.00	0.00
ATOM	76	H	UNK	1	1.769	4.446	0.818	1.00	0.00
ATOM	77	H	UNK	1	-1.828	-0.210	3.248	1.00	0.00
ATOM	78	H	UNK	1	-2.007	1.459	5.051	1.00	0.00
ATOM	79	H	UNK	1	-2.394	3.864	4.509	1.00	0.00
ATOM	80	H	UNK	1	-2.546	4.579	2.122	1.00	0.00
ATOM	81	H	UNK	1	-2.357	2.915	0.313	1.00	0.00
ATOM	82	H	UNK	1	-4.689	1.237	0.739	1.00	0.00
ATOM	83	H	UNK	1	-6.500	1.947	-0.784	1.00	0.00
ATOM	84	H	UNK	1	-6.245	1.674	-3.249	1.00	0.00
ATOM	85	H	UNK	1	-4.154	0.676	-4.171	1.00	0.00
ATOM	86	H	UNK	1	-2.341	-0.048	-2.643	1.00	0.00
ATOM	87	H	UNK	1	1.616	-2.803	-0.003	1.00	0.00
ATOM	88	H	UNK	1	3.983	-2.791	-0.667	1.00	0.00
ATOM	89	H	UNK	1	5.774	-2.790	1.068	1.00	0.00
ATOM	90	H	UNK	1	5.160	-2.799	3.485	1.00	0.00
ATOM	91	H	UNK	1	2.746	-2.782	4.151	1.00	0.00
ATOM	92	H	UNK	1	-4.684	-1.166	0.656	1.00	0.00
ATOM	93	H	UNK	1	-5.598	-3.071	1.921	1.00	0.00
ATOM	94	H	UNK	1	-4.038	-4.597	3.151	1.00	0.00

```
ATOM      95  H   UNK     1       -1.601  -4.197   3.069  1.00  0.00
CONECT     1    2    3    4   10
CONECT     2    1   16   27   33
CONECT     3    1   39   45   52
CONECT     4    1    8   21
CONECT     5   15   57   58
CONECT     6    8
CONECT     7   15
CONECT     8    4    6    9
CONECT     9    8   10   14
CONECT    10    1    9   11
CONECT    11   10   12   59
CONECT    12   11   13   60
CONECT    13   12   14   61
CONECT    14    9   13   62
CONECT    15    5    7   51
CONECT    16    2   17   21
CONECT    17   16   18   63
CONECT    18   17   19   64
CONECT    19   18   20   65
CONECT    20   19   21   66
CONECT    21    4   16   20
CONECT    22   23   27   67
CONECT    23   22   24   68
CONECT    24   23   25   69
CONECT    25   24   26   70
CONECT    26   25   27   71
CONECT    27    2   22   26
CONECT    28   29   33   72
CONECT    29   28   30   73
CONECT    30   29   31   74
CONECT    31   30   32   75
CONECT    32   31   33   76
CONECT    33    2   28   32
CONECT    34   35   39   77
CONECT    35   34   36   78
CONECT    36   35   37   79
CONECT    37   36   38   80
CONECT    38   37   39   81
CONECT    39    3   34   38
CONECT    40   41   45   82
CONECT    41   40   42   83
CONECT    42   41   43   84
CONECT    43   42   44   85
```

```
CONECT   44   43   45   86
CONECT   45    3   40   44
CONECT   46   47   51   87
CONECT   47   46   48   88
CONECT   48   47   49   89
CONECT   49   48   50   90
CONECT   50   49   51   91
CONECT   51   15   46   50
CONECT   52    3   53   57
CONECT   53   52   54   92
CONECT   54   53   55   93
CONECT   55   54   56   94
CONECT   56   55   57   95
CONECT   57    5   52   56
CONECT   58    5
CONECT   59   11
CONECT   60   12
CONECT   61   13
CONECT   62   14
CONECT   63   17
CONECT   64   18
CONECT   65   19
CONECT   66   20
CONECT   67   22
CONECT   68   23
CONECT   69   24
CONECT   70   25
CONECT   71   26
CONECT   72   28
CONECT   73   29
CONECT   74   30
CONECT   75   31
CONECT   76   32
CONECT   77   34
CONECT   78   35
CONECT   79   36
CONECT   80   37
CONECT   81   38
CONECT   82   40
CONECT   83   41
CONECT   84   42
CONECT   85   43
CONECT   86   44
CONECT   87   46
```

```
CONECT    88    47
CONECT    89    48
CONECT    90    49
CONECT    91    50
CONECT    92    53
CONECT    93    54
CONECT    94    55
CONECT    95    56
MASTER          0     0     0     0     0     0     0     0    95     0    95     0
END
```

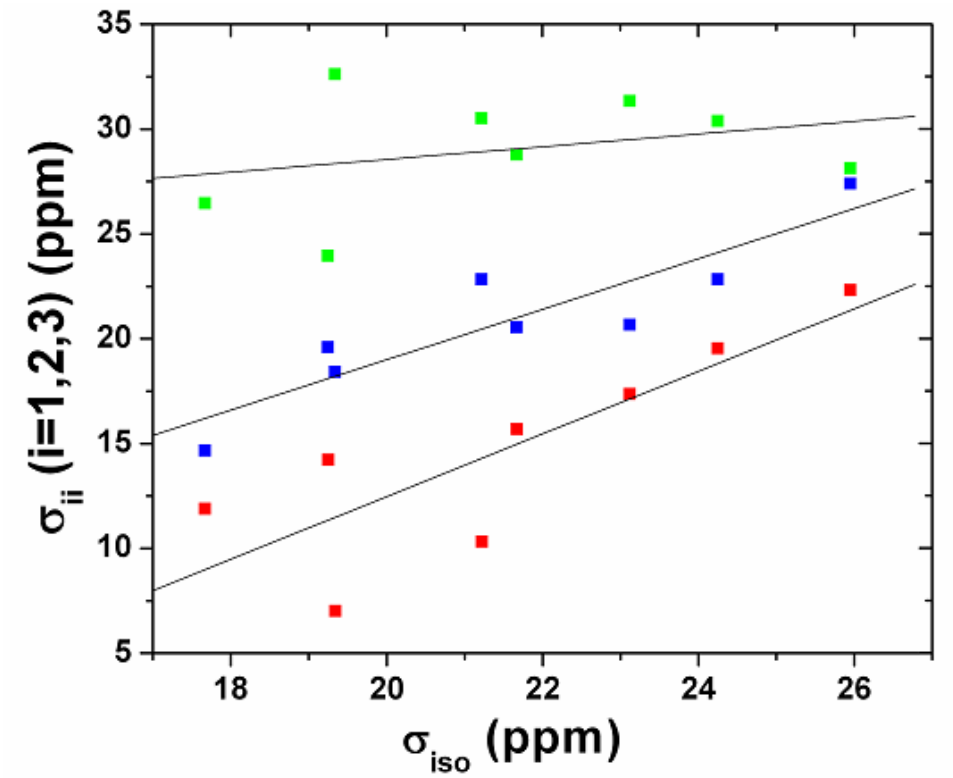

Figure S1. Computed ^{1}H NMR chemical shift tensor elements as a function of the isotropic shielding. σ_{11}, σ_{22}, σ_{33} are represented by red, blue, and green data points, respectively.

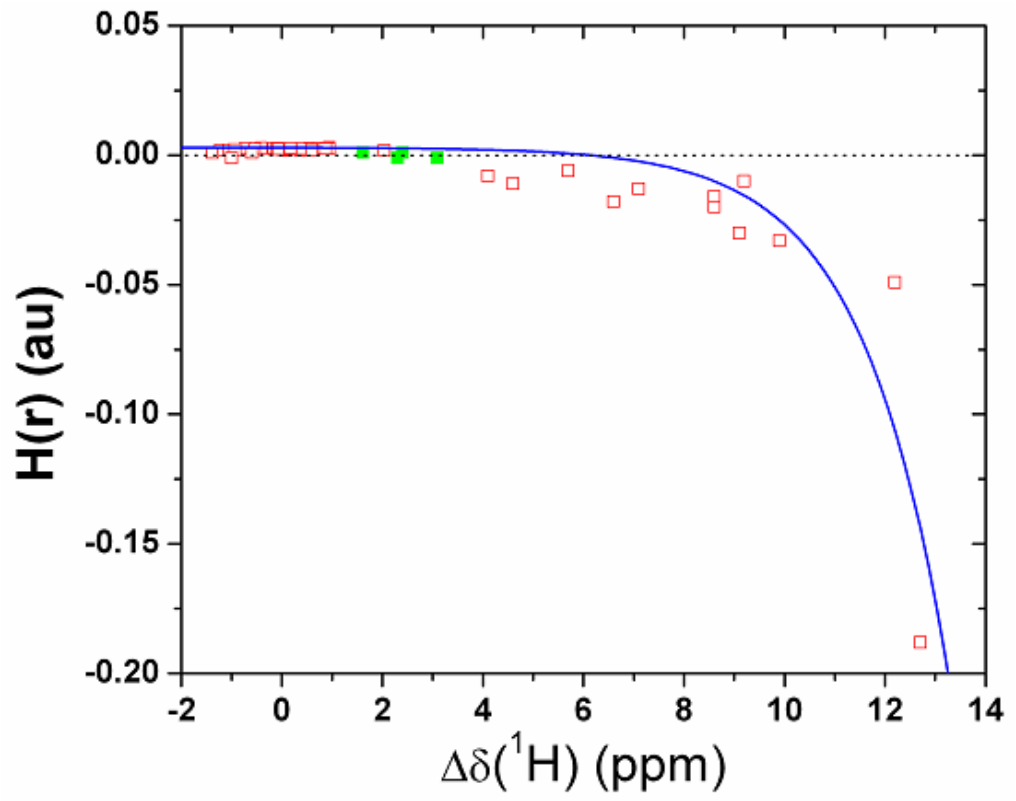

Figure S2. Plot of H(**r**)'s and experimental ^{1}H NMR chemical shift changes ($\Delta\delta$) in metal complexes **1-4** (green) and non-metal HB systems from ref.15 (red). Here $\Delta\delta$ rather than δ (as used in ref.15) is used to include both the metal and non-metal systems on the same graph. The $\Delta\delta$ values of non-metal HB systems (mostly protein backbone HBs) from ref.15 were calculated from original δ values by subtracting 8.3 ppm (an average value of amide proton shifts, ref.21). The blue line was adapted from ref.15 accordingly. The dotted line divides the regions of purely electrostatic and covalent interactions in AIM terminology.