### Computational Characterization of Bidentate P-donor Ligands: Direct Comparison to Tolman’s Electronic Parameters

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Cartesian coordinates of palladium-diphosphine complexes occurring in this study

All energy values are given in a.u.

| Complex                      | Pd  | C1 | C2 | C3 | C4 | H1 | H2 | H3 | H4 | H5 | H6 |
|------------------------------|-----|----|----|----|----|----|----|----|----|----|----|
| Pd(dppe)(CO) (Pd(13)(CO))   |     |    |    |    |    |    |    |    |    |    |    |
| Pd                           | 15.1972 | -27.52594 | -16.77965 |     |    |    |    |    |    |    |    |
| P                             | 15.8169 | -26.31602 | -18.73061 |     |    |    |    |    |    |    |    |
| C                             | 15.43896 | -24.81242 | -14.13540 |     |    |    |    |    |    |    |    |
| C                             | 15.05119 | -25.61455 | -13.03987 |     |    |    |    |    |    |    |    |
| C                             | 14.9612 | -25.0331 | -11.89379 |     |    |    |    |    |    |    |    |
| H                             | 15.64579 | -28.4033 | -12.9249 |     |    |    |    |    |    |    |    |
| C                             | 14.29813 | -23.6407 | -11.83323 |     |    |    |    |    |    |    |    |
| H                             | 15.15213 | -26.7029 | -13.10119 |     |    |    |    |    |    |    |    |
| H                             | 15.5292 | -22.77135 | -14.90114 |     |    |    |    |    |    |    |
| H                             | 14.20358 | -25.66749 | -11.04835 |     |    |    |    |    |    |    |
| H                             | 14.40934 | -21.75525 | -12.88362 |     |    |    |    |    |    |    |
| H                             | 13.85210 | -23.18906 | -10.94017 |     |    |    |    |    |    |    |
| P                             | 14.40479 | -23.5250 | -19.39087 |     |    |    |    |    |    |    |
| C                             | 14.40679 | -24.77426 | -20.68782 |     |    |    |    |    |    |    |
| C                             | 13.30241 | -25.08978 | -18.54217 |     |    |    |    |    |    |    |
| C                             | 13.32644 | -23.99463 | -21.12517 |     |    |    |    |    |    |    |
| C                             | 12.22915 | -24.29871 | -18.97766 |     |    |    |    |    |    |    |
| H                             | 12.03309 | -24.65210 | -11.2405 |     |    |    |    |    |    |    |
| P                             | 12.23772 | -23.75156 | -20.27046 |     |    |    |    |    |    |    |
| H                             | 12.25262 | -24.96358 | -21.35907 |     |    |    |    |    |    |    |
| H                             | 13.28395 | -25.54511 | -17.52476 |     |    |    |    |    |    |    |
| H                             | 13.33135 | -23.57586 | -22.13862 |     |    |    |    |    |    |    |
| H                             | 11.3788 | -24.11979 | -18.3063 |     |    |    |    |    |    |    |
| H                             | 11.39298 | -23.14288 | -20.61512 |     |    |    |    |    |    |    |
| H                             | 17.87772 | -26.04169 | -15.05617 |     |    |    |    |    |    |    |
| H                             | 18.52141 | -27.18450 | -15.58091 |     |    |    |    |    |    |    |
| H                             | 18.58411 | -25.18073 | -14.20145 |     |    |    |    |    |    |    |
| P                             | 18.86547 | -25.45595 | -15.24674 |     |    |    |    |    |    |    |
| H                             | 19.55647 | -26.59554 | -14.38525 |     |    |    |    |    |    |    |
| H                             | 19.76890 | -27.86398 | -16.23859 |     |    |    |    |    |    |    |
| H                             | 18.08733 | -24.29508 | -13.78758 |     |    |    |    |    |    |    |
| H                             | 20.34780 | -28.34854 | -15.65157 |     |    |    |    |    |    |    |
| H                             | 20.45700 | -28.7877 | -13.18453 |     |    |    |    |    |    |    |
| H                             | 21.59452 | -26.81337 | -14.11480 |     |    |    |    |    |    |    |
| H                             | 16.62267 | -26.96985 | -20.24926 |     |    |    |    |    |    |    |
| H                             | 17.75494 | -26.39322 | -20.85961 |     |    |    |    |    |    |    |
| H                             | 16.06106 | -26.13780 | -20.80952 |     |    |    |    |    |    |    |
| H                             | 18.31048 | -26.97276 | -22.01181 |     |    |    |    |    |    |    |
| H                             | 16.60744 | -28.70389 | -21.96789 |     |    |    |    |    |    |    |
| H                             | 17.73637 | -28.12380 | -22.57097 |     |    |    |    |    |    |    |
| H                             | 18.20856 | -25.48755 | -20.44651 |     |    |    |    |    |    |    |
| H                             | 15.19599 | -28.60199 | -20.31959 |     |    |    |    |    |    |    |
| H                             | 19.19442 | -25.51885 | -22.47507 |     |    |    |    |    |    |    |
| H                             | 16.15980 | -29.60866 | -22.39490 |     |    |    |    |    |    |    |
| H                             | 18.17007 | -28.57191 | -23.47226 |     |    |    |    |    |    |    |
| H                             | 16.96338 | -24.93584 | -18.15934 |     |    |    |    |    |    |    |
| H                             | 16.44131 | -23.33089 | -16.85143 |     |    |    |    |    |    |    |
| H                             | 17.96875 | -25.39102 | -18.00033 |     |    |    |    |    |    |    |
| H                             | 17.05813 | -24.15889 | -18.93844 |     |    |    |    |    |    |    |

Pd(dppe)(CO) (Pd(13)(CO))
Pd(dpdpf)(CO) (Pd(26)(CO))

Pd(xantphos)(CO) (Pd(25)(CO))
Pd(PM$_2$Ph)$_2$(CO) (Pd(2)$_2$(CO))

Pd ($^{1}(1)$) 0.04662  0.81206  -1.67522
P  -1.89874  -0.05305  -0.57770
P  1.87456  0.11185  -0.49066
C  -1.89773  -0.05086  1.26712
C  -2.50308  -1.06475  2.05121
C  -1.14643  0.92484  1.95768
C  -2.42373  -0.09331  3.41450
H  -3.1025  -1.84636  1.50936
C  -1.04704  0.90071  3.35294
H  -0.61879  1.70404  1.39722
C  -1.68510  -0.11058  4.08839
H  -2.92319  -1.98048  3.97906
N  -0.65116  1.65296  3.86806
H  -1.59563  -0.13768  5.18114
C  1.8809  -0.29579  1.31292
C  1.18997  -1.44856  1.72435
C  2.55625  0.47823  2.28048
C  1.16533  -1.82385  3.07334
H  0.64650  -2.03515  0.97425
C  2.52977  0.10955  3.63374
C  3.10908  1.38967  1.98562
C  1.82875  -1.04306  4.03165
C  0.60893  -2.71641  3.38082
C  3.09300  0.72647  4.38011
C  1.79684  -1.32738  5.09040
C  3.60542  -0.36511  -0.97690
C  4.36345  0.12160  -0.33631
C  3.70006  -1.46058  -0.89163
C  3.76675  -0.08127  -2.03147
C  2.01030  1.96417  -0.53041
C  2.92999  2.34341  -0.03961
C  2.01965  2.27929  -1.58784
C  1.12494  2.08968  -0.04664
C  -3.50035  -0.89461  -0.98817
C  -3.67379  -0.75606  -2.06923
C  -3.40782  -1.97784  -0.80305
C  -4.35249  -0.48673  -0.41511
C  -2.33184  1.71224  -0.97006
C  -2.50563  1.78512  -2.05746

Pd(PEt$_2$Ph)$_2$ (CO) (Pd(2)$_2$(CO))

Pd  -0.02836  -0.50874  -1.81045
P  2.02247  -0.10729  -0.60515
P  1.88534  -0.18544  -0.45699
C  -1.94007  0.18703  1.21911
C  -2.71022  -0.50016  2.17862
C  -0.99319  1.13140  1.66873
C  -2.52724  -0.25752  3.54792
H  3.45705  1.23874  1.86974
C  0.82296  0.38189  3.03318
H  0.36659  1.66471  0.93232
C  -1.58469  0.68531  3.98015
H  -3.12654  -0.81183  4.28040
H  -0.07392  2.11826  3.36242
C  -1.43556  0.86647  5.05128
C  1.75575  -0.64645  1.32766
C  0.82237  -1.64669  1.67312
C  2.51404  -0.04394  2.34932
C  0.66413  -2.03031  3.00851
H  0.21275  -2.09788  0.88107
C  2.32824  -0.41814  3.88881
H  3.24897  0.73218  2.10279
C  1.39403  -1.40622  4.02105
H  -0.09287  -2.79956  3.26215
H  2.91440  0.70107  4.47669
H  1.24349  1.69567  5.06913
C  3.40337  1.15441  -0.96486
C  4.21886  -0.93953  -2.24737
C  3.70199  -0.74834  -1.94930
C  2.55087  1.55846  -0.41168
C  3.58256  1.54877  -0.01258
H  1.92838  2.11561  0.31243
C  -3.27726  -1.46977  -0.79141
H  -3.60553  -1.40122  -1.84516
H  -4.16695  -1.27631  -0.16374
C  -2.95695  1.41072  -1.17657
H  -3.11421  1.26334  -2.26202
H  -2.23649  2.24497  -1.08332
C  -0.00197  -1.02618  -3.65086
G  0.01534  -1.30758  -4.77924
C  2.49981  2.22570  -1.79048
C  3.10656  1.67519  -2.53072
C  1.46379  2.25237  -2.17392
C  2.88428  3.26084  -1.74257
C  3.12603  -2.66491  -1.06264
H  4.01998  -3.20271  -1.41253
C  2.83719  -3.07266  -0.08157
C  2.29987  -2.85216  -1.77049
C  -2.67836  -2.85235  -0.51315
C  -3.42157  -3.65118  -0.68992
H  -1.80899  -3.03406  -1.17004
C  -2.33044  -2.94201  0.53143
C  -4.26299  1.72897  -0.44823
C  -5.00977  0.92437  -0.57567
C  -4.09393  1.86301  0.63500
C  -4.71169  2.66063  -0.84034

Pd(PEt$_2$Ph)$_2$ (CO) (Pd(2)$_2$(CO))
| Atom  | X    | Y    | Z    |
|-------|------|------|------|
| Pd(PEt)₂ | -0.20247 | -0.50874 | -1.81045 |
| P      | -1.09027 | -0.60515 |
| C      | 0.09854 | -0.45699 |
| C      | -2.71022 | 0.00016 | 2.17682 |
| C      | -0.99319 | 1.13160 | 1.66873 |
| C      | -2.57272 | -0.25752 | 3.34792 |
| H      | -3.45705 | -1.23784 | 1.86374 |
| C      | -0.82206 | 1.38819 | 3.03318 |
| H      | -0.36459 | 1.64671 | 0.93323 |
| C      | 1.58469 | 0.68531 | 3.98015 |
| H      | -3.15825 | -0.81183 | 4.20840 |
| C      | 0.70327 | 2.11826 | 3.36042 |
| H      | -1.43556 | 0.86647 | 5.05128 |
| C      | 1.75575 | -0.64845 | 1.32766 |
| C      | 0.82237 | -1.64669 | 1.67312 |
| C      | 2.51404 | -0.04394 | 2.34932 |
| C      | 0.64613 | -2.03031 | 3.00851 |
| C      | 0.21277 | -2.09788 | 0.88107 |
| C      | 2.32824 | -0.41814 | 3.68881 |
| C      | 3.24897 | 0.73218 | 2.10729 |
| C      | 1.39403 | -1.41062 | 4.02105 |
| C      | -0.09287 | -2.79956 | 3.26215 |
| C      | 2.91400 | 0.07017 | 4.47669 |
| C      | 1.24349 | -1.69567 | 5.06913 |
| C      | 3.40337 | -1.15441 | -0.96486 |
| C      | 4.21886 | -0.93953 | -0.24737 |
| C      | 3.70199 | -0.74834 | -1.94930 |
| C      | 2.55087 | 1.55846 | -0.41188 |
| C      | 3.58256 | 1.54877 | -0.01258 |
| C      | 4.28338 | 2.11561 | 0.31243 |
| C      | -3.27726 | -1.46977 | -0.79414 |
| C      | -3.60553 | -1.40122 | -1.84516 |
| C      | -4.16695 | -1.27631 | -0.19374 |
| C      | -2.96056 | 1.41072 | -1.17687 |
| C      | -3.14211 | 2.16334 | -2.26202 |
| C      | -2.23649 | 2.26497 | 0.30832 |
| C      | -0.00197 | -1.02618 | 0.35068 |
| H      | 0.01534 | -1.30758 | -9.77924 |
| C      | 2.49981 | 2.22570 | -1.79048 |
| C      | 3.10655 | 1.67519 | -2.55072 |
| C      | 1.46279 | 2.29237 | -2.17922 |
| C      | 2.88428 | 3.26084 | -1.74257 |
| C      | 3.12603 | 2.65491 | -0.36264 |
| H      | 4.01998 | -3.20271 | -1.41253 |
| H      | 2.83719 | -3.07266 | -0.08157 |
| H      | 2.29987 | -2.85216 | -1.77049 |
| C      | 3.67836 | -2.85238 | -0.51315 |
| H      | -3.42157 | -3.65118 | -0.69992 |
| H      | -1.80899 | -3.03406 | -1.17004 |
| H      | -2.33044 | -2.94201 | 0.53143 |
| C      | -4.26299 | 1.72897 | -0.44825 |
| H      | -5.00977 | 0.92437 | -2.57587 |
| H      | -4.09393 | 1.86301 | 0.63500 |
| H      | -4.71699 | 2.66063 | -0.84034 |

**Pd(PEt)$_2$(CO)**

| Atom  | X    | Y    | Z    |
|-------|------|------|------|
| Pd    | -0.05427 | 1.17105 | -1.61266 |
| P      | -1.89423 | 0.07145 | -0.62267 |
| P      | 1.87985 | 0.23668 | -0.63146 |
| C      | 1.94574 | -1.61311 | 0.45852 |
| C      | 2.88974 | 1.91287 | -0.98123 |
| C      | 1.04836 | -2.08456 | -1.43102 |
| C      | 3.52839 | 0.55554 | -1.42445 |
| C      | 4.36237 | 0.08451 | 0.87066 |
| C      | 3.68660 | 1.64633 | -1.47878 |
| C      | -2.17235 | 1.66845 | -1.22115 |
| H      | 1.27175 | -2.26961 | -1.01671 |
| H      | 2.32877 | -1.64269 | -2.31315 |
| C      | 3.58937 | 0.79732 | -0.84467 |
| H      | 3.79728 | 0.68534 | -1.92488 |
| C      | 3.58773 | 1.81600 | -0.45181 |
| C      | -0.12883 | 2.93715 | -2.95088 |
| D      | -0.17819 | 3.36151 | -3.76921 |
| C      | 2.21179 | 0.78374 | 1.11135 |
| C      | 3.12628 | 0.31754 | 1.52290 |
| C      | 2.32235 | 1.88167 | 1.12346 |
| C      | 1.87097 | -0.18911 | 1.21841 |
| C      | -1.78972 | 0.78986 | 1.72079 |
| C      | -2.77940 | -0.70760 | 1.57866 |
| C      | -3.04710 | -1.23341 | -0.73313 |
| C      | -4.37613 | -1.8795 | -0.36108 |
| C      | -0.89301 | -0.78743 | 1.48625 |
| C      | 1.34907 | 0.51910 | 1.74724 |
| C      | 3.50677 | 0.16453 | -2.95376 |
| C      | 1.09680 | 1.94040 | 0.18512 |
|Element| X | Y | Z |
|-------|---|---|---|
| C     | -3.2687 | -2.2775 | -5.2313 |
| H     | -1.93162 | -3.0519 | -6.76058 |
| H     | -0.07279 | -1.48196 | -6.16017 |
| H     | -0.37795 | 0.18170 | -4.33342 |
| Pd    | 0.78274 | -2.28544 | -1.54011 |
| C     | 0.70044 | -3.17303 | 0.99169 |
| C     | 3.07160 | -1.26242 | -2.21068 |
| C     | -1.27211 | -3.68367 | -2.53906 |
| C     | 0.30560 | -2.64813 | 3.71484 |
| C     | -0.58037 | -3.49133 | 3.02349 |
| C     | -0.39475 | -3.74684 | 1.65726 |
| C     | 1.60265 | -2.34340 | 1.67683 |
| C     | 1.39925 | -2.07566 | 3.03760 |
| H     | 0.14837 | -2.43833 | 4.77920 |
| Pd    | 0.87491 | 0.29110 | 0.59384 |
| P     | 0.87491 | 0.29110 | 0.59384 |
| P     | -0.40987 | 1.38524 | -0.97429 |
| C     | 0.87491 | 0.29110 | 0.59384 |
| C     | -0.40987 | 1.38524 | -0.97429 |
| C     | 1.66115 | -2.34340 | -1.54011 |
| C     | 3.07160 | -1.26242 | -2.21068 |
| Pd    | 0.78274 | -2.28544 | -1.54011 |
| C     | 0.70044 | -3.17303 | 0.99169 |
| C     | 3.07160 | -1.26242 | -2.21068 |
| C     | -1.27211 | -3.68367 | -2.53906 |
| C     | 0.30560 | -2.64813 | 3.71484 |
| C     | -0.58037 | -3.49133 | 3.02349 |
| C     | -0.39475 | -3.74684 | 1.65726 |
| C     | 1.60265 | -2.34340 | 1.67683 |
| C     | 1.39925 | -2.07566 | 3.03760 |
| H     | 0.14837 | -2.43833 | 4.77920 |
| O     | 0.02875 | -3.24708 | -2.67499 |
| O     | 0.87547 | -3.46752 | -0.39468 |
| O     | 2.27740 | -2.40669 | -2.27205 |
| O     | -2.61772 | 0.37990 | -2.80254 |
| O     | -2.38825 | 1.78853 | -0.78199 |
| O     | -1.08818 | 2.32875 | -2.93194 |
| O     | 1.42175 | 0.78155 | 0.43527 |
| O     | 2.05857 | 1.33219 | 1.22590 |

Pd(PCl₂)(CO)(Pd(9)(CO))

Pd 0.87491 0.29110 0.59384
P -0.40987 1.38524 -0.97429
P 0.87491 0.29110 0.59384
C 1.66115 1.04135 2.21801
D 2.10851 1.48454 3.18006

Pd(PCl₃)(CO)(Pd(10)(CO))

Pd 0.87491 0.29110 0.59384
P -0.40987 1.38524 -0.97429
P 0.87491 0.29110 0.59384
C 1.66115 1.04135 2.21801
D 2.10851 1.48454 3.18006

Pd(PF₂)(CO)(Pd(11)(CO))

Pd 0.72692 0.17896 0.39357
P -0.67602 1.38085 -0.93887
P 1.18494 -1.96676 -0.22082
C 1.52283 0.97704 2.00655
D 1.99381 1.44288 2.94514
F -2.16484 1.58357 -0.37098
F -0.33083 2.91549 -1.27180
F 1.44836 -3.09367 0.89613
F -1.06244 0.93410 -2.43819
F 0.19352 -2.83288 -1.14608
F 2.52904 -2.16094 -1.07962

Pd(PCl₃)(CO)(Pd(12)(CO))

Pd 0.87491 0.29110 0.59384
P -0.40987 1.38524 -0.97429
P 0.87491 0.29110 0.59384
C 1.66115 1.04135 2.21801
D 2.10851 1.48454 3.18006

Pd(PCl₂)(OEt)(CO)(Pd(27)(CO))

Pd 0.87491 0.29110 0.59384
P -0.40987 1.38524 -0.97429
P 0.99632 -1.87771 -0.17604
C 1.66115 1.04135 2.21801
D 2.10851 1.48454 3.18006

Pd(PCl₃)(OEt)(CO)(Pd(27)(CO))

Pd 0.87491 0.29110 0.59384
P -0.40987 1.38524 -0.97429
P 0.99632 -1.87771 -0.17604
C 1.66115 1.04135 2.21801
D 2.10851 1.48454 3.18006