Insight into metal-phosphorus bonding from analysis of the electronic structure of redox pairs of metal-phosphine complexes

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## Supporting Information

Tables containing relative energies of different spin states of the target compounds (S1 and S2), followed by Tables containing the average bond lengths and angles in reduced and oxidized complexes, together with the changes in bond lengths and angles (S3 to S15)

Table S1 B3LYP Computed relative energies $\left(\mathrm{kcal} \mathrm{mol}^{-1}\right)$ for different spin states of the target compounds.

| Compound | charge | Oxidation <br> state | multiplicity |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  | 1 | 2 | 3 | 4 | 5 | 6 |
| trans $-\left[\mathrm{MoCl}_{2}(\mathrm{dmpe})_{2}\right]$ | +1 | III ( $\mathrm{d}^{3}$ ) |  | 5.43 |  | 0.00 |  | 1 |
|  | 0 | II ( $\mathrm{d}^{4}$ ) | 12.74 |  | 0.00 |  | 48.42 |  |
| trans $-\left[\mathrm{CrCl}_{2}(\mathrm{dmpe})_{2}\right]$ | +1 | III ( $\mathrm{d}^{3}$ ) |  | 31.92 |  | 0.00 |  |  |
|  | 0 | II ( $\mathrm{d}^{4}$ ) | 27.34 |  | 0.00 |  | -0.54 |  |
| trans $-\left[\mathrm{TcCl}_{2}(\mathrm{dppe})_{2}\right]$ | +1 | III ( $\mathrm{d}^{4}$ ) | 19.15 |  | 0.00 |  | 36.42 |  |
|  | 0 | II ( $\mathrm{d}^{5}$ ) |  | 0.00 |  | 34.09 |  | 49.72 |
| [ $\mathrm{Mn}(\mathrm{CO})($ dppe $\left.)\left(\eta^{5}-\mathrm{C}_{6} \mathrm{H}_{6} \mathrm{Ph}\right)\right]$ | +1 | II ( $\mathrm{d}^{5}$ ) |  | 0.00 |  | 11.69 |  | 14.48 |
|  | 0 | I ( $\mathrm{d}^{6}$ ) | 0.00 |  | 22.42 |  | 39.21 |  |
| $\left[\mathrm{FeCp}^{*}\left(\mathrm{C} \equiv \mathrm{C}-\mathrm{C}_{6} \mathrm{H}_{4} \mathrm{NO}_{2}\right)(\right.$ dppe $\left.)\right]$ | +1 | III ( $\mathrm{d}^{5}$ ) |  | 0.00 |  | 16.57 |  | 41.00 |
|  | 0 | II ( $\mathrm{d}^{6}$ ) | 0.00 |  | 11.44 |  | 15.66 |  |
| $\left[\mathrm{Fe}\left(\mathrm{P}\left(\mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{PPh}_{2}\right)_{3}\right)(\mathrm{C} \equiv \mathrm{C}-\mathrm{Ph})\right]$ | +1 | II ( $\mathrm{d}^{6}$ ) | 14.03 |  | 0.00 |  | 10.30 |  |
|  | 0 | $\mathrm{I}\left(\mathrm{d}^{7}\right)$ |  | 0.00 |  | 9.11 |  |  |
| [FeCp*(dppe)] | +1 | II ( $\mathrm{d}^{6}$ ) | 14.16 |  | 0.00 |  | -0.26 |  |
|  | 0 | $\mathrm{I}\left(\mathrm{d}^{7}\right)$ |  | 0.00 |  | 4.20 |  |  |
| $\left[\mathrm{Cp}^{*} \mathrm{MoCl}_{2}\left(\mathrm{PMe}_{2} \mathrm{Ph}\right)_{2}\right]$ | +1 | $\operatorname{IV}\left(\mathrm{d}^{2}\right)$ | 12.47 | 0.00 |  |  |  |  |
|  | 0 | III ( $\mathrm{d}^{3}$ ) |  | 0.00 |  | 17.86 |  |  |
| $\left[\eta^{7}-\left(\mathrm{C}_{7} \mathrm{H}_{7}\right) \mathrm{Mo}(\mathrm{C} \equiv \mathrm{CPh})(\right.$ dppe $\left.)\right]$ | +1 | I ( $\mathrm{d}^{5}$ ) |  | 0.00 |  | 29.95 |  | 52.46 |
|  | 0 | $0\left(d^{6}\right)$ | 0.00 |  | 33.15 |  | 50.32 |  |

Table S2 BP86 relative single-point energies ( $\mathrm{kcal} \mathrm{mol}^{-1}$ ) for different spin states of target compounds.

| Compound | charge | Oxidation state | multiplicity |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  | 1 | 2 | 3 | 4 | 5 | 6 |
| trans $-\left[\mathrm{CrCl}_{2}(\mathrm{dmpe})_{2}\right]$ | +1 | III ( $\mathrm{d}^{3}$ ) |  | 22.27 |  | 0.00 |  |  |
|  | 0 | II ( $\mathrm{d}^{4}$ ) | 24.74 |  | 0.00 |  | 16.37 |  |
| $\left[\mathrm{Mn}(\mathrm{CO})(\right.$ dppe $\left.)\left(\eta^{5}-\mathrm{C}_{6} \mathrm{H}_{6} \mathrm{Ph}\right)\right]$ | +1 | II ( $\mathrm{d}^{5}$ ) |  | 0.00 |  | 24.57 |  | 50.16 |
|  | 0 | I ( $\mathrm{d}^{6}$ ) | 0.00 |  | 34.78 |  | 67.94 |  |
| $\left[\mathrm{FeCp}{ }^{*}\left(\mathrm{C} \equiv \mathrm{C}-\mathrm{C}_{6} \mathrm{H}_{4} \mathrm{NO}_{2}\right)(\right.$ dppe $\left.)\right]$ | +1 | III ( $\mathrm{d}^{5}$ ) |  | 0.00 |  | 28.63 |  | 66.37 |
|  | 0 | II ( $\mathrm{d}^{6}$ ) | 0.00 |  | 28.08 |  | 50.43 |  |
| $\left[\mathrm{Fe}\left(\mathrm{P}\left(\mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{PPh}_{2}\right)_{3}\right)(\mathrm{C} \equiv \mathrm{C}-\mathrm{Ph})\right]$ | +1 | II ( $\mathrm{d}^{6}$ ) | 4.38 |  | 0.00 |  | 30.65 |  |
|  | 0 | $\mathrm{I}\left(\mathrm{d}^{7}\right)$ |  | 0.00 |  | 29.36 |  |  |
| [FeCp*(dppe)] | +1 | II ( $\mathrm{d}^{6}$ ) | 5.00 |  | 0.00 |  | 0.36 |  |
|  | 0 | $\mathrm{I}\left(\mathrm{d}^{7}\right)$ |  | 0.00 |  | 20.62 |  |  |

In Tables S3 - S15, all bond lengths are averages of the relevant values throughout the structure. E.g. for trans$\left[\mathrm{MoCl}_{2}(\mathrm{dmpe})_{2}\right], \mathrm{r}(\mathrm{Mo}-\mathrm{Cl})$ refers to the average of the two $\mathrm{Mo}-\mathrm{Cl}$ distances, $\mathrm{r}(\mathrm{Mo}-\mathrm{P})$ is the average of the four $\mathrm{Mo}-\mathrm{P}$ distances, $\mathrm{r}(\mathrm{P}-\mathrm{Me})$ is the average of the eight $\mathrm{P}-\mathrm{C}(\mathrm{Me})$ distances, $\mathrm{r}\left(\mathrm{P}-\mathrm{CH}_{2}\right)$ is the average of the four $\mathrm{P}-\mathrm{C}\left(\mathrm{CH}_{2}\right)$ distances, and $\alpha(\mathrm{MePMe})$ is the average of the $4 \mathrm{C}(\mathrm{Me})-\mathrm{P}-\mathrm{C}(\mathrm{Me})$ angles. Also, distances to rings refer to distances between a metal and the centroid of a ligand.

Table S3. Experimental and computational average bond lengths ( $\AA$ ) and angles (degrees) for reduced and oxidized trans- $\left[\mathrm{MoCl}_{2}(\mathrm{dmpe})_{2}\right]$, and changes upon oxidation. In this case, as discussed in ref. 15 of the paper, some of the crystal structures seem to be affected by disorder, and the agreement between experiment and theory is poor. However, the computed trends are in good agreement with those found for the other complexes, and are probably more reliable than the experimental values.

|  | Calculated |  |  | Experimental |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | Reduced | Oxidized | Change | Reduced | Oxidized | Change |
| $\mathrm{r}(\mathrm{Mo}-\mathrm{Cl})$ | 2.498 | 2.443 | -0.055 | 2.443 | 2.436 | -0.007 |
| $\mathrm{r}(\mathrm{Mo}-\mathrm{P})$ | 2.515 | 2.605 | 0.090 | 2.463 | 2.462 | -0.001 |
| $\mathrm{r}(\mathrm{P}-\mathrm{Me})$ | 1.852 | 1.842 | -0.010 | 1.806 | 1.818 | 0.013 |
| $\mathrm{r}\left(\mathrm{P}-\mathrm{CH}_{2}\right)$ | 1.880 | 1.865 | -0.015 | 1.819 | 1.841 | 0.022 |
| $\alpha(\mathrm{MePMe})$ | 102.5 | 104.70 | 2.20 | 101.75 | 101.30 | -0.45 |

Table S4. Experimental and computational average bond lengths $(\AA)$ and angles (degrees) for reduced and oxidized trans- $\left.\left[\mathrm{CrCl}_{2} \text { (dmpe) }\right)_{2}\right]$, and changes upon oxidation.

|  | Calculated |  |  | Experimental |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | Reduced | Oxidized | Change | Reduced | Oxidized | Change |
| $\mathrm{r}(\mathrm{Cr}-\mathrm{Cl})$ | 2.402 | 2.328 | -0.074 | 2.345 | 2.292 | -0.053 |
| $\mathrm{r}(\mathrm{Cr}-\mathrm{P})$ | 2.444 | 2.515 | 0.071 | 2.370 | 2.445 | 0.076 |
| $\mathrm{r}(\mathrm{P}-\mathrm{Me})$ | 1.851 | 1.840 | -0.010 | 1.824 | 1.809 | -0.015 |
| $\mathrm{r}\left(\mathrm{P}-\mathrm{CH}_{2}\right)$ | 1.875 | 1.862 | -0.013 | 1.858 | 1.821 | -0.037 |
| $\alpha(\mathrm{MePMe})$ | 102.30 | 104.80 | 2.50 | 100.85 | 103.70 | 2.85 |

Table S5. Experimental and computational average bond lengths $(\AA)$ and angles (degrees) for reduced and oxidized trans- $\left[\mathrm{TcCl}_{2}(\mathrm{dppe})_{2}\right]$, and changes upon oxidation.

|  | Calculated |  |  | Experimental |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | Reduced | Oxidized | Change | Reduced | Oxidized | Change |
| $\mathrm{r}(\mathrm{Tc}-\mathrm{Cl})$ | 2.493 | 2.372 | -0.121 | 2.424 | 2.319 | -0.105 |
| $\mathrm{r}(\mathrm{Tc}-\mathrm{P})$ | 2.475 | 2.541 | 0.066 | 2.429 | 2.501 | 0.072 |
| $\mathrm{r}(\mathrm{P}-\mathrm{Ph})$ | 1.853 | 1.840 | -0.013 | 1.838 | 1.827 | -0.011 |
| $\mathrm{r}\left(\mathrm{P}-\mathrm{CH}_{2}\right)$ | 1.880 | 1.876 | -0.004 | 1.850 | 1.839 | -0.011 |
| $\alpha(\mathrm{PhPPh})$ | 102.10 | 104.95 | 2.85 | 100.80 | 101.65 | 0.85 |

Table S6. Experimental and computational average bond lengths $(\AA)$ and angles (degrees) for reduced and oxidized $\left[\mathrm{Mn}(\mathrm{CO})(\right.$ dppe $\left.)\left(\eta^{5}-\mathrm{C}_{6} \mathrm{H}_{6} \mathrm{Ph}\right)\right]$, and changes upon oxidation.

|  | Calculated |  |  | Experimental |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | Reduced | Oxidized | Change | Reduced | Oxidized | Change |
| $\mathrm{r}\left(\mathrm{Mn}-\left(\eta^{5}-\mathrm{C}_{6} \mathrm{H}_{6} \mathrm{Ph}\right)\right)$ | 1.676 | 1.675 | -0.001 | 1.703 | 1.708 | 0.005 |
| $\mathrm{r}(\mathrm{Mn}-\mathrm{P})$ | 2.273 | 2.394 | 0.121 | 2.221 | 2.334 | 0.112 |
| $\mathrm{r}(\mathrm{Mn}-\mathrm{C}(\mathrm{CO}))$ | 1.770 | 1.811 | 0.041 | 1.773 | 1.803 | 0.030 |
| $\mathrm{r}(\mathrm{C}-\mathrm{O})$ | 1.172 | 1.155 | -0.017 | 1.176 | 1.145 | -0.031 |
| $\mathrm{r}(\mathrm{P}-\mathrm{Ph})$ | 1.856 | 1.836 | -0.020 | 1.850 | 1.817 | -0.033 |
| $\mathrm{r}\left(\mathrm{P}-\mathrm{CH}_{2}\right)$ | 1.882 | 1.867 | -0.015 | 1.864 | 1.827 | -0.037 |
| $\alpha(\mathrm{PhPPh})$ | 100.81 | 104.74 | 3.93 | 98.66 | 104.14 | 5.49 |

Table S7. Experimental and computational average bond lengths $(\AA)$ and angles (degrees) for reduced and oxidized $\left[\mathrm{FeCp}{ }^{*}\left(\mathrm{C} \equiv \mathrm{C}-\mathrm{C}_{6} \mathrm{H}_{4} \mathrm{NO}_{2}\right)(\right.$ dppe $\left.)\right]$, and changes upon oxidation.

|  | Calculated |  |  | Experimental |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | Reduced | Oxidized | Change | Reduced | Oxidized | Change |
| $\mathrm{r}\left(\mathrm{Fe}-\mathrm{Cp}^{*}\right)$ | 1.792 | 1.808 | 0.016 | 1.739 | 1.780 | 0.041 |
| $\mathrm{r}(\mathrm{Fe}-\mathrm{C}(\mathrm{CC}))$ | 1.890 | 1.892 | 0.002 | 1.876 | 1.893 | 0.017 |
| $\mathrm{r}(\mathrm{Fe}-\mathrm{P})$ | 2.260 | 2.350 | 0.090 | 2.188 | 2.271 | 0.083 |
| $\mathrm{r}(\mathrm{C}-\mathrm{C})$ | 1.237 | 1.231 | -0.006 | 1.220 | 1.214 | -0.005 |
| $\mathrm{r}(\mathrm{P}-\mathrm{Ph})$ | 1.856 | 1.842 | -0.014 | 1.840 | 1.823 | -0.017 |
| $\mathrm{r}\left(\mathrm{P}-\mathrm{CH}_{2}\right)$ | 1.879 | 1.869 | -0.010 | 1.848 | 1.843 | -0.005 |
| $\alpha(\mathrm{PhPPh})$ | 100.83 | 102.82 | 1.98 | 99.77 | 102.25 | 2.47 |

Table S8. Experimental and computational average bond lengths ( $\AA$ ) and angles (degrees) for reduced and oxidized [ $\mathrm{Fe}\left(\mathrm{P}^{\left.\left.\left(\mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{PPh}_{2}\right)_{3}\right)(\mathrm{C} \equiv \mathrm{C}-\mathrm{Ph})\right] \text {, and changes upon oxidation. The phosphorus atom that is not linked to any of the }}\right.$ phenyl groups is represented by $\mathrm{P}^{*}$.

|  | Calculated |  |  | Experimental |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | Reduced | Oxidized | Change | Reduced | Oxidized | Change |
| $\mathrm{r}(\mathrm{Fe}-\mathrm{C})$ | 1.925 | 1.907 | -0.018 | 1.916 | 1.882 | -0.034 |
| $\mathrm{r}(\mathrm{Fe}-\mathrm{P})$ | 2.277 | 2.414 | 0.136 | 2.204 | 2.302 | 0.098 |
| $\mathrm{r}\left(\mathrm{Fe}-\mathrm{P}^{*}\right)$ | 2.186 | 2.290 | 0.105 | 2.153 | 2.224 | 0.071 |
| $\mathrm{r}(\mathrm{C}-\mathrm{C})$ | 1.237 | 1.233 | -0.004 | 1.213 | 1.202 | -0.011 |
| $\mathrm{r}(\mathrm{P}-\mathrm{Ph})$ | 1.853 | 1.838 | -0.014 | 1.840 | 1.817 | -0.023 |
| $\mathrm{r}\left(\mathrm{P}-\mathrm{CH}_{2}\right)$ | 1.890 | 1.867 | -0.023 | 1.842 | 1.847 | 0.005 |
| $\mathrm{r}\left(\mathrm{P}^{*}-\mathrm{CH}_{2}\right)$ | 1.874 | 1.863 | -0.012 | 1.833 | 1.805 | -0.028 |
| $\alpha(\mathrm{PhPPh})$ | 100.06 | 104.36 | 4.29 | 99.22 | 103.00 | 3.79 |
| $\alpha\left(\mathrm{CH}_{2} \mathrm{P}^{*} \mathrm{CH}_{2}\right)$ | 105.59 | 105.86 | 0.28 | 105.71 | 105.38 | -0.33 |

Table S9. Experimental and computational average bond lengths ( $\AA$ ) and angles (degrees) for reduced and oxidized [ FeCp *(dppe)], and changes upon oxidation.

|  | Calculated |  |  | Experimental |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | Reduced | Oxidized | Change | Reduced | Oxidized | Change |
| $\mathrm{r}\left(\mathrm{Fe}-\mathrm{Cp}^{*}\right)$ | 1.808 | 1.820 | 0.012 | 1.722 | 1.768 | 0.046 |
| $\mathrm{r}(\mathrm{Fe}-\mathrm{P})$ | 2.186 | 2.317 | 0.130 | 2.137 | 2.246 | 0.110 |
| $\mathrm{r}(\mathrm{P}-\mathrm{Ph})$ | 1.859 | 1.833 | -0.026 | 1.844 | 1.806 | -0.038 |
| $\mathrm{r}\left(\mathrm{P}-\mathrm{CH}_{2}\right)$ | 1.887 | 1.875 | -0.012 | 1.855 | 1.830 | -0.025 |
| $\alpha(\mathrm{PhPPh})$ | 101.65 | 106.04 | 4.39 | 100.40 | 104.45 | 4.05 |

Table S10. Experimental and computational average bond lengths ( $\AA$ ) and angles (degrees) for reduced and oxidized $\left[\mathrm{Cp}^{*} \mathrm{MoCl}_{2}\left(\mathrm{PMe}_{2} \mathrm{Ph}\right)_{2}\right]$, and changes upon oxidation. $\alpha(\mathrm{MePPh})$ is the average of the $4 \mathrm{C}(\mathrm{Me})-\mathrm{P}-\mathrm{C}(\mathrm{Ph})$ angles.

|  | Calculated |  |  | Experimental |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | Reduced | Oxidized | Change | Reduced | Oxidized | Change |
| $\mathrm{r}(\mathrm{Mo}-\mathrm{Cl})$ | 2.551 | 2.433 | -0.118 | 2.480 | 2.383 | -0.097 |
| $\mathrm{r}\left(\mathrm{Mo}-\mathrm{Cp}^{*}\right)$ | 2.023 | 2.087 | 0.064 | 1.966 | 2.034 | 0.068 |
| $\mathrm{r}(\mathrm{Mo}-\mathrm{P})$ | 2.573 | 2.625 | 0.051 | 2.527 | 2.566 | 0.039 |
| $\mathrm{r}(\mathrm{P}-\mathrm{Me})$ | 1.851 | 1.843 | -0.008 | 1.817 | 1.804 | -0.014 |
| $\mathrm{r}(\mathrm{P}-\mathrm{Ph})$ | 1.844 | 1.832 | -0.012 | 1.823 | 1.811 | -0.012 |
| $\alpha(\mathrm{MePMe})$ | 101.20 | 102.54 | 1.34 | 101.17 | 102.39 | 1.22 |
| $\alpha(\mathrm{MePPh})$ | 102.85 | 104.81 | 1.96 | 102.23 | 104.62 | 2.39 |

Table S11. Experimental and computational average bond lengths ( $\AA$ ) and angles (degrees) for reduced and oxidized $\left[\eta^{7}-\left(\mathrm{C}_{7} \mathrm{H}_{7}\right) \mathrm{Mo}(\mathrm{C} \equiv \mathrm{CPh})(\right.$ dppe $\left.)\right]$, and changes upon oxidation.

|  | Calculated |  |  | Experimental |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | Reduced | Oxidized | Change | Reduced | Oxidized | Change |
| $\mathrm{r}\left(\mathrm{Mo}-\eta^{7}\right)$ | 1.672 | 1.682 | 0.010 | 1.636 | 1.624 | -0.012 |
| $\mathrm{r}(\mathrm{Mo}-\mathrm{C}(\mathrm{CC}))$ | 2.131 | 2.075 | -0.056 | 2.137 | 2.067 | -0.070 |
| $\mathrm{r}(\mathrm{Mo}-\mathrm{P})$ | 2.502 | 2.567 | 0.065 | 2.472 | 2.533 | 0.061 |
| $\mathrm{r}(\mathrm{C}-\mathrm{C})$ | 1.235 | 1.237 | 0.001 | 1.205 | 1.195 | -0.011 |
| $\mathrm{r}(\mathrm{P}-\mathrm{Ph})$ | 1.853 | 1.841 | -0.012 | 1.838 | 1.817 | 0.021 |
| $\mathrm{r}\left(\mathrm{PCH}_{2}\right)$ | 1.878 | 1.873 | -0.006 | 1.845 | 1.829 | -0.016 |
| $\alpha(\mathrm{PhPPh})$ | 101.19 | 103.09 | 1.90 | 100.42 | 102.00 | 1.59 |

Table S12. Computational average bond lengths $(\AA)$ and angles (degrees) for reduced and oxidized $\left[\mathrm{Cr}(\mathrm{CO})_{5} \mathrm{PH}_{3}\right]$, and changes upon oxidation. $\mathrm{r}\left(\mathrm{Cr}-\mathrm{C}_{c i s}\right)$ refers to the average of the four cis $\mathrm{Cr}-\mathrm{C}$ distances, $\mathrm{r}\left(\mathrm{C}_{c i s}-\mathrm{O}\right)$ refers to the average of the four cis $\mathrm{C}-\mathrm{O}$ distances.

|  | Reduced | Oxidized | Change |
| :---: | :---: | :---: | :---: |
| $\mathrm{r}\left(\mathrm{Cr}-\mathrm{C}_{\text {cis }}\right)$ | 1.912 | 1.975 | 0.063 |
| $\mathrm{r}\left(\mathrm{C}_{\text {cis }}-\mathrm{O}\right)$ | 1.153 | 1.140 | -0.014 |
| $\mathrm{r}\left(\mathrm{Cr}-\mathrm{C}_{\text {trans }}\right)$ | 1.880 | 1.983 | 0.104 |
| $\mathrm{r}\left(\mathrm{C}_{\text {trans }}-\mathrm{O}\right)$ | 1.155 | 1.137 | -0.018 |
| $\mathrm{r}(\mathrm{Cr}-\mathrm{P})$ | 2.400 | 2.493 | 0.094 |
| $\mathrm{r}(\mathrm{P}-\mathrm{H})$ | 1.416 | 1.409 | -0.007 |
| $\alpha(\mathrm{HPH})$ | 96.83 | 99.89 | 3.06 |

Table S13. Computational average bond lengths $(\AA)$ and angles (degrees) for reduced and oxidized $\left[\mathrm{Mo}(\mathrm{CO})_{5} \mathrm{PH}_{3}\right]$, and changes upon oxidation. $\mathrm{r}\left(\mathrm{Mo}-\mathrm{C}_{c i s}\right)$ refers to the average of the four cis $\mathrm{Mo}-\mathrm{C}$ distances, $\mathrm{r}\left(\mathrm{C}_{c i s}-\mathrm{O}\right)$ refers to the average of the four cis $\mathrm{C}-\mathrm{O}$ distances.

|  | Reduced | Oxidized | Change |
| :---: | :---: | :---: | :---: |
| $\mathrm{r}\left(\mathrm{Mo}-\mathrm{C}_{\text {cis }}\right)$ | 2.057 | 2.118 | 0.043 |
| $\mathrm{r}\left(\mathrm{C}_{\text {cis }}-\mathrm{O}\right)$ | 1.153 | 1.140 | -0.012 |
| $\mathrm{r}\left(\mathrm{Mo}-\mathrm{C}_{\text {trans }}\right)$ | 2.035 | 2.117 | 0.082 |
| $\mathrm{r}\left(\mathrm{C}_{\text {trans }}-\mathrm{O}\right)$ | 1.155 | 1.139 | -0.016 |
| $\mathrm{r}(\mathrm{Mo}-\mathrm{P})$ | 2.547 | 2.604 | 0.058 |
| $\mathrm{r}(\mathrm{P}-\mathrm{H})$ | 1.416 | 1.409 | -0.006 |
| $\alpha(\mathrm{HPH})$ | 96.80 | 99.88 | 3.09 |

Table S14. Computational average bond lengths ( $\AA$ ) and angles (degrees) for reduced and oxidized $\left[\mathrm{Cr}(\mathrm{CO})_{5} \mathrm{NH}_{3}\right]$, and changes upon oxidation. $\mathrm{r}\left(\mathrm{Cr}-\mathrm{C}_{c i s}\right)$ refers to the average of the four cis $\mathrm{Cr}-\mathrm{C}$ distances, $\mathrm{r}\left(\mathrm{C}_{c i s}-\mathrm{O}\right)$ refers to the average of the four cis $\mathrm{C}-\mathrm{O}$ distances.

|  | Reduced | Oxidized | Change |
| :---: | :---: | :---: | :---: |
| $\mathrm{r}\left(\mathrm{Cr}-\mathrm{C}_{\text {cis }}\right)$ | 1.913 | 1.981 | 0.068 |
| $\mathrm{r}\left(\mathrm{C}_{\text {cis }}-\mathrm{O}\right)$ | 1.155 | 1.140 | -0.015 |
| $\mathrm{r}\left(\mathrm{Cr}-\mathrm{C}_{\text {trans }}\right)$ | 1.869 | 1.987 | 0.118 |
| $\mathrm{r}\left(\mathrm{C}_{\text {trans }}-\mathrm{O}\right)$ | 1.158 | 1.138 | -0.020 |
| $\mathrm{r}(\mathrm{Cr}-\mathrm{N})$ | 2.239 | 2.190 | -0.050 |
| $\mathrm{r}(\mathrm{N}-\mathrm{H})$ | 1.019 | 1.022 | 0.003 |
| $\alpha(\mathrm{HNH})$ | 106.76 | 105.75 | -1.01 |

Table S15. Computational average bond lengths $(\AA)$ and angles (degrees) for reduced and oxidized $\left[\mathrm{Mo}(\mathrm{CO})_{5} \mathrm{NH}_{3}\right]$, and changes upon oxidation. $\mathrm{r}\left(\mathrm{Mo}-\mathrm{C}_{c i s}\right)$ refers to the average of the four cis $\mathrm{Mo}-\mathrm{C}$ distances, $\mathrm{r}\left(\mathrm{C}_{c i s}-\mathrm{O}\right)$ refers to the average of the four cis $\mathrm{C}-\mathrm{O}$ distances.

|  | Reduced | Oxidized | Change |
| :---: | :---: | :---: | :---: |
| $\mathrm{r}\left(\mathrm{Mo}-\mathrm{C}_{\text {cis }}\right)$ | 2.072 | 2.119 | 0.046 |
| $\mathrm{r}\left(\mathrm{C}_{\text {cis }}-\mathrm{O}\right)$ | 1.154 | 1.141 | -0.014 |
| $\mathrm{r}\left(\mathrm{Mo}-\mathrm{C}_{\text {trans }}\right)$ | 2.010 | 2.100 | 0.090 |
| $\mathrm{r}\left(\mathrm{C}_{\text {trans }}-\mathrm{O}\right)$ | 1.159 | 1.141 | -0.018 |
| $\mathrm{r}(\mathrm{Mo}-\mathrm{P})$ | 2.385 | 2.328 | -0.057 |
| $\mathrm{r}(\mathrm{P}-\mathrm{H})$ | 1.019 | 1.022 | 0.004 |
| $\alpha(\mathrm{HNH})$ | 106.77 | 105.78 | -0.99 |

Table S16. Computational average bond lengths $(\AA)$ and angles (degrees) for reduced and oxidized $\left[\mathrm{Cr}(\mathrm{CO})_{5} \mathrm{PMe}_{3}\right]$, and changes upon oxidation. $\mathrm{r}\left(\mathrm{Cr}-\mathrm{C}_{c i s}\right)$ refers to the average of the four cis $\mathrm{Cr}-\mathrm{C}$ distances, $\mathrm{r}\left(\mathrm{C}_{\mathrm{cis}}-\mathrm{O}\right)$ refers to the average of the four cis $\mathrm{C}-\mathrm{O}$ distances.

|  | Reduced | Oxidized | Change |
| :---: | :---: | :---: | :---: |
| $\mathrm{r}\left(\mathrm{Cr}-\mathrm{C}_{\text {cis }}\right)$ | 1.906 | 1.963 | 0.057 |
| $\mathrm{r}\left(\mathrm{C}_{\text {cis }}-\mathrm{O}\right)$ | 1.156 | 1.142 | -0.014 |
| $\mathrm{r}\left(\mathrm{Cr}-\mathrm{C}_{\text {trans }}\right)$ | 1.878 | 1.980 | 0.102 |
| $\mathrm{r}\left(\mathrm{C}_{\text {trans }}-\mathrm{O}\right)$ | 1.156 | 1.138 | -0.018 |
| $\mathrm{r}(\mathrm{Cr}-\mathrm{P})$ | 2.426 | 2.500 | 0.074 |
| $\mathrm{r}(\mathrm{P}-\mathrm{C})$ | 1.850 | 1.843 | -0.008 |
| $\alpha(\mathrm{CPC})$ | 101.60 | 104.00 | 2.04 |

Table S17. Computational average bond lengths ( $\AA$ ) and angles (degrees) for reduced and oxidized $\left[\mathrm{Mo}(\mathrm{CO})_{5} \mathrm{PMe}_{3}\right]$, and changes upon oxidation. $\mathrm{r}\left(\mathrm{Mo}-\mathrm{C}_{c i s}\right)$ refers to the average of the four cis Mo-C distances, $\mathrm{r}\left(\mathrm{C}_{\mathrm{cis}}-\mathrm{O}\right)$ refers to the average of the four cis $\mathrm{C}-\mathrm{O}$ distances.

|  | Reduced | Oxidized | Change |
| :---: | :---: | :---: | :---: |
| $\mathrm{r}\left(\mathrm{Mo}-\mathrm{C}_{\text {cis }}\right)$ | 2.071 | 2.110 | 0.040 |
| $\mathrm{r}\left(\mathrm{C}_{\text {cis }}-\mathrm{O}\right)$ | 1.155 | 1.143 | -0.012 |
| $\mathrm{r}\left(\mathrm{Mo}-\mathrm{C}_{\text {trans }}\right)$ | 2.039 | 2.130 | 0.091 |
| $\mathrm{r}\left(\mathrm{C}_{\text {trans }}-\mathrm{O}\right)$ | 1.156 | 1.140 | -0.016 |
| $\mathrm{r}(\mathrm{Mo}-\mathrm{P})$ | 2.569 | 2.616 | 0.047 |
| $\mathrm{r}(\mathrm{P}-\mathrm{C})$ | 1.851 | 1.843 | -0.008 |
| $\alpha(\mathrm{CPC})$ | 101.77 | 103.90 | 2.13 |

