**SI: σ → σ* Transitions in Mn₂(CO)₈L₂ complexes (L = P-donor ligands):**

**π-acidity and oxygen pendant group effects in phosphite ligands**

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**Table S1** Results of regression analyses of values of $h\nu(\sigma \rightarrow \sigma^*)$ for Mn₂(CO)₈L₂ complexes.

<table>
<thead>
<tr>
<th>#</th>
<th>Obs</th>
<th>α (kJ mol⁻¹)</th>
<th>β</th>
<th>$\gamma$ (kJ mol⁻¹ deg⁻¹)</th>
<th>δ (kJ mol⁻¹)</th>
<th>φ</th>
<th>Ω (kJ mol⁻¹)</th>
<th>σ(hv)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>e</td>
<td>14</td>
<td>329(2)</td>
<td>-0.296(22)</td>
<td>-3.44(35)</td>
<td>-</td>
<td>13.4(1)</td>
<td>0.776</td>
<td>0.990</td>
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<tr>
<td>d</td>
<td>17</td>
<td>332(1)</td>
<td>0.104(25)</td>
<td>-3.51(34)</td>
<td>-1.09(18)</td>
<td>8.21(153)</td>
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<td>0.147(36)</td>
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<td>9.43(253)</td>
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</tr>
<tr>
<td>f</td>
<td>19</td>
<td>329(3)</td>
<td>0.096(58)</td>
<td>-3.66(86)</td>
<td>-0.702(313)</td>
<td>8.60(149)</td>
<td>1.26</td>
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<td>g</td>
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<td>329(1)</td>
<td>-0.282(31)</td>
<td>-3.55(26)</td>
<td>-0.559(166)</td>
<td>8.39(136)</td>
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<td>329(1)</td>
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<td>-</td>
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<td>12.05(44)</td>
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<td>0.977</td>
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<td>i</td>
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<td>329(1)</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<td>1.44</td>
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<td>j</td>
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<td>323(2)</td>
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<td>-2.44(52)</td>
<td>8.12(95)</td>
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<td>k</td>
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<td>-12.71(70)</td>
<td>1.96</td>
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*a* Number of observations. *b* All cone angles are referenced to 130°. *c* Non π-acceptor phosphines. *d* Including P(OR)₃ ligands. ($θ_h = 130°$). *e* Including P(OR)₃ ligands and PPh₃₋ₓ(OMe)ₓ ($θ_h = 130$) (This shows that the phosphinites are the cause of a poorer fit). *f* Including P(OR)₃ ligands and PPh₃₋ₓ(OMe)ₓ, but with no $θ_h$ (comparison with e shows the improvement resulting from the introduction of a steric threshold). *g* Including P(OR)₃ ligands and PPh₃₋ₓ(OMe)ₓ ($θ_h = 130$), the value of $β$ is taken as 0.109; see h). *h* Including P(OR)₃ ligands and PPh₃₋ₓ(OMe)ₓ, ($θ_h = 130$), values for the coefficients $β = 0.109, γ = -0.296, δ = -3.44$ are taken from h). *i* Including P(OR)₃ ligands and PPh₃₋ₓ(OMe)ₓ ($θ_h = 130$), values for the coefficient $φ = -1.06$ is taken from Table 2, #3). *j* Not including $φ$ in analysis. *k* Including P(OR)₃ ligands and PPh₃₋ₓ(OMe)ₓ ($θ_h = 0$, values for the coefficient $φ = -1.06$ is taken from Table 2, #3). *l* Including P(OR)₃ ligands and PPh₃₋ₓ(OMe)ₓ ($θ_h = 130$, values for the coefficient $φ = -1.06$ is taken from Table 2, #3).
Table S2 The influence of each individual effect on the $\sigma \rightarrow \sigma^*$ energies.

<table>
<thead>
<tr>
<th>Name</th>
<th>$\nu$ (kJ mol$^{-1}$)</th>
<th>$\alpha$ (kJ mol$^{-1}$)</th>
<th>$\beta(pK_a')$ (kJ mol$^{-1}$)</th>
<th>$\gamma(\theta - 130)$ (kJ mol$^{-1}$)</th>
<th>$\delta(E_{av})$ (kJ mol$^{-1}$)</th>
<th>$\phi(pK_a'p)$ (kJ mol$^{-1}$)</th>
<th>$\Omega(E_{ox})$ (kJ mol$^{-1}$)</th>
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<td>P($p$-CF$_3$Ph)$_3$</td>
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<td>327</td>
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<td>327</td>
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<td>-9.19</td>
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<td>P($p$-MePh)$_3$</td>
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<td>327</td>
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<td>-9.19</td>
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<td>P($p$-MeOPh)$_3$</td>
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SI: $\sigma \rightarrow \sigma^*$ Transitions in Mn$_2$(CO)$_8$L$_2$ complexes...
Fig. S1 Steric profile including π and oxygen effects. Non-π-acids (Solid diamonds), phosphites and phosphinites (Open circles).

SI: σ → σ* Transitions in Mn₂(CO)₈L₂ complexes…
**Fig. S2** Colour version of Fig 6. Contributions of various terms to $hn$ for complexes with each individual ligand. $\beta(pK_a')$ (red fill), $\gamma(\theta - 130)$ (no fill), $\delta(E_{ar})$ (green fill), $\phi(pK_a'\pi)$ (dark blue fill), $\Omega(E_{ox})$ (Light blue fill).

SI: $\sigma \rightarrow \sigma^*$ Transitions in Mn$_2$(CO)$_8$L$_2$ complexes…