Supporting Information for

The influence of reversible trianionic pincer OCO\(^{3-}\) \(\mu\)-oxo Cr\(^{IV}\) dimer formation ([Cr\(^{IV}\)]\(_2\)(\(\mu\)-O)) and donor ligands in oxygen-atom-transfer (OAT)†

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- ['BuOCO]Cr(O)(THF) (2) reduction:
  - Variable Temperature
  - Solvent Effect: MeCN, CH\(_2\)Cl\(_2\), and THF

- {['BuOCO]Cr\(^{IV}\)(THF)}\(_2\)(\(\mu\)-O) (3) reduction:
  - Proposed mechanism
  - Rate law derivation
  - \(\ln[3]\) vs time
  - \(2[3] – [Cr]_{tot}\ln[3]\) vs time

- IR of ['BuOCO]Cr\(^{V}\)(O)(CH\(_2\)PPh\(_3\)) (4)
- \(^1\)H NMR of ['BuOCO]Cr\(^{V}\)(O)(CH\(_2\)PPh\(_3\)) (4)
- UV-vis of ['BuOCO]Cr\(^{V}\)(O)(CH\(_2\)PPh\(_3\)) (4)
- \(^1\)H NMR of 3 with OPPh\(_3\)
- EPR of 2 and 2a with MeCN
Table S1. Reduction of 2. Variable Temperature vs. \( k_{\text{obs}} \) (M/s)

<table>
<thead>
<tr>
<th>Temp. (K)</th>
<th>1/T (K(^{-1}))</th>
<th>k</th>
<th>k</th>
<th>k</th>
<th>Avg. k</th>
<th>ln(k/T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>273.15</td>
<td>0.003661</td>
<td>14.2</td>
<td>15.5</td>
<td>13.0</td>
<td>14.2</td>
<td>-2.95</td>
</tr>
<tr>
<td>283.15</td>
<td>0.003532</td>
<td>31.7</td>
<td>36.4</td>
<td>37.0</td>
<td>35.1</td>
<td>-2.08</td>
</tr>
<tr>
<td>293.15</td>
<td>0.003411</td>
<td>59.2</td>
<td>55.4</td>
<td>49.6</td>
<td>54.7</td>
<td>-1.68</td>
</tr>
<tr>
<td>313.15</td>
<td>0.003193</td>
<td>159</td>
<td>157</td>
<td>167</td>
<td>161</td>
<td>-0.665</td>
</tr>
</tbody>
</table>

Figure S1. Eyring plot for the OAT from 2a (0.186 mM) to PPh\(_3\) (1.59 mM) in THF between 0 – 40 °C. Intercept (b) = -2(2); slope (m) = -4.6(5) x 10\(^3\). Calculated \( \Delta S^\ddagger = -18(3) \) cal/mol; \( \Delta H^\ddagger = 9.4(8) \) kcal/mol.

Figure S2. [2] vs time in MeCN, THF, and DCM/THF.
Scheme S1. Mechanism of OAT from 3.

\[
\frac{d[5]}{dt} = k_2 [PPh_3][2]_{ss} \quad (S1)
\]

\[
\Delta[2]_{ss} = 0 = k_1[3] - k_{-1}[5][2] - k_2[2][PPh_3] \quad (S2)
\]

\[
[2]_{ss} = \frac{k_1[3]}{k_{-1}[5] + k_2[PPh_3]} \quad (S3)
\]

\[
\frac{d[5]}{dt} = \frac{k_1 k_2[PPh_3][3]}{k_{-1}[5] + k_2[PPh_3]} \quad (S4)
\]

*At late reaction times assume: \( k_1[5] \gg k_2[PPh_3] \)

\[
\frac{d[5]}{dt} = \frac{k_1 k_2[PPh_3][3]}{k_{-1}[5]} \quad (S5)
\]

*Mass-balance equation*

\[
[Cr]_{tot} = 2[3] + [5] + [2] \quad (S6)
\]

Since \([2] = [2]_{ss} \approx 0\)

\[
[Cr]_{tot} = 2[3] + [5] \quad (S7)
\]

\[
\frac{d[5]}{dt} = -\frac{d[3]}{dt} = \frac{k_1 k_2[PPh_3]}{k_{-1}([Cr]_{tot} - 2[3])} \quad (S8)
\]

\[
\frac{-[Cr]_{tot} + 2[3]}{[3]} \frac{d[3]}{dt} = \frac{k_1 k_2[PPh_3]}{k_{-1}} dt \quad (S9)
\]
**Integrated rate law**

\[-[Cr]_\text{tot} \ln[3] + 2[3] = \frac{k_1 k_2 [\text{PPh}_3]}{k_{-1}} t \]  
(S10)

*At early reaction times assume: \(k_2 [\text{PPh}_3] \gg k_{-1} [5]\)*

\[\frac{d[5]}{dt} = -\frac{d[3]}{dt} = k_1[3] \]  
(S11)

**Figure S2.** Averaged plots of \(\ln[3]\) vs time between reaction times 0-150 s for \([3] = 0.78 \times 10^{-4} \text{ M}\) and \(1.56 \times 10^{-4} \text{ M}\) and for 0-300 s for \([3] = 3.31 \times 10^{-4} \text{ M}\) upon addition of \(\text{PPh}_3\) (1.1 \times 10^{-3} \text{ M}).

**Table S2.** \(k_1\) (s\(^{-1}\)) values obtained from the slope of the \(\ln[3]\) vs time (0 - 150 s) plots for [3] (0.31, 0.16, and 0.08 mM); \(\text{PPh}_3\) (1.10 mM) in \(\text{CH}_2\text{Cl}_2\) (22°C).

<table>
<thead>
<tr>
<th>([3] \times 10^{-4})</th>
<th>(k_1 \times 10^4)</th>
<th>(k_1 \times 10^4)</th>
<th>(k_1 \times 10^4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.78</td>
<td>26.1</td>
<td>21.9</td>
<td>22.7</td>
</tr>
<tr>
<td>1.56</td>
<td>14.0</td>
<td>14.4</td>
<td>13.4</td>
</tr>
<tr>
<td>3.31</td>
<td>9.14</td>
<td>7.81</td>
<td>8.19</td>
</tr>
</tbody>
</table>
Figure S3. The average $2[3] \text{ [Cr]}_{\text{tot}}\ln[3]$ vs time upon the addition of PPh$_3$ ($1.1 \times 10^{-3}$ M) into a solution of 3 (0.78, 1.56, and 3.31 ($\times 10^{-4}$) M) in CH$_2$Cl$_2$.

Table S3. Slopes obtained from the plot of the [Cr]$_{\text{tot}}\ln[3] - 2[3]$ vs time for [3] (0.78, and 1.56, 3.11 ($\times 10^{-4}$) M); PPh$_3$ ($1.10 \times 10^{-3}$ M) in CH$_2$Cl$_2$ (22 °C).

<table>
<thead>
<tr>
<th>[3] x10$^{-4}$</th>
<th>m x10$^8$</th>
<th>m x10$^8$</th>
<th>m x10$^8$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.78</td>
<td>3.10</td>
<td>3.51</td>
<td>3.59</td>
</tr>
<tr>
<td>1.56</td>
<td>3.14</td>
<td>2.42</td>
<td>2.29</td>
</tr>
<tr>
<td>3.31</td>
<td>9.14</td>
<td>7.81</td>
<td>8.19</td>
</tr>
</tbody>
</table>
Supporting Information for [tBuOCO]CrV(O(CH2PPh3) (4).

Figure S4. IR spectrum of [tBuOCO]CrV(O(CH2PPh3) (4) (thin-film).

Figure S5. 1H NMR of [tBuOCO]CrV(O(CH2PPh3) (4) in C6D6 with 0.01 mL THF-d8.
Figure S6. UV-vis of 4 in THF (0.057 mM, red; 0.113 mM, blue).
**Figure S7.** $^1$H NMR of 3 (2.43 x10$^{-5}$ mol) in C$_6$D$_6$ (red) and with OPPh$_3$ (5.82 x10$^{-5}$) in C$_6$D$_6$ (blue).

**Figure S8.** Solution EPR spectra of a mixture of 2 and 2a (5.0 x10$^{-3}$ M) in toluene (blue) and a 2 and 2a solution (1.6 x10$^{-3}$ M) in toluene (blue) after addition of 6 equivalents of MeCN (red)