## Supporting Information for The influence of reversible trianionic pincer $OCO^{3-} \mu$ -oxo $Cr^{IV}$ dimer formation ([ $Cr^{IV}$ ]<sub>2</sub>( $\mu$ -O)) and donor ligands in oxygen-atomtransfer (OAT)<sup>†</sup>

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Index	Page
[ <sup>t</sup> BuOCO]Cr(O)(THF) ( <b>2</b> ) reduction:	
Variable Temperature	S2
Solvent Effect: MeCN, CH <sub>2</sub> Cl <sub>2</sub> , and THF	S2
${[^{t}BuOCO]Cr^{IV}(THF)}_{2}(\mu-O)(3)$ reduction:	
Proposed mechanism	S3
Rate law derivation	S3-S4
ln[ <b>3</b> ] vs time	S4
$2[3] - [Cr]_{tot} \ln[3]$ vs time	S5
IR of $[^{t}BuOCO]Cr^{V}(O)(CH_{2}PPh_{3})$ (4)	S6
<sup>1</sup> H NMR of [ <sup><i>t</i></sup> BuOCO]Cr <sup>V</sup> (O)(CH <sub>2</sub> PPh <sub>3</sub> ) (4)	S6
UV-vis of [ <sup>t</sup> BuOCO]Cr <sup>V</sup> (O)(CH <sub>2</sub> PPh <sub>3</sub> ) (4)	S7
<sup>1</sup> H NMR of <b>3</b> with OPPh <sub>3</sub>	S8
EPR of <b>2</b> and <b>2a</b> with MeCN	S8

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

**Table S1.** Reduction of **2**. Variable Temperature vs. k<sub>obs</sub> (M/s)



**Figure S1.** Eyring plot for the OAT from **2a** (0.186 mM) to PPh<sub>3</sub> (1.59 mM) in THF between 0 – 40 °C. Intercept (b) = -2(2); slope (m) = -4.6(5) x10<sup>3</sup>. 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.

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

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

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

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

At late reaction times assume: k<sub>-1</sub>[**5**]>>k<sub>2</sub>[PPh<sub>3</sub>]

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

Mass-balance equation

$$[Cr]_{tot} = 2[3] + [5] + [2] \quad (S6)$$
  
Since  $[2] = [2]_{ss} \approx 0$   
$$[Cr]_{tot} = 2[3] + [5] \quad (S7)$$
  
$$\frac{d[5]}{dt} = -\frac{d[3]}{dt} = \frac{k_1 k_2 [3] [PPh_3]}{k_{-1} ([Cr]_{tot} - 2[3])} \quad (S8)$$

$$\frac{-[Cr]_{tot}+2[3]}{[3]}d[\mathbf{3}] = \frac{k_1 k_2 [PPh_3]}{k_{-1}}dt$$
(S9)

Integrated rate law

$$-[Cr]_{tot}\ln[3] + 2[3] = \frac{k_1 k_2 [PPh_3]}{k_{-1}} t \quad (S10)$$

At early reaction times assume:  $k_2[PPh_3] \gg k_{-1}[5]$ 

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



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

**Table S2.**  $k_1$  (s<sup>-1</sup>) 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); PPh<sub>3</sub> (1.10 mM) in CH<sub>2</sub>Cl<sub>2</sub> (22°C).

<b>[3</b> ] x10 <sup>4</sup>	$k_1x10^4$	$k_1x10^4$	$k_1 \ x 10^4$
0.78	26.1	21.9	22.7
1.56	14.0	14.4	13.4
3.31	9.14	7.81	8.19



**Figure S3.** The average  $2[3] - [Cr]_{tot}ln[3]$  vs time upon the addition of PPh<sub>3</sub> (1.1 x10<sup>-3</sup> M) into a solution of **3** (0.78, 1.56, and 3.31 (x10<sup>-4</sup>) M) in CH<sub>2</sub>Cl<sub>2</sub>.

**Table S3.** Slopes obtained from the plot of the  $[Cr]_{tot}ln[3] - 2[3]$  vs time for [3] (0.78, and 1.56, 3.11 (x10<sup>-4</sup>) M); PPh<sub>3</sub> (1.10 x10<sup>-3</sup> M) in CH<sub>2</sub>Cl<sub>2</sub> (22 °C).

$[3] \times 10^4$	m x10 <sup>8</sup>	m x10 <sup>8</sup>	m x10 <sup>8</sup>
0.78	3.10	3.51	3.59
1.56	3.14	2.42	2.29
3.31	9.14	7.81	8.19



## Supporting Information for [<sup>t</sup>BuOCO]Cr<sup>V</sup>O(CH<sub>2</sub>PPh<sub>3</sub>) (4).



							6/9/2010 10:51:48 AM
Acquisition Time (sec)	1.2800	Comment	mment 1H Standard Parameters			Date	Jun 8 2010
Date Stamp	Jun 8 2010	File Name	C:\Users\Matth	ew\Documents\(OCO)Cr(C	)(CH2PPh3)\100	608A.fid\fid	
Frequency (MHz)	300.15	Nucleus	1H	Number of Transients	16	Original Points Count	64000
Points Count	65536	Pulse Sequence	s2pul	Receiver Gain	22.00	Solvent	Benzene
Spectrum Offset (Hz)	2061.7407	Spectrum Type	STANDARD	Sweep Width (Hz)	50000.00	Temperature (degree C	25.000
1.0 1.0 1.0 1.0 1.0 1.0 1.0 1.0	Vertic	alScaleFactor = 1		7 6 5	Ph <sub>3</sub> P		
Chemical Shift (ppm)							

**Figure S5.** <sup>1</sup>H NMR of [<sup>*t*</sup>BuOCO]Cr<sup>V</sup>O(CH<sub>2</sub>PPh<sub>3</sub>) (**4**) in C<sub>6</sub>D<sub>6</sub> with 0.01 mL THF- $d_8$ .



Figure S6. UV-vis of 4 in THF (0.057 mM, red; 0.113 mM, blue).



**Figure S7.** <sup>1</sup>H NMR of **3** (2.43  $\times 10^{-5}$  mol) in C<sub>6</sub>D<sub>6</sub> (red) and with OPPh<sub>3</sub> (5.82  $\times 10^{-5}$ ) in C<sub>6</sub>D<sub>6</sub> (blue).



3.53E+03 3.55E+03 3.57E+03 3.59E+03

**Figure S8.** Solution EPR spectra of a mixture of **2** and **2a** (5.0 x10<sup>-3</sup> M) in toluene (blue) and a **2** and **2a** solution (1.6 x10<sup>-3</sup> M) in toluene (blue) after addition of 6 equivalents of MeCN (red)