Supplementary materials for

Title: Mechanism and Activation Parameters for the κ*O* to $\mu,\kappa^2 O,O'$ Bonding Mode of the Maleic Acid Ligand on an Osmium Carbonyl Cluster

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Table S1. First order rate constants (k_{obs}) for conversion of **2** to **3**.
For a 1st order reaction,

$$\ln[A]_t = -kt + \ln[A]_0 \qquad (1)$$

where, $[A]_t$ is the concentration of **A** at any given time, t (in sec), and $[A]_0$ is the initial concentration. [A] can be replaced by $[I_A/(I_A + I_B)]$ and a linear plot of $\ln\{[I_A/(I_A + I_B)]\}$ vs time yields the rate constant as the gradient, where I_A is the integral of the hydride resonance of A and I_B is that for B. The first order rate constants obtained at different temperatures are:

entry	Temp (K)	$10^6\ k_{obsd}$ (s^{-1})
1	298	1.9 ± 0.1
2	308	9.5 ± 0.4
3	313	20.5 ± 0.1
4	318	40.6 ± 0.2
5	323	67.3 ± 0.3
6	328	121.9 ± 0.2

Figure S1. Plot of R ln($h.k.T/k_B$) vs (1/T).

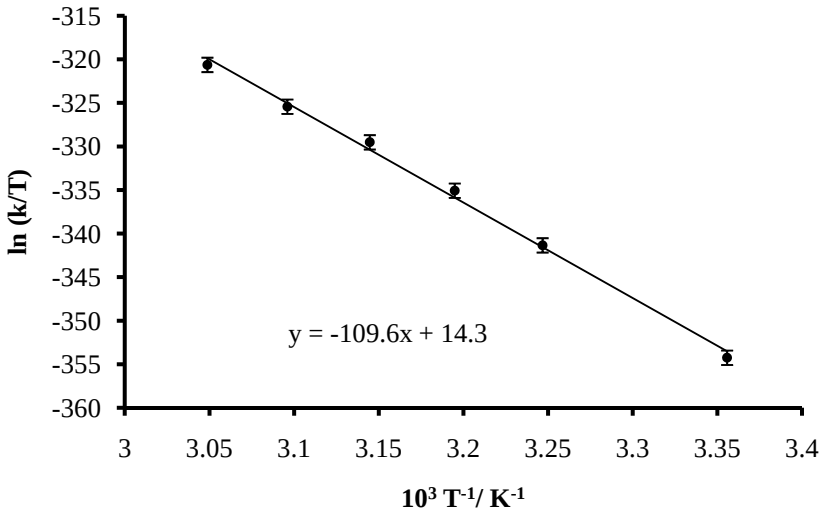
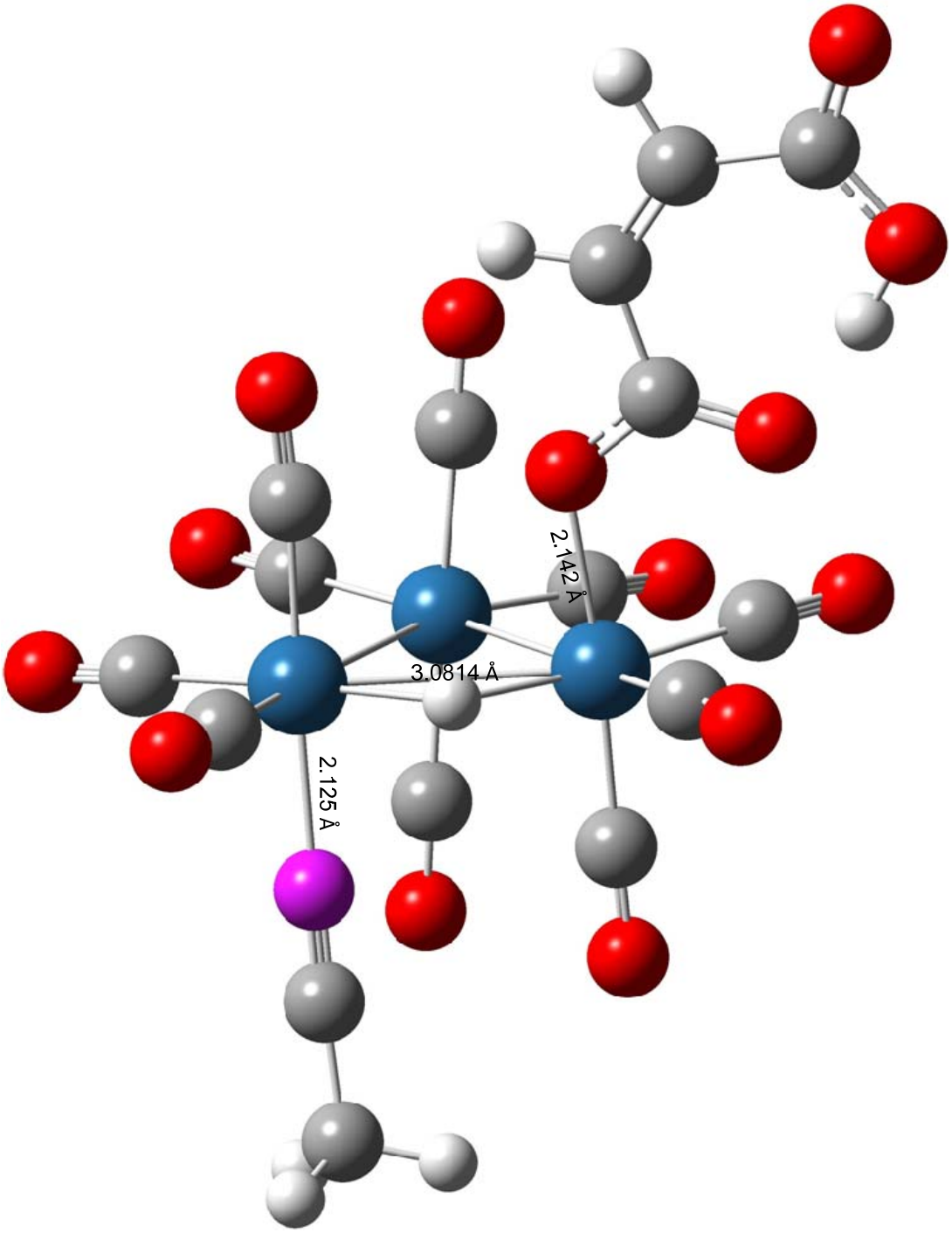


Table S2. Crystal and refinement data for clusters **2** and **3**.

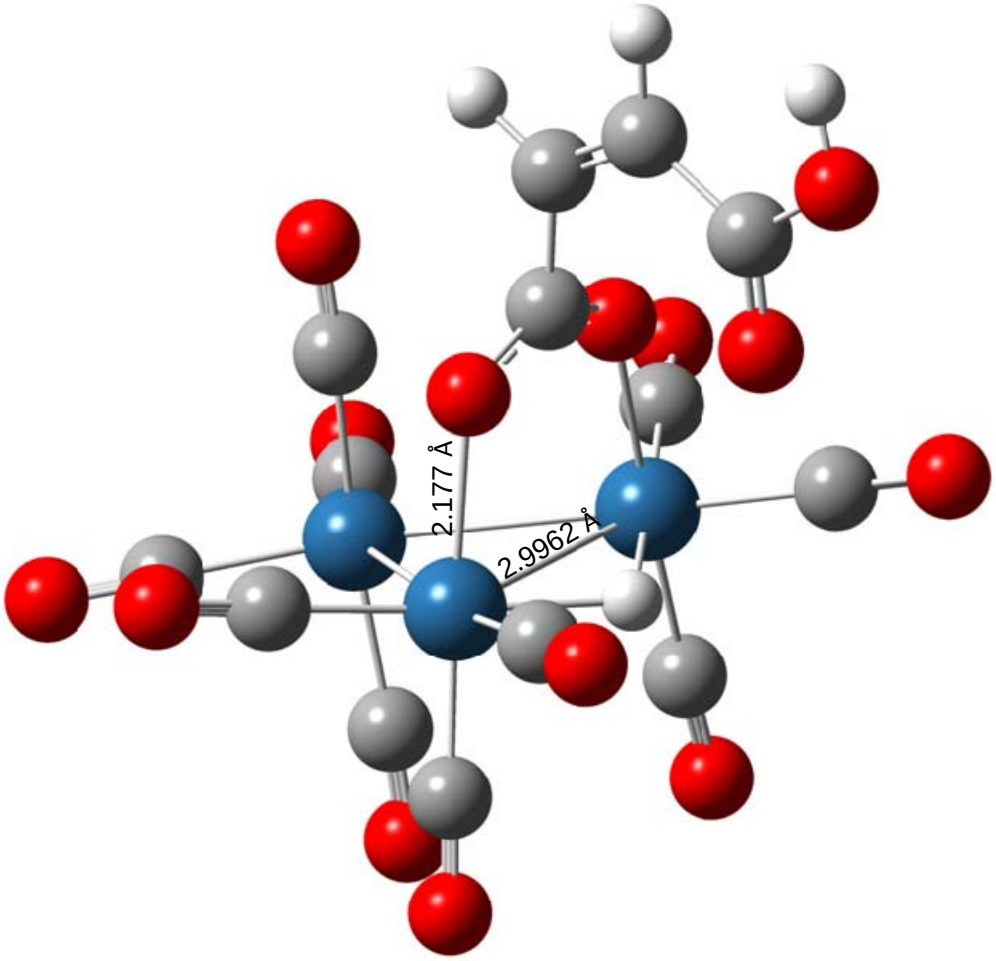
	2	**3**
empirical formula	C16 H7 N O14 Os3.$CHCl_3$	C14 H4 O14 Os3
formula weight	1127.19	966.77
crystal system	Triclinic	Triclinic
Space group	P $\bar{1}$	P $\bar{1}$
a (Å)	8.5814(7)	7.8243(7)
b (Å)	12.6977(10)	7.9415(7)
c (Å)	13.1890(11)	17.3870(15)
α (deg)	70.675(4)	100.792(4)
ß (deg)	72.549(4)	90.777(4)
γ (deg)	82.261(4)	108.646(4)
V ($Å^3$)	1292.73(18)	1002.42(15)
Z	2	2
ρ_{calc} (Mg/m^3)	2.896	3.203
μ (mm^{-1})	15.086	19.038
F(000)	1016	856
Reflections collected	43939	32778
Max. and min. transmission	0.5837 and 0.0649	0.3946 and 0.0489
Data / restraints / parameters	7879 / 0 / 345	4090 / 96 / 281
Goodness-of-fit on F^2	1.215	1.058
Final R indices [I>2sigma(I)]	R1 = 0.0181, wR2 = 0.0492	R1 = 0.0634, wR2 = 0.2090
R indices (all data)	R1 = 0.0230, wR2 = 0.0587	R1 = 0.0655, wR2 = 0.2129
Largest diff. peak and hole (e $Å^{-3}$)	1.224 and -1.945	5.922 and -8.049

Figure S2. Optimized structures for $[Os_3(\mu\text{-}H)(CO)_{10}(O_2CCH{=}CHCO_2H)(CH_3CN)]$ (**2**), $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}O_2CCH{=}CHCO_2H)]$ (**3**), and intermediate (**IN**).

Cluster **2**



Cluster **3**



Intermediate **IN**