Electronic supplementary information for:

Electronic and steric effects in fragmentation reactions of $Os_3(CO)_9(\mu\text{-}C_4Ph_4)$†

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Table S1. Values of k_{obs} and k_2 for the reaction of P-donor nucleophiles with $Os_3(CO)_9(\mu\text{-}C_4Ph_4)$ at various temperatures.

10^4[L] (M^{-1})	10^4 k_{obs} (s^{-1})	k_2
P(*p*-$F_3CC_6H_4)_3$		
40°C		
9.04	0.094	0.0129(7)
9.04	0.105	
23.0	0.159	
26.5	0.335	
35.0	0.326	
39.7	0.472	
45.0	0.427	
52.9	0.621	
56.0	1.03	
79.4	1.09	
95.3	1.37	
103.4	1.39	
50°		
20.1	0.641	0.021(2)
40.2	0.923	
60.3	1.45	
80.4	1.90	
60°		
40.2	1.37	0.032(3)
60.3	1.92	
80.4	2.75	
80.4	2.68	
70°		
47.1	3.78	0.048

62.8	4.38	
70.6	4.67	
78.4	5.50	
P(*p*-ClC$_6$H$_4$)$_3$		
40°		
34.7	1.98	0.057(1)
34.7	1.99	
49.8	2.76	
60.4	3.41	
77.8	4.44	
86.4	4.90	
97.4	5.56	
50°		
24.8	2.60	0.103(2)
49.5	5.10	
74.3	7.73	
99.0	9.98	
60°		
24.8	4.60	0.180(4)
49.5	9.17	
74.3	13.54	
99.0	18.1	
P(*p*-FC$_6$H$_4$)$_3$		
30°		
72.4	Original Data Missing	0.0534(3)
86.9		
115.9		
144.8		
40°		
9.05	0.860	0.107(2)
9.54	1.00	
15.9	1.67	

22.6	2.36	
33.5	3.58	
45.0	4.78	
56.6	6.01	
143.2	14.4	
50°		
34.7	6.66	0.182(9)
69.3	13.2	
104.0	18.7	
138.6	24.3	
60°		
34.7	12.8	0.32(2)
69.3	23.0	
104.0	33.6	
138.6	46.4	
PPh_3		
40°		
8.67	3.41	0.393
11.5	4.51	
19.8	7.80	
10.2	4.02	
17.7	6.94	
26.2	10.3	
37.2	14.6	
50°		
17.5	11.5	0.70(2)
26.3	17.6	
35.1	23.1	
43.8	30.1	
60°		
13.0	14.5	1.25(3)
17.5	21.2	
21.7	25.2	

26.3	32.0	
32.6	38.8	
32.6	38.7	
43.5	52.5	
43.5	53.0	
43.8	62.9	
P(*i*-Pr)Ph$_2$		
40°		
18.2	19.4	0.93(2)
22.7	24.7	
36.4	37.1	
46.8	46.8	
54.6	55.4	
72.7	68.9	
73.9	70.7	
90.9	87.5	
90.9	83.3	
110.9	90.3	
121.5	94.4	
130.8	107.4	
151.9	109.5	
169.0	124.9	
50°		
18.1	30.3	1.6(2)
36.4	63.3	
54.6	93.6	
72.7	122.1	
60°		
13.4	28.2	2.4(3)
20.1	45.1	
33.5	76.2	
46.8	107.0	
60.2	133.6	
PCyPh$_2$		

40°		
12.7	11.9	0.90(4)
19.1	18.9	
25.4	24.1	
25.4	25.4	
31.8	30.6	
38.1	40.2	
50.8	46.2	
63.5	51.8	
63.5	55.3	
63.5	54.8	
50°		
11.2	20.2	1.65(8)
22.4	40.5	
33.5	59.0	
44.7	74.8	
44.7	75.9	
60°		
22.4	61.9	2.9(1)
33.5	95.0	
33.5	94.5	
44.7	125.9	
$P(NMe_2)_3$		
40°		
13.8	51.7	4.3
19.3	73.4	
24.8	91.2	
27.5	109.0	
27.5	126.3	
38.5	164.0	
57.8	251.8	
50°		
13.8	72.8	5.7(3)
27.5	152	

41.3	233	
55.0	324	
68.8	403	
60°		
13.8	87.5	7.3(4)
20.6	132	
27.5	182	
34.4	246	
34.4	242	
PCy_2Ph		
50°		
10.8	5.48	0.33(3)
13.0	6.31	
17.3	7.52	
21.6	8.76	
13.0	6.55	
10.8	5.35	
21.6	8.93	
17.3	7.93	
60°		
9.0	3.88	0.47(4)
13.5	6.51	
19.4	9.52	
22.5	10.75	
70°		
10.8	4.91	0.64(8)
13.0	6.29	
17.3	8.31	
21.6	12.84	
21.6	12.67	
PCy_3		
50°		
35.6	73.7	1.4(2)

66.7	117	
71.1	188	
106.7	258	
133.4	177	
178	392	
60°		
17.8	29.4	2.2(3)
35.6	73.8	
71.1	188	
107	258	
142	328	
178	392	
70°		
16.9	38.7	3.3(1)
16.9	44.3	
50.7	167	
84.5	261	
118	373	
169	529	
$P(o\text{-}MeOC_6H_4)Ph_2$		
40°		
10.4	3.08	0.26(1)
17.4	4.99	
20.8	6.06	
24.3	6.68	
27.8	7.38	
34.7	9.32	
50°		
14.0	7.11	0.49(1)
20.9	10.8	
27.9	13.8	
34.9	17.5	
60°		

14.0	12.6	0.884(1)
20.9	18.8	
27.9	25.0	
34.9	31.1	
P(*t*-Bu)$_3$		
70°		
210	1.32	0.0021(9)
388	0.851	
669	1.12	
863	3.01	
1035	3.56	
1697	5.23	
80°		
145	0.238	0.0050(3)
296	1.11	
407	1.82	
501	1.52	
669	2.14	
929	3.19	
948	3.98	
1697	7.16	
90°		
145	0.270	0.884(1)
443	3.72	
532	4.77	
863	9.81	
1022	10.1	
2002	17.1	

Table S2. Kinetic data[a] and physical parameters for the reaction of P-donor nucleophiles with $Os_3(CO)_9(\mu\text{-}C_4Ph_4)$ at 13.6°C, where $\theta \leq 143°$.

L	**log(k_{+L})**	**log(k_{-CO})**	**p*K*a'+4**	***θ*(deg)**	***E*ar**	**p*K*a'π**
etpb	1.358	-0.752	3.70	101	0	8.50
P(OMe)$_3$	1.301	-0.694	4.83	107	0	2.80
P(OEt)$_3$	1.509	-1.147	5.64	109	0	2.90
P(OMe)$_2$Ph	1.336	-1.292	5.48	120	1	2.37
P(OEt)$_2$Ph	1.403	-1.409	5.99	121	1	1.97
PMe$_2$Ph	2.149	-1.415	9.07	122	1	0
PPh$_2$H	1.524	-	4.52	126	2	0
P(OPh)$_3$	0.421	-1.456	1.21	128	0	5.33
P(O-*i*-Pr)$_3$	1.509	-1.504	7.38	130	0	4.00
PEt$_3$	1.966	-2.046	11.96	132	0	0.00
P(*n*-Pr)$_3$	1.603	-2.377	12.57	132	0	0.00
P(*n*-Bu)$_3$	1.656	-1.757	12.67	132	0	0.00
P(OMe)Ph$_2$	1.061	-0.943	6.09	133	2	0.86
P(OEt)Ph$_2$	1.009	-2.055	6.35	133	2	0.65
PMePh$_2$	1.695	-2.260	8.06	136	2	0.00
PEtPh$_2$	1.338	-1.620	8.60	140	2	0.00
PCy$_2$H	1.199	-1.824	10.08	143	0	0.00

a From ref. 14.

Table S3. Recalculated QALE analysis of the values of log(k_{+L}) and log(k_{-co}) for the reaction of small P-donor nucleophiles ($\theta \leq 143°$) with $Os_3(CO)_9(\mu\text{-}C_4Ph_4)$ at 13.6°C.[a]

N[b]	α	β	γ/deg	θ_{th} /deg	σlog(k_{+L})	R^2
6[c]	0.564(217)	0.163(36)	–	–	0.145	0.837
7[d]	5.42(118)	0.163	-0.040(9)	122	0.116	0.809
13[e]	3.281(503)	0.164(20)	-0.024(4)	–	0.167	0.868
13[e]	0.557(93)	0.163(15)	-0.044(6)	122	0.125	0.928
N[b]	**α**	**β**	**γ**	**θ_{th}**	**σlog(k_{-CO})**	**R^2**
16[f]	–0.77(25)	–0.10(3)			0.394	0.434
16[f]	1.74(95)	–0.06(3)	–0.023(8)		0.327	0.636

a) Rate data from ref 14. *b*) Number of P-donors used in calculation. *c*) Analysis of the data for nucleophiles with $\theta \leq 122°$ that experience no steric effects. *d*) Calculated from data for nucleophiles with cone angles $\theta \geq 123°$ that do experience steric effects and using β = 0.163 as found for the smaller group of nucleophiles. *e*) Omitting 'outlying' P-donors as in ref 14, and assuming no steric threshold. *f*) All P-donors from ref. 14, and allowing for a steric threshold. This analysis seems to be the best available, but only marginally so.

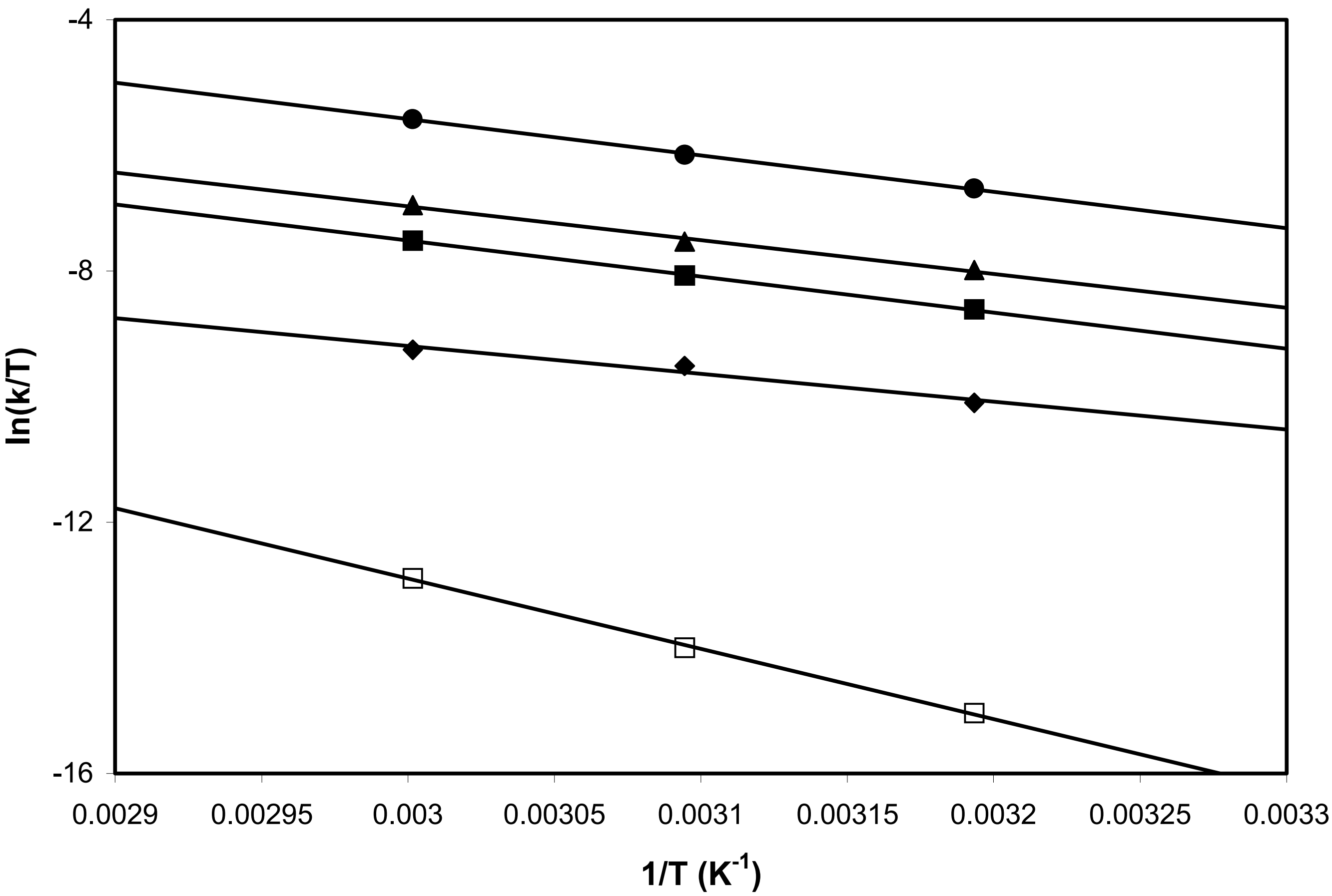

Figure S1. Eyring plots for representative reactions of P-donor nucleophiles with $Os_3(CO)_9(\mu\text{-}C_4Ph_4)$ where $\theta \geq 143°$. PPh_3 (solid circles), P(*p*-FC_6H_4)$_3$ (solid triangles), P(*p*-ClC_6H_4)$_3$ (solid squares), P(*p*-$F_3CC_6H_4$)$_3$ (solid diamonds), P(*t*-Bu)$_3$ (open squares).

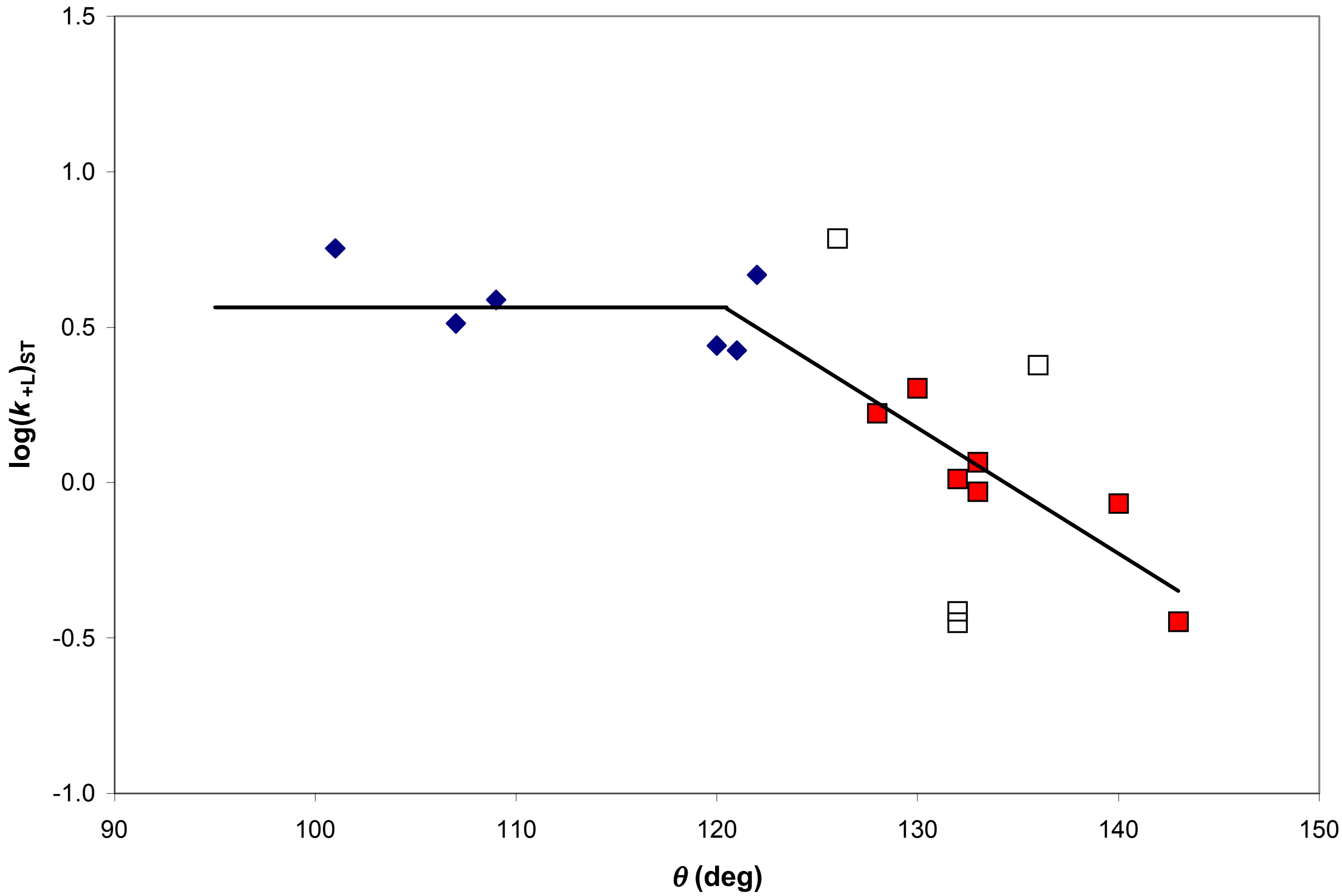

Figure S2. Steric profile for the reaction of smaller P-donor nucleophiles (SNs) with $Os_3(CO)_9(\mu\text{-}C_4Ph_4)$ at 13.6°C, where $\theta \leq 143°$ and $\theta_{th} = 122°$. Outliers are the same as in ref. 14.

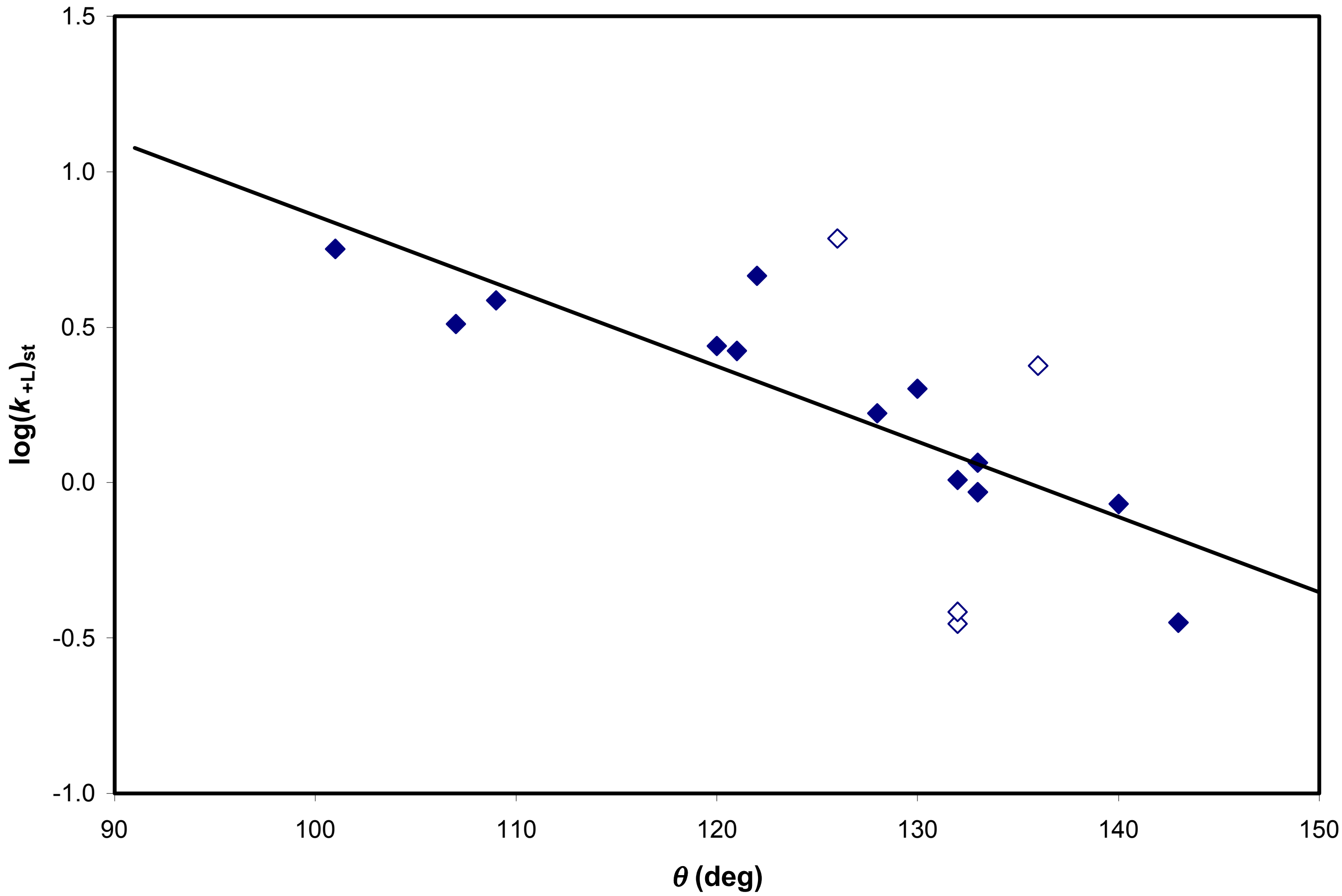

Figure S3. Steric profile for the reaction of smaller P-donor nucleophiles with $Os_3(CO)_9(\mu\text{-}C_4Ph_4)$ at 13.6°C, where $\theta \leq 143°$ and no steric threshold is thought to be operating. Outliers are the same as in ref. 14.