Electronic supplementary information for:

Electronic and steric effects in fragmentation reactions of Os₃(CO)₉(µ-C₄Ph₄)[†]

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Table S1. Values of k_{obs} and k_2 for the reaction of P-donor nucleophiles with Os₃(CO)₉(μ -C₄Ph₄) at various temperatures.

$10^{4}[L] (M^{-1})$	$10^4 k_{\rm obs} ({\rm s}^{-1})$	<i>k</i> ₂
P(p-F ₃ CC ₆ H 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

70.6 4.67 78.4 5.50 40° 34.7 1.98 $0.057(1)$ 34.7 1.99 $0.057(1)$ 34.7 1.99 $0.057(1)$ 34.7 1.99 $0.057(1)$ 34.7 1.99 $0.057(1)$ 34.7 1.99 $0.057(1)$ 34.7 1.99 $0.057(1)$ 34.7 1.99 $0.057(1)$ 34.7 1.99 $0.057(1)$ 44.8 2.76 $0.057(1)$ 50° 2.76 $0.013(2)$ 510 7.73 $0.103(2)$ 74.3 7.73 $0.103(2)$ 99.0 9.98 $0.180(4)$ 90.0 18.1 $0.180(4)$ 99.0 18.1 $0.0534(3)$ 86.9 $0.15.9$ 0.860 $0.107(2)$ 115.9 1.467 $0.107(2)$	62.8	4.38	
78.4 5.50 $P(p-ClC_6H_4)_3$ 40° 44° 1.98 $0.057(1)$ 34.7 1.99 $0.057(1)$ 34.7 1.99 $0.057(1)$ 34.7 1.99 $0.057(1)$ 34.7 1.99 $0.057(1)$ 34.7 1.99 $0.057(1)$ 34.7 1.99 $0.057(1)$ 44.8 2.76 $0.0103(2)$ 60° 2.60 $0.103(2)$ 49.5 5.10 $0.103(2)$ 74.3 7.73 9.90 9.0 9.98 $0.180(4)$ 49.5 9.17 $0.180(4)$ 49.5 9.17 $0.180(4)$ 99.0 18.1 $0.0534(3)$ 72.4 $Original$ $0.0534(3)$ 86.9 115.9 144.8 40° 0.860 $0.107(2)$ 9.54 1.00 1.67	70.6	4.67	
$P(p-ClC_6H_4)_3$ Image: second symbolsImage: second symbolsImage: second symbols 34.7 1.980.057(1) 34.7 1.990.057(1) 34.7 1.990.057(1) 34.7 1.990.057(1) 34.7 1.990.057(1) 49.8 2.760.001 60.4 3.410.001 7.4 5.560.103(2) 50° 2.600.103(2) 24.8 2.600.103(2) 49.5 5.100.180(4) 9.0 9.980.180(4) 49.5 9.170.180(4) 99.0 18.10.0534(3) $P(p-FC_6H_4)_3$ 0.0534(3) 30° 72.40.0534(3) 86.9 0.1500.8600.107(2) 115.9 1.001.67	78.4	5.50	
$P(p-ClC_6H_4)_3$ Image: second symbols 40° 1.980.057(1) 34.7 1.990.057(1) 34.7 1.990.057(1) 34.7 1.990.057(1) 49.8 2.760.0101 60.4 3.410.0101 77.8 4.440.0101 86.4 4.900.103(2) 97.4 5.560.103(2) 50° 0.103(2) 24.8 2.600.103(2) 49.5 5.100.103(2) 74.3 7.73 99.0 9.98 60° 0.180(4) 24.8 4.600.180(4) 49.5 9.17 74.3 13.54 99.0 18.1 $P(p-FC_6H_4)_3$ 0.0534(3) 30° 0.0534(3) 72.4 Original Data Missing 86.9 0.107(2) 115.9 1.467			
40° 1.980.057(1) 34.7 1.990.057(1) 34.7 1.990.057(1) 34.7 1.990.057(1) 49.8 2.760.0101 60.4 3.410.0101 71.8 4.440.0101 86.4 4.900.103(2) 97.4 5.560.103(2) 49.5 5.100.103(2) 74.3 7.730.103(2) 99.0 9.980.180(4) 99.0 9.1713.54 99.0 18.10.0534(3) $P(p-FC_6H_4)_3$ 0.0534(3) 30° 72.4Original Data Missing 86.9 115.90.460 115.9 0.8600.107(2) 144.8 1.001.67	P(<i>p</i> -ClC ₆ H ₄) ₃		
34.7 1.98 $0.057(1)$ 34.7 1.99 2.76 60.4 3.41 77.8 4.44 86.4 4.90 97.4 5.56 50° 2.60 24.8 2.60 49.5 5.10 74.3 7.73 99.0 9.98 60° 4.60 24.8 4.60 9.90 9.98 60° 9.17 74.3 13.54 99.0 18.1 $P(p-FC_6H_4)_3$ $0.0534(3)$ 30° 72.4 86.9 $0.107(2)$ 115.9 1.467	40°		
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° 24.8 260 $0.103(2)$ 49.5 5.10 74.3 7.73 99.0 9.98 60° $0.180(4)$ 24.8 4.60 9.17 74.3 9.17 74.3 13.54 99.0 18.1 $P(p-FC_6H_4)_3$ $0.0534(3)$ 30° $0.0534(3)$ 72.4 $Original Data Missing$ 86.9 $0.107(2)$ 115.9 1.47	34.7	1.98	0.057(1)
49.82.76 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 $P(p-FC_6H_4)_3$ $0.0534(3)$ 30° 72.4 90.5 0.860 $0.107(2)$ 9.54 1.00 15.9 1.67	34.7	1.99	
60.4 3.41 77.8 4.44 86.4 4.90 97.4 5.56 50° 2.60 24.8 2.60 49.5 5.10 74.3 7.73 99.0 9.98 60° 24.8 4.60 $0.103(2)$ 49.5 9.17 74.3 9.17 74.3 9.17 74.3 13.54 99.0 18.1 $P(p-FC_6H_4)_3$ $0.0534(3)$ 30° 72.4 $Original Data Missing$ 86.9 115.9 0.860 $0.107(2)$ 9.54 1.00 1.67	49.8	2.76	
77.8 4.44 86.4 4.90 97.4 5.56 50° 24.8 24.8 2.60 49.5 5.10 74.3 7.73 99.0 9.98 60° 24.8 4.60 $0.103(2)$ 99.0 9.98 60° $0.180(4)$ 24.8 4.60 9.9 9.17 74.3 9.17 74.3 13.54 99.0 18.1 $P(p-FC_6H_4)_3$ $0.0534(3)$ 30° 72.4 $Original$ $Data Missing$ $0.0534(3)$ 86.9 115.9 144.8 40° 0.860 $0.107(2)$ 9.54 1.00 1.67	60.4	3.41	
86.4 4.90 97.4 5.56 50° 24.8 24.8 2.60 49.5 5.10 74.3 7.73 99.0 9.98 60° $0.103(2)$ 24.8 4.60 99.0 9.98 60° $0.180(4)$ 24.8 4.60 99.0 9.17 74.3 9.17 74.3 13.54 99.0 18.1 $P(p-FC_6H_4)_3$ $0.0534(3)$ 30° 72.4 $Original$ 86.9 $0.15.9$ $0.0534(3)$ 40° 9.05 0.860 $0.107(2)$ 9.54 1.00 1.67	77.8	4.44	
97.4 5.56 50° 24.8 2.60 $0.103(2)$ 49.5 5.10 $0.103(2)$ 74.3 7.73 99.0 99.0 9.98 $0.180(4)$ 49.5 9.17 $0.180(4)$ 49.5 9.17 $0.180(4)$ 49.5 9.17 13.54 99.0 18.1 $0.0534(3)$ $P(p-FC_6H_4)_3$ $0.0534(3)$ 30° 72.4 $Original Data Missing$ 86.9 $0.15.9$ $0.0534(3)$ 115.9 144.8 $0.107(2)$ 40° 0.905 0.860 $0.107(2)$ 9.54 1.00 1.67	86.4	4.90	
50° 2.60 $0.103(2)$ 24.8 2.60 $0.103(2)$ 49.5 5.10 7.73 99.0 9.98 $0.180(4)$ 60° $0.180(4)$ 24.8 4.60 $0.180(4)$ 49.5 9.17 74.3 13.54 99.0 18.1 $P(p-FC_6H_4)_3$ $0.0534(3)$ 30° $0.0534(3)$ 72.4 $Original Data Missing$ 86.9 $0.15.9$ 115.9 0.860 $0.107(2)$ 9.05 0.860 $0.107(2)$ 9.54 1.00 1.67	97.4	5.56	
50° 24.82.600.103(2) 49.5 5.10 7.73 9.90 9.98 $0.103(2)$ 60° 9.98 $0.180(4)$ 9.98 $0.180(4)$ 49.5 9.17 $0.180(4)$ 9.990 18.1 $P(p-FC_6H_4)_3$ 13.54 99.0 $0.0534(3)$ 30° 72.4 0.131 $0.0534(3)$ 86.9 115.9 $0.0534(3)$ $0.0534(3)$ 144.8 40° $0.107(2)$ 9.05 0.860 $0.107(2)$ 9.54 1.00 1.67			
24.8 2.60 $0.103(2)$ 49.5 5.10 7.73 99.0 9.98 $0.180(4)$ 60° 4.60 $0.180(4)$ 24.8 4.60 $0.180(4)$ 49.5 9.17 13.54 99.0 18.1 $0.0534(3)$ $P(p-FC_6H_4)_3$ $0.0534(3)$ 30° $0.0534(3)$ 72.4 $0riginal$ $B6.9$ 0.159 115.9 0.860 144.8 $0.107(2)$ 9.05 0.860 9.05 1.67	50°		
49.5 5.10 74.3 7.73 99.0 9.98 60° $0.180(4)$ 24.8 4.60 49.5 9.17 74.3 13.54 99.0 18.1 $P(p-FC_6H_4)_3$ $0.0534(3)$ 30° $0.0534(3)$ 72.4 $Original Data Missing$ 86.9 $0.0534(3)$ 115.9 $0.0534(3)$ 144.8 $0.0017(2)$ 9.05 0.860 $0.107(2)$ 9.54 1.00 15.9 1.67	24.8	2.60	0.103(2)
74.3 7.73 99.0 9.98 60° 9.98 24.8 4.60 $0.180(4)$ 49.5 9.17 $0.180(4)$ 49.5 9.17 13.54 99.0 18.1 $0.0534(3)$ $P(p-FC_6H_4)_3$ $0.0534(3)$ 30° 72.4 $Original Data Missing$ 86.9 115.9 $0.0534(3)$ 115.9 144.8 $0.107(2)$ 9.05 0.860 $0.107(2)$ 9.54 1.00 1.67	49.5	5.10	
99.0 9.98 60° 0.180(4) 24.8 4.60 0.180(4) 49.5 9.17 0.180(4) 49.5 9.17 13.54 99.0 18.1 0.0534(3) P(p-FC ₆ H ₄) ₃ 0.0534(3) 30° 72.4 Original Data Missing 86.9 0.0534(3) 115.9 144.8 40° 0.860 0.107(2) 9.54 1.00 1.67	74.3	7.73	
60° 4.600.180(4) 49.5 9.17 0.180(4) 49.5 9.17 13.54 99.0 18.1 0.180(4) P(p-FC_6H_4)3 0.181 30° 0.0534(3) 72.4 Original Data Missing0.0534(3) 86.9 0.115.90.0534(3) 144.8 0.05340.107(2) 9.05 0.8600.107(2) 9.54 1.001.67	99.0	9.98	
60° 4.600.180(4) 24.8 4.60 $0.180(4)$ 49.5 9.17 74.3 13.54 99.0 18.1 $P(p-FC_6H_4)_3$ Original Data Missing $0.0534(3)$ 30° $0.0534(3)$ 72.4 Original Data Missing $0.0534(3)$ 86.9 115.9 0.860 $0.107(2)$ 9.05 0.860 $0.107(2)$ 9.54 1.00 1.67			
24.8 4.60 $0.180(4)$ 49.5 9.17 74.3 13.54 99.0 18.1 $P(p-FC_6H_4)_3$ $0.0534(3)$ 30° $0.0534(3)$ 72.4 $0riginal$ 86.9 115.9 144.8 $0.0534(3)$ 40° 0.860 9.54 1.00 15.9 1.67	60°		
49.5 9.17 74.3 13.54 99.0 18.1 $P(p-FC_6H_4)_3$ $0.0534(3)$ 30° $0.0534(3)$ 72.4 $0.0534(3)$ 86.9 $0.0534(3)$ 115.9 144.8 40° 0.860 $0.107(2)$ 9.54 1.00 1.67	24.8	4.60	0.180(4)
74.3 13.54 99.0 18.1 $P(p-FC_6H_4)_3$ $0.0534(3)$ 30° $0.0534(3)$ 72.4 $0riginal$ $0.0534(3)$ $0.0534(3)$ 86.9 115.9 115.9 0.860 9.05 0.860 9.05 0.860 9.54 1.00 15.9 1.67	49.5	9.17	
99.0 18.1 $P(p-FC_6H_4)_3$ Original Data Missing 0.0534(3) 30° 72.4 Original Data Missing 0.0534(3) 86.9 115.9 144.8 0.0534(3) 40° 0.055 0.860 0.107(2) 9.54 1.00 1.67 0.107(2)	74.3	13.54	
$P(p-FC_6H_4)_3$ Original Data Missing $0.0534(3)$ 72.4 Original Data Missing $0.0534(3)$ 86.9 115.9 144.8 40° 0.055 0.860 $0.107(2)$ 9.54 1.00 1.67	99.0	18.1	
$P(p-FC_6H_4)_3$ Original Data Missing $0.0534(3)$ 72.4 Original Data Missing $0.0534(3)$ 86.9 115.9 144.8 40° 0.860 $0.107(2)$ 9.05 0.860 $0.107(2)$ 9.54 1.00 1.67			
30° Original Data Missing 0.0534(3) 86.9 Data Missing 0.0534(3) 115.9 144.8 0.0534(3) 40° 0.0534(3) 0.0534(3) 9.05 0.860 0.107(2) 9.54 1.00 1.67	P(<i>p</i> -FC ₆ H ₄) ₃		
72.4 Original Data Missing 0.0534(3) 86.9 115.9 144.8 40° 9.05 0.860 9.54 1.00 15.9 1.67	30°		
Bata Missing 86.9 115.9 144.8 40° 9.05 0.860 9.54 1.00 15.9	72.4	Original	0.0534(3)
86.9 115.9 144.8 40° 9.05 0.860 9.54 1.00 15.9 1.67		Data Missing	
115.9 144.8 40° 9.05 0.860 9.54 1.00 15.9 1.67	86.9		
144.8 40° 9.05 0.860 9.54 1.00 15.9 1.67	115.9		
40°	144.8		
9.05 0.860 0.107(2) 9.54 1.00 15.9 1.67	40°		
9.54 1.00 15.9 1.67	9.05	0 860	0.107(2)
15.9 1.67	9.54	1.00	
1.07	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°		
10		
8.67	3.41	0.393
8.67 11.5	3.41 4.51	0.393
8.67 11.5 19.8	3.41 4.51 7.80	0.393
8.67 11.5 19.8 10.2	3.41 4.51 7.80 4.02	0.393
8.67 11.5 19.8 10.2 17.7	3.41 4.51 7.80 4.02 6.94	0.393
8.67 11.5 19.8 10.2 17.7 26.2	3.41 4.51 7.80 4.02 6.94 10.3	0.393
8.67 11.5 19.8 10.2 17.7 26.2 37.2	3.41 4.51 7.80 4.02 6.94 10.3 14.6	0.393
8.67 11.5 19.8 10.2 17.7 26.2 37.2	3.41 4.51 7.80 4.02 6.94 10.3 14.6	0.393
8.67 11.5 19.8 10.2 17.7 26.2 37.2 50°	3.41 4.51 7.80 4.02 6.94 10.3 14.6	0.393
8.67 11.5 19.8 10.2 17.7 26.2 37.2 50° 17.5	3.41 4.51 7.80 4.02 6.94 10.3 14.6	0.393
8.67 11.5 19.8 10.2 17.7 26.2 37.2 50° 17.5 26.3	3.41 4.51 7.80 4.02 6.94 10.3 14.6 11.5 17.6	0.393
8.67 11.5 19.8 10.2 17.7 26.2 37.2 50° 17.5 26.3 35.1	3.41 4.51 7.80 4.02 6.94 10.3 14.6 11.5 17.6 23.1	0.393
8.67 11.5 19.8 10.2 17.7 26.2 37.2 50° 17.5 26.3 35.1 43.8	3.41 4.51 7.80 4.02 6.94 10.3 14.6 11.5 17.6 23.1 30.1	0.393
8.67 11.5 19.8 10.2 17.7 26.2 37.2 50° 17.5 26.3 35.1 43.8	3.41 4.51 7.80 4.02 6.94 10.3 14.6 11.5 17.6 23.1 30.1	0.393
8.67 11.5 19.8 10.2 17.7 26.2 37.2 50° 17.5 26.3 35.1 43.8 60°	3.41 4.51 7.80 4.02 6.94 10.3 14.6 11.5 17.6 23.1 30.1	0.393
8.67 11.5 19.8 10.2 17.7 26.2 37.2 50° 17.5 26.3 35.1 43.8 60° 13.0	3.41 4.51 7.80 4.02 6.94 10.3 14.6 11.5 17.6 23.1 30.1	0.393 0.70(2) 1.25(3)
8.67 11.5 19.8 10.2 17.7 26.2 37.2 50° 17.5 26.3 35.1 43.8 60° 13.0 17.5	3.41 4.51 7.80 4.02 6.94 10.3 14.6 11.5 17.6 23.1 30.1 14.5 21.2	0.393 0.70(2) 1.25(3)

 $\textit{Electronic supplementary information for: Electronic and steric effects in fragmentation reactions of Os_3(CO)_9 (\mu-C_4Ph_4)^{\dagger}$

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>i</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		

 $\textit{Electronic supplementary information for: Electronic and steric effects in fragmentation reactions of Os_3(CO)_9 (\mu-C_4Ph_4)^{\dagger}$

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 ₂ Ph		
50°	5 40	0.22/2
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	
DCy		
ГUУ3 50°		
3U 35.6	ד בד	1 A(2)
55.0	13.1	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-MeOC ₆ H 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(<i>t</i> -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	

L	$\log(k_{+L})$	log(k _{-CO})	p <i>K</i> a'+4	θ(deg)	Ear	p <i>K</i> 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>i</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(<i>n</i> -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

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

a From ref. 14.

Table S3. R	ecalculated Q	ALE analysis	of the values	of $\log(k_{+L})$	and $log(k_{-co})$	for the reaction of	of small P-
donor nucle	ophiles ($\theta \le 1$	43°) with $Os_3($	$CO)_9(\mu - C_4Pl$	h_4) at 13.6°	$\mathrm{C.}^{a}$		

N ^b	α	β	γ/deg	$ heta_{ ext{th}}$	$\sigma \log(k_{+L})$	R ²
				/deg		
6 ^{<i>c</i>}	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	$\theta_{\rm th}$	$\sigma \log(k_{-CO})$	\mathbf{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 $\theta \le 122^{\circ}$ that experience no steric effects. *d*) Calculated from data for nucleophiles with cone angles $\theta \ge 123^{\circ}$ that do experience steric effects and using $\beta = 0.163$ 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 $Os_3(CO)_9(\mu-C_4Ph_4)$ where $\theta \ge 143^\circ$. PPh₃ (solid circles), P(*p*-FC₆H₄)₃ (solid triangles), P(*p*-ClC₆H₄)₃ (solid squares), P(*p*-F₃CC₆H₄)₃ (solid diamonds), P(*t*-Bu)₃ (open squares).



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



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