

## Supplementary Information

### **Combined Experiment and Theoretical Investigation into C-H Activation of Cyclic Alkanes by Cp'Rh(CO)<sub>2</sub> (Cp' = $\eta^5$ -C<sub>5</sub>H<sub>5</sub> or $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)**

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Table S1. Calculated relative energies (kcal/mol) and experimental lifetimes in the reaction  
 $\text{Cp}'\text{Rh}(\text{CO}) + (\text{alkane}) \rightarrow \text{Cp}'\text{Rh}(\text{CO})(\text{alkane}) \rightarrow \text{Cp}'\text{Rh}(\text{CO})(\text{alkyl})\text{H}$  (std.state: mol/L)

	Separated reactants $\Delta E, H, G$	$\sigma$ -complex			TS			Product			Lifetime (ns)
		$\Delta E$	$\Delta H$	$\Delta G$	$\Delta E$	$\Delta H$	$\Delta G$	$\Delta E$	$\Delta H$	$\Delta G$	
<b>B3LYP</b>											
Cp + CyP	0.00	-9.49	-8.53	0.74	0.24	-1.26	9.94	-10.22	-10.77	0.82	<b>4.41</b>
Cp + NeP	0.00	-8.08	-7.05	1.09	2.52	1.19	11.51	-7.38	-7.69	3.19	<b>18.40</b>
Cp + CyH	0.00	-9.03	-8.09	0.36	1.04	-0.48	10.06	-8.74	-9.29	1.43	<b>8.76</b>
Cp* + CyP	0.00	-7.46	-6.49	2.67	3.09	1.52	12.94	-7.42	-8.03	3.82	<b>10.86</b>
Cp* + NeP	0.00	-6.44	-5.45	2.71	4.64	3.18	13.95	-5.56	-5.96	5.23	
Cp* + CyH	0.00	-6.99	-6.02	2.83	4.28	2.66	13.19	-6.01	-6.67	4.27	<b>22.06</b>
<b>BMK</b>											
Cp + CyP	0.00	-12.50	-11.16	-1.58	-2.68	-4.19	6.34	-17.50	-17.77	-6.32	<b>4.41</b>
Cp + NeP	0.00	-11.60	-10.36	-0.97	-1.17	-2.68	8.61	-14.67	-14.53	-2.92	<b>18.40</b>
Cp + CyH	0.00	-12.18	-10.88	-1.47	-1.97	-3.13	7.29	-15.77	-15.91	-4.50	<b>8.76</b>
Cp* + CyP	0.00	-11.68	-10.46	0.35	-2.01	-3.92	8.05	-17.55	-18.28	-6.08	<b>10.86</b>
Cp* + NeP	0.00	-10.66	-9.79	-1.11	-0.34	-2.11	8.22	-15.69	-15.56	-3.35	
Cp* + CyH	0.00	-11.26	-10.05	0.22	-0.94	-1.74	9.90	-15.92	-16.49	-4.46	<b>22.06</b>
<b>TPSSTPSS</b>											
Cp + CyP	0.00	-12.56	-11.80	-2.26	-6.47	-8.09	3.34	-17.96	-18.62	-6.97	<b>4.41</b>
Cp + NeP	0.00	-11.08	-10.19	-1.28	-4.72	-6.21	4.40	-15.58	-16.07	-5.33	<b>18.40</b>
Cp + CyH	0.00	-12.03	-11.27	-2.28	-5.79	-7.44	3.18	-16.78	-17.47	-6.60	<b>8.76</b>
Cp* + CyP	0.00	-10.18	-9.38	0.40	-3.41	-5.21	6.51	-14.97	-15.74	-3.94	<b>10.86</b>
Cp* + NeP	0.00	-9.16	-8.33	0.29	-2.33	-3.97	6.66	-13.65	-14.26	-2.89	
Cp* + CyH	0.00	-9.56	-8.79	0.39	-2.34	-4.11	6.63	-13.86	-14.68	-3.56	<b>22.06</b>
<b>wB97XD</b>											
Cp + CyP	0.00	-16.31	-14.74	-7.36	-7.86	-8.66	0.92	-17.75	-17.65	-8.01	<b>4.41</b>
Cp + NeP	0.00	-15.70	-14.56	-5.10	-6.50	-7.56	3.90	-15.57	-15.77	-4.94	<b>18.40</b>
Cp + CyH	0.00	-16.13	-15.14	-6.08	-7.26	-8.63	2.29	-16.30	-16.71	-5.46	<b>8.76</b>
Cp* + CyP	0.00	-16.39	-14.81	-6.23	-7.65	-8.45	1.62	-18.15	-18.10	-7.99	<b>10.86</b>
Cp* + NeP	0.00	-15.44	-14.51	-5.57	-6.43	-7.67	3.38	-17.05	-17.32	-5.47	
Cp* + CyH	0.00	-16.20	-15.15	-5.31	-6.93	-8.56	2.98	-16.97	-17.45	-5.47	<b>22.06</b>

Cp = CpRh(CO), CyP = Cyclopentane, CyH = Cyclohexane, NeP = Neopentane