

Results of VT-NMR measurements of $(\text{Cp}^*\text{Ru})_3(\mu\text{-H})_2(\mu_3\text{-CCH}_3)\{\mu_3\text{-}\eta^2\text{-}(\text{E})\text{-CH=CH}\}$ (5)**Table S1.** Rate of the exchange of the ethyne proton signals at various temperatures

Temp. (°C)	$k_{(\text{C-H})}$	$\ln(k_{\text{C-H}}/T)$
-35	0	
-15	2.9	-4.489
0	18	-2.719
10	55	-1.638
15	77	-1.320
30	370	0.199
45	1360	1.453
60	4400	2.581
75	13000	3.620
100	65500	5.168

Table S2. Rate of the exchange of the hydride signals at various temperatures

Temp. (°C)	$k_{(\text{Ru-H})}$	$\ln(k_{\text{Ru-H}}/T)$
-35	0	
-25	0.6	-6.025
-15	2	-4.860
-5	5.8	-3.834
0	9.2	-3.391
10	25	-2.427
15	37	-2.052
20	60	-1.586
25	85	-1.255
30	130	-0.847
40	285	-0.094
45	420	0.278
50	590	0.602
55	835	0.934
60	1200	1.282
75	3050	2.170
100	13000	3.551

Table S3. Rate of the exchange of the Cp* signals at various temperatures

Temp. (°C)	<i>K</i> 1	<i>K</i> 2	ln (<i>k</i> 1/ <i>T</i>)	ln (<i>k</i> 2/ <i>T</i>)
-35	0	0		
-25	0.4	0	-6.430	
-15	2.2	0	-4.788	
0	16.2	0	-2.825	
15	81	0.2	-1.269	-7.273
20	150	0.4	-0.670	-6.597
30	360	1.5	0.172	-5.309
40	880	4.8	1.033	-4.178
45	1200	8.85	1.328	-3.582
50	2000	14	1.823	-3.139
60	4800	32.5	2.668	-2.327
75	13200	135	3.635	-0.947
100	68000	1300	5.205	1.248

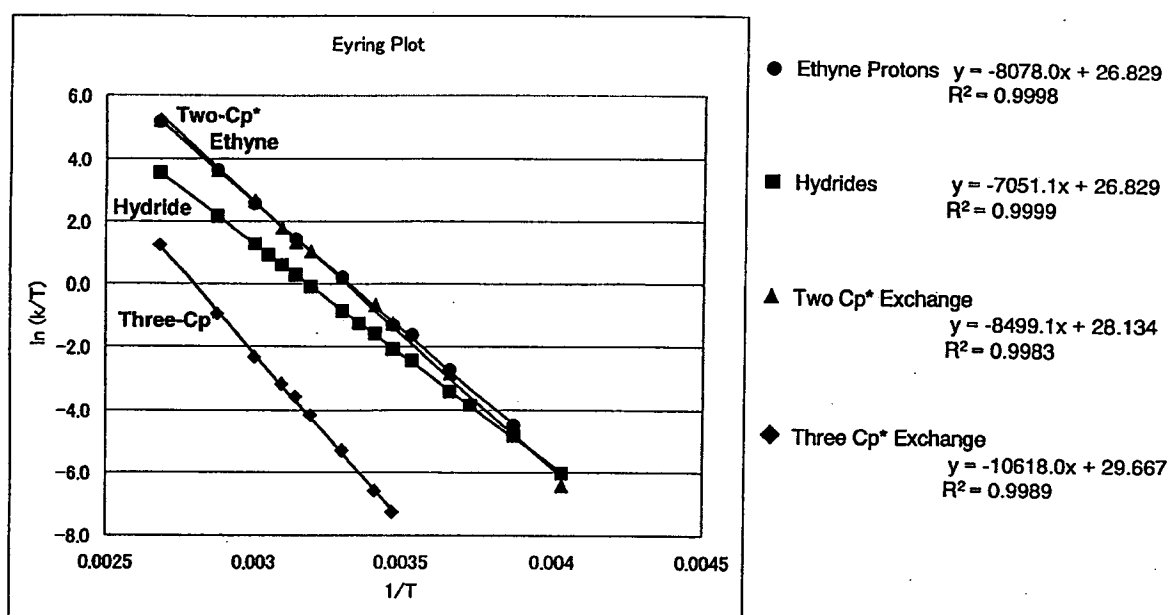
**Figure S1.** Eyring Plots for the fluxional processes of **5**; (a) Exchange for the ethyne protons (?), (b) Exchange for the hydrides (■), (c) Exchange for the two Cp* signals (?), and (d) Exchange for the three Cp* signals (◆).

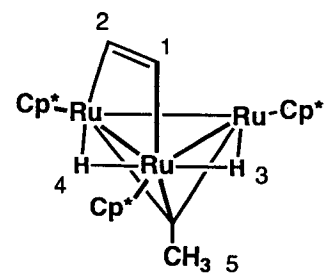
Table S4. Estimated coupling parameters between each signals at low-temperature limit (-35 °C).

(a) Ethyne protons and hydrides

	δ	$W_{1/2}$ (Hz)	1	2	3	4
1 (Ethyne)	6.106	0.95				
2 (Ethyne)	8.618	0.75	$J = 2.92$ Hz			
3 (Hydride)	-17.250	1.17	$J = 3.96$ Hz	$J = 0.20$ Hz		
4 (Hydride)	-21.737	1.17	$J = 0.42$ Hz	$J = 0.42$ Hz	$J = 2.85$ Hz	
5 (Ethyldyne)	3.390	0.90	$J = 0.00$ Hz	$J = 0.00$ Hz	$J = 0.70$ Hz	$J = 0.75$ Hz

(b) Cp*

	δ	$W_{1/2}$ (Hz)	1	2
1(Cp*)	1.923	0.90		
2(Cp*)	1.821	0.99	$J = 0.00$ Hz	
3(Cp*)	1.781	0.90	$J = 0.00$ Hz	$J = 0.00$ Hz

**Complex 5**

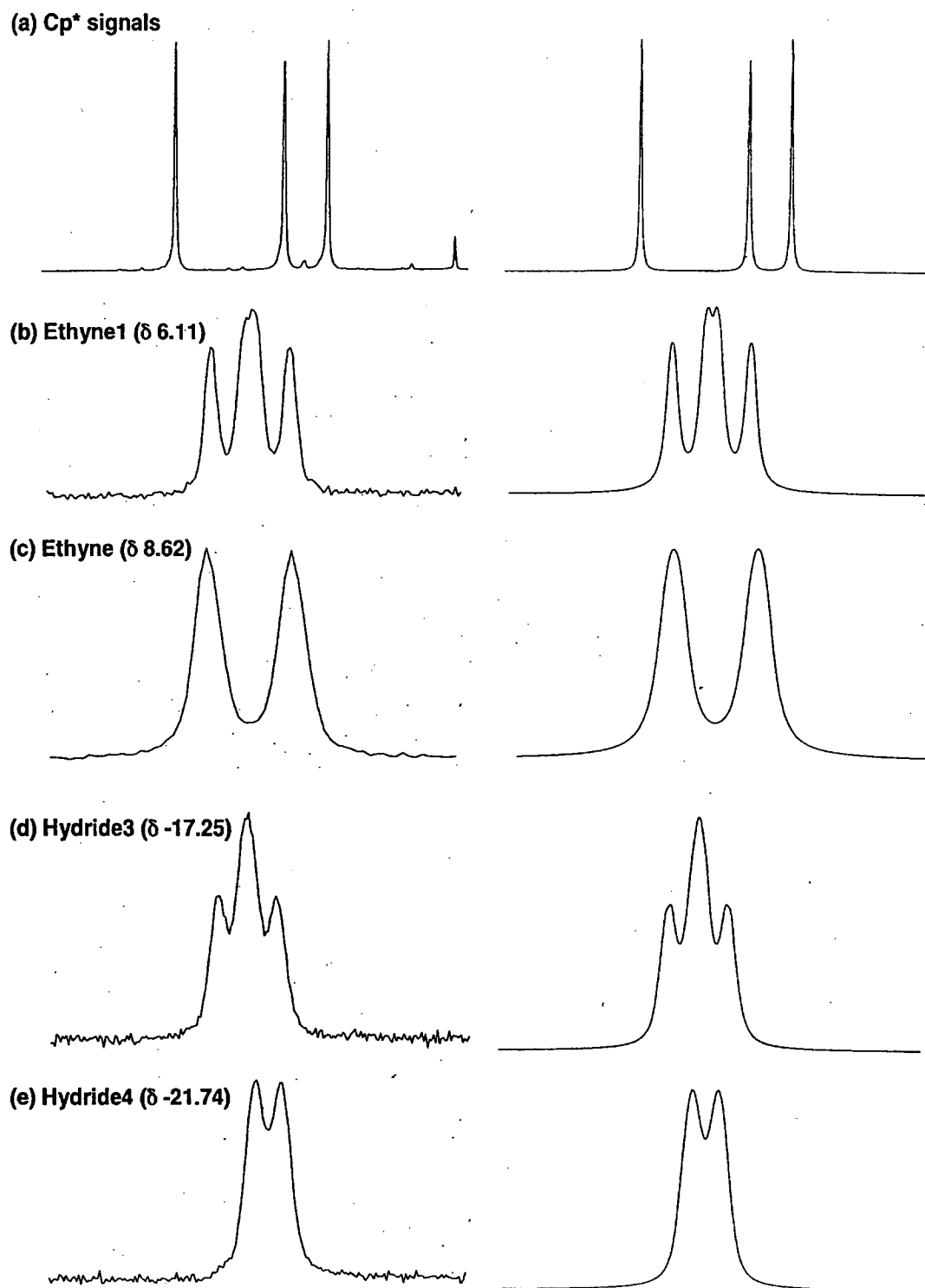


Figure S2. Results of curve fitting of the each signal of **5** at low-temperature limit; left: measured line, right: simulated line.

Results of VT-NMR measurements of $(\text{Cp}^*\text{Ru})_3(\mu\text{-H})(\mu_3\text{-C=CH}_2)(\mu_3\text{-}\eta^2\text{-}(\text{E})\text{-CH=CH})$ (**6**)

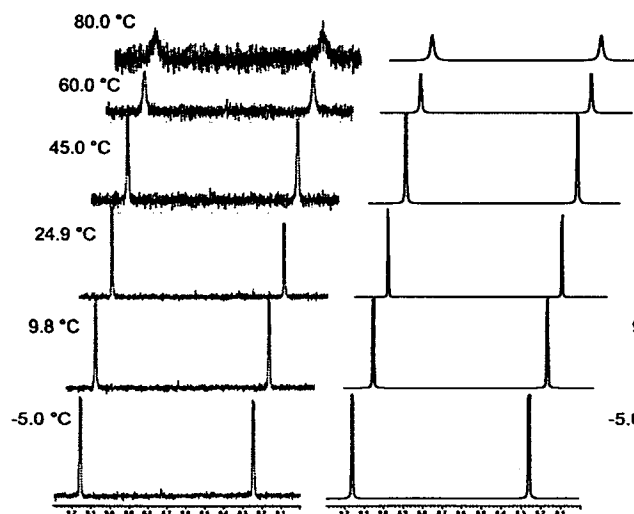
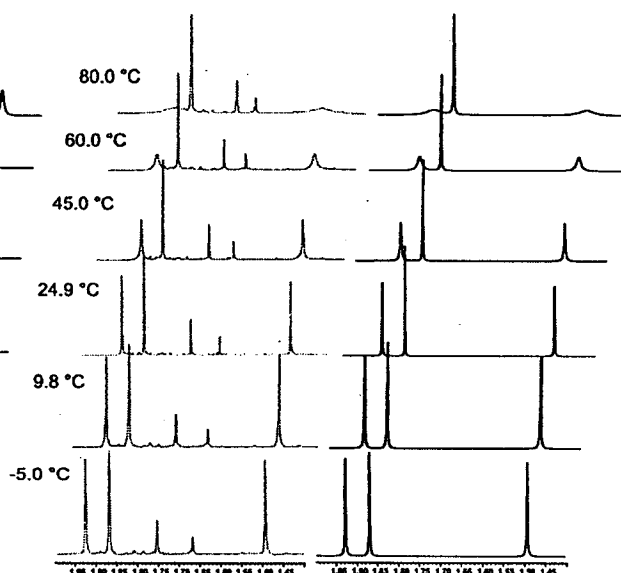
Table S5. Rate of the exchange of the ethyne proton signals at various temperatures

Temp. (°C)	$k_{(\text{C-H})}$	$\ln(k_{\text{C-H}}/T)$
-5.0	0.02	-9.791
9.8	0.07	-8.304
24.9	0.18	-7.411
45.0	0.82	-5.961
60.0	3.50	-4.556
80.0	16.0	-3.094

Table S6. Rate of the exchange of the Cp^* -methyl proton signals at various temperatures

Temp. (°C)	$k_{(\text{C-H})}$	$\ln(k_{\text{C-H}}/T)$
-5.0	0.02	-9.791
9.8	0.07	-8.304
24.9	0.18	-7.411
45.0	0.82	-5.961
60.0	3.20	-4.645
80.0	13.0	-3.302

(a) Ethyne

(b) Cp^* Figure S3. Variable-temperature ^1H NMR spectra of $(\text{Cp}^*\text{Ru})_3(\mu\text{-H})(\mu_3\text{-C=CH}_2)(\mu_3\text{-}\eta^2\text{-}(\text{E})\text{-HC=CH})$ (**6**) showing (a) ethyne proton, and (b) Cp^* -methyl together with the results of the simulation at right.

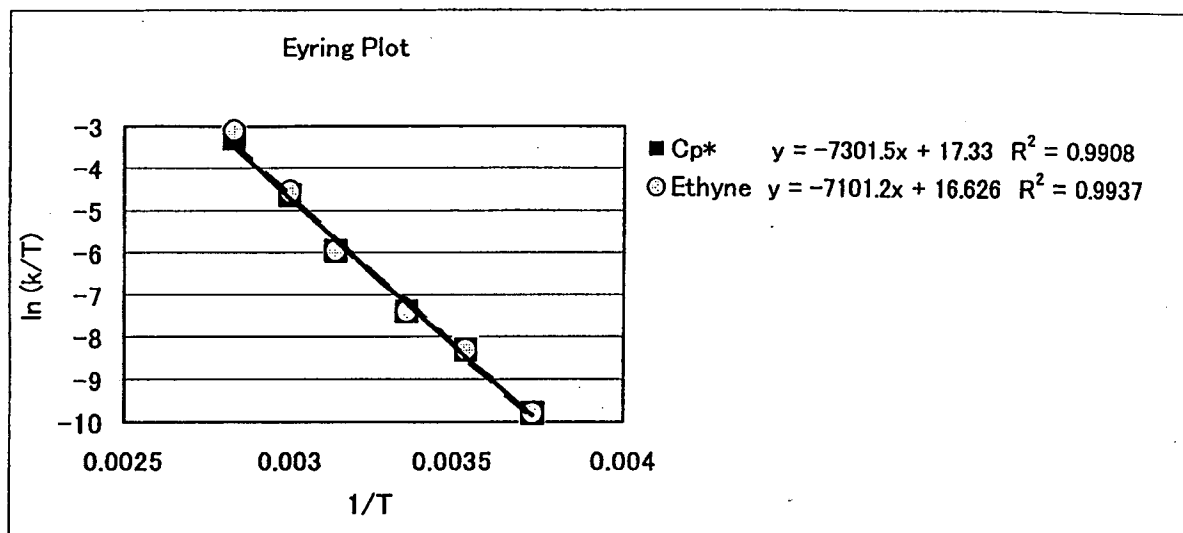


Figure S4. Eyring Plots for the fluxional processes of **6**; (a) Exchange for the ethyne protons (?), (b) Exchange for the two Cp* signals (■).