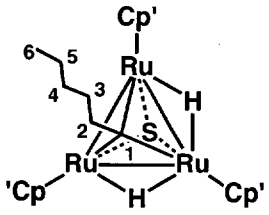
(1) Spectral and analytical data for **2**



^{1}H NMR (500 MHz, C_6D_6, TMS/ppm, 298 K)

-20.00 (s, 2H, Ru-*H*)

1.10 (t, *J* = 7.5 Hz, 3H, C6-*H*)

1.60 (m, 2H, C5-*H*)

1.62 (m, 2H, C3-*H* or C4-*H*)

1.62 (m, 2H, C3-*H* or C4-*H*)

1.93 (s, 45H, C_5*Me*$_5$)

3.18 (m, 2H, C2-*H*)

^{13}C NMR (68 MHz, C_6D_6, TMS/ppm, 298 K)

12.3 (q, J_{CH} = 126 Hz, Cp*Me*)

14.9 (q, J_{CH} = 125 Hz, *C6*)

23.8 (t, J_{CH} = 124 Hz, *C5*)

33.3 (t, J_{CH} = 127 Hz, *C4* or C*3*)

33.3 (t, J_{CH} = 125 Hz, *C4* or C*3*)

57.1 (t, J_{CH} = 123 Hz, *C2*)

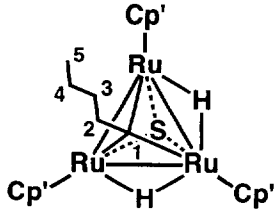
94.2 (s, Cp'*ring*)

315.6 (s, *C1*)

IR (KBr, cm^{-1}) 2956, 2906, 2796, 2716, 2520, 2056, 1556, 1457, 1376, 1107, 1028, 924, 679

Anal. Found (cacd for $C_{36}H_{58}SRu_3$) : C, 52.25 (52.34); H, 7.22 (7.08)

(2) Spectral data for **3**



^{1}H NMR (500 MHz, C_6D_6, TMS/ppm, 298 K)

-20.01 (s, 2H, Ru-*H*)

1.17 (t, *J* = 7.0 Hz, 3H, C5-*H*)

1.65 (m, 2H, C3-*H* or C4-*H*)

1.65 (m, 2H, C3-*H* or C4-*H*)

1.92 (s, 45H, C_5*Me*$_5$)

^{13}C NMR (68 MHz, C_6D_6, TMS/ppm, 298 K)

12.5 (q, J_{CH} = 126 Hz, Cp*Me*)

14.8 (q, J_{CH} = 124 Hz, *C5*)

24.0 (t, J_{CH} = 125 Hz, *C4* or C*3*)

35.6 (t, J_{CH} = 125 Hz, *C4* or C*3*)

56.7 (t, J_{CH} = 124 Hz, C2)

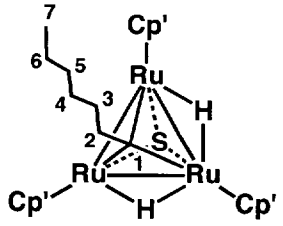
3.18 (m, 2H, C2-*H*)

94.2 (s, Cp'*ring*)

315.6 (s, *C1*)

IR (KBr / cm^{-1}) 2959, 2901, 1373, 1261, 1023, 876, 802, 683

(3) Spectral data for **4**



^{1}H NMR (500 MHz, C_6D_6, TMS/ppm, 298 K)

-20.01 (s, 2H, Ru-*H*)

1.03 (t, *J* = 7.5 Hz, 3H, C7-*H*)

1.51 (quint, *J* = 7.5 Hz 2H, C6-*H*)

1.56 (br, $\Delta w_{1/2}$ = 23 Hz, 2H, C5-*H*)

1.66 (br, $\Delta w_{1/2}$ = 16 Hz, 2H, C3-*H* or C4-*H*)

1.66 (br, $\Delta w_{1/2}$ = 16 Hz, 2H, C3-*H* or C4-*H*)

1.94 (s, 45H, C_5Me_5)

3.20 (br, $\Delta w_{1/2}$ = 18 Hz, 2H, C2-*H*)

^{13}C NMR (125 MHz, C_6D_6, TMS/ppm, 298 K)

12.3 (q, J_{CH} = 126 Hz, Cp*Me*)

14.5 (tq, J_{CH} = 4, 125 Hz, *C7*)

23.6 (t, J_{CH} = 124 Hz, *C6*)

30.8 (t, J_{CH} = 122 Hz, *C3* or C*4*)

33.1 (t, J_{CH} = 128 Hz, *C5*)

33.5 (t, J_{CH} = 125 Hz, *C3* or C*4*)

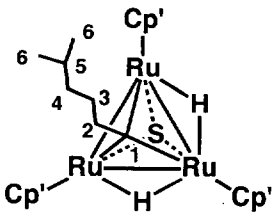
57.2 (t, J_{CH} = 123 Hz, *C2*)

94.2 (s, Cp'*ring*)

315.6 (s, *C1*)

IR (KBr / cm^{-1}) 2956, 2898, 2852, 1449, 1373, 1070, 1024

(4) Spectral data for **5**



^{1}H NMR (500 MHz, C_6D_6, TMS/ppm, 298 K)

-20.00 (s, 2H, Ru-*H*)

^{13}C NMR (125 MHz, C_6D_6, TMS/ppm, 298 K)

12.4 (q, J_{CH} = 126 Hz, Cp*Me*)

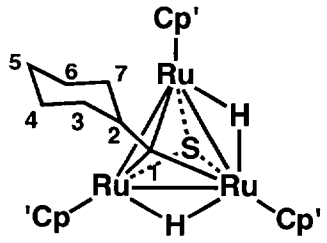
1.10 (d, J = 7.5 Hz, 6H, C6-*H*)
1.57* (2H, C4-*H*)
1.64* (2H, C3-*H*)
1.77* (1H, C5-*H*)
1.95 (s, 45H, C_5Me_5)
3.19 (m, 2H, C2-*H*)

* confirmed by H-H, C-H COSY spectra

23.5 (q, J_{CH} = 123 Hz, *C6*)
29.4 (d, J_{CH} = 126 Hz, *C5*)
31.4 (t, J_{CH} = 125 Hz, *C4*)
40.4 (t, J_{CH} = 126 Hz, *C3*)
57.7 (t, J_{CH} = 124 Hz, *C2*)
94.2 (s, Cp'*ring*)
315.4 (s, *C1*)

IR (KBr / cm^{-1}) 2956, 2900, 2852, 1450, 1373, 1023

(5) Spectral and analytical data for **6**



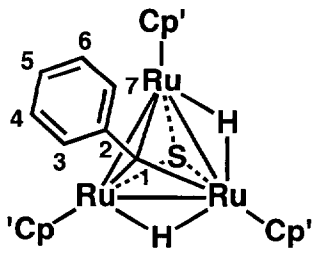
^{1}H NMR (300 MHz, C_6D_6, TMS/ppm, 298 K)
-20.27 (s, 2H, Ru-*H*)
1.16 (dq, J = 3, 12 Hz, 2H, C5-*H*)
1.5～1.6 (m, 8H, C3-*H*, C4-*H*, C6-*H*, C7-*H*)
1.93 (s, 45H, C_5Me_5)
2.59 (t, J = 11.3, 3.2 Hz, 1H, C2-*H*)

^{13}C NMR (75 MHz, C_6D_6, TMS/ppm, 298 K)
12.7 (q, J_{CH} = 126 Hz, Cp*Me*)
27.3 (t, J_{CH} = 124 Hz, *C5*)
27.9 (t, J_{CH} = 127 Hz, *C3, C6* or *C4, C7*)
33.3 (t, J_{CH} = 125 Hz, *C3, C6* or *C4, C7*)
62.4 (d, J_{CH} = 123 Hz, *C2*)
94.3 (s, Cp'*ring*)
324.6 (s, *C1*)

IR (KBr / cm^{-1}) 2956, 2898, 1776, 1450, 1373, 1024

Anal. Found (cacd for $C_{37}H_{58}SRu_3$) : C, 52.84 (53.03); H, 6.90 (6.98)

(6) Spectral data for **7**



^{1}H NMR (300 MHz, THF-d_8, TMS/ppm, 298 K)

-20.15 (s, 2H, Ru-*H*)

1.75 (s, 45H, C_5*Me*$_5$)

6.80 (tt, *J* = 7 , 2 Hz, 1H, *p*-Ph*H*)

6.97 (t, *J* = 7 Hz, 2H, *m*-Ph*H*)

7.00 (d, *J* = 7 Hz, 2H, *o*-Ph*H*)

^{13}C NMR (75 MHz, C_6D_6, TMS/ppm, 298 K)

11.5 (q, J_{CH} = 127 Hz, Cp*Me*)

94.7 (s, Cp'*ring*)

122.1 (d, J_{CH} = 160 Hz, *C5*)

126.6 (d, J_{CH} = 158 Hz, *C4, C6*)

126.6 (d, J_{CH} = 158 Hz, *C3, C7*)

162.1 (s, *ipso-Ph*)

297.0 (s, *C1*)

IR (KBr, cm^{-1}) 2973, 2898, 1583, 1450, 1371, 1261, 1068, 1025, 905, 799

Reaction of $\{(C_5Me_5)Ru\}_3(\mu_3\text{-}S)(\mu\text{-}H)_3$ (**1**) with hexane

All manipulations were carried out under an argon atmosphere with use of standard Schlenk techniques.

A 50-mL glass autoclave was charged with 55.1 mg of $\{(C_5Me_5)Ru\}_3(\mu_3\text{-}S)(\mu\text{-}H)_3$ (**1**) (0.074 mmol), and the reactor was evacuated to admit atmospheric pressure argon. Then 5 mL of hexane was added to the reactor under argon atmosphere. The color of the solution changed from dark green to brown after heating for 4.5 days at 170 °C. Removal of the solvent under reduced pressure gave brown solid. The solid was dissolved in toluene and the product was purified by the use of column chromatography on neutral alumina. Removal of solvent under reduced pressure afforded 40.3 mg of **2** as brown solid (66 % yield). Pure **2** was obtained from cold pentane solution as a red single-crystal.