Supporting Information for the article

Synthesis of Diruthenium μ-η^4-α-Diimine Complex via Dehydrogenative Coupling of Cyclic Amines and Its Role in Dehydrogenative Oxidation of Pyrrolidine

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Contents

1. NMR Spectra of Compounds

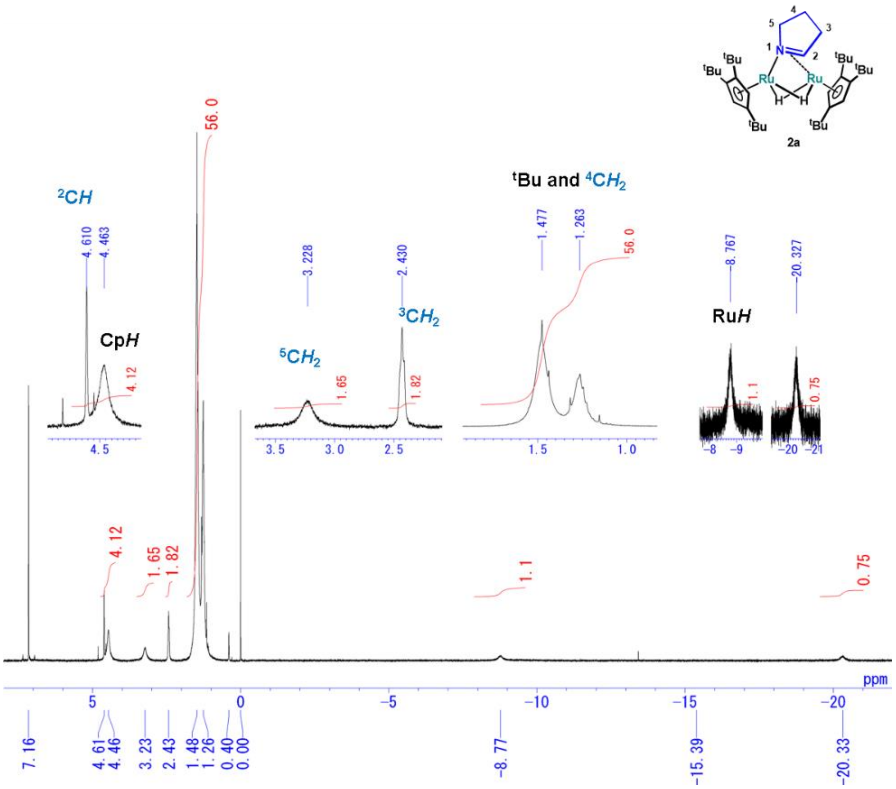

Figure S1. ^{1}H NMR spectrum of **2a** (400 MHz, C_6D_6, 25 °C).

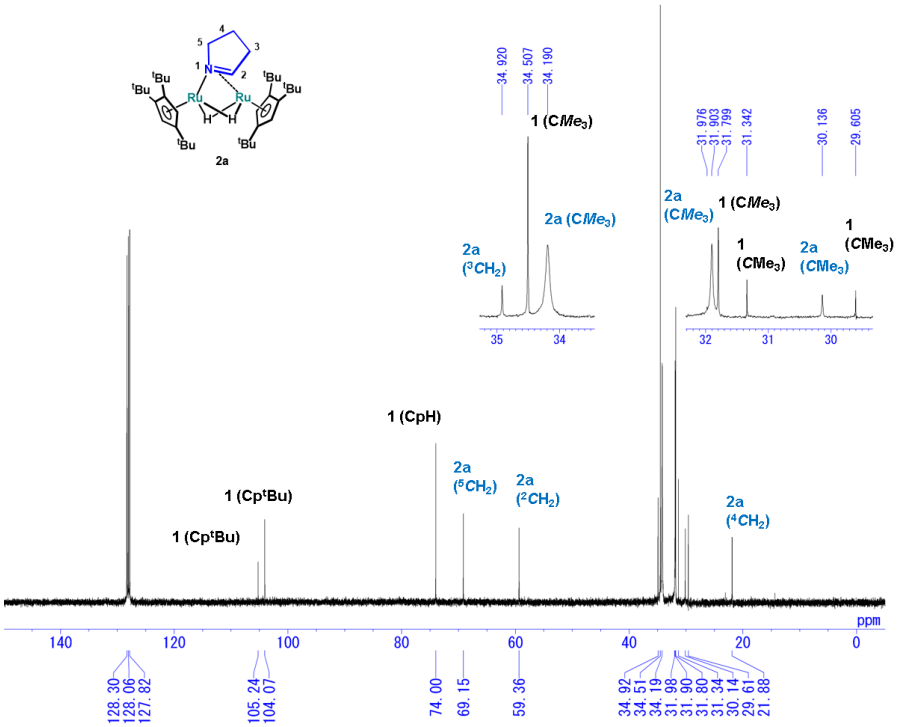

Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum of the mixture of **2a** and **1** in a molar ratio of 1/0.3. (100 MHz, C_6D_6, 25 °C).

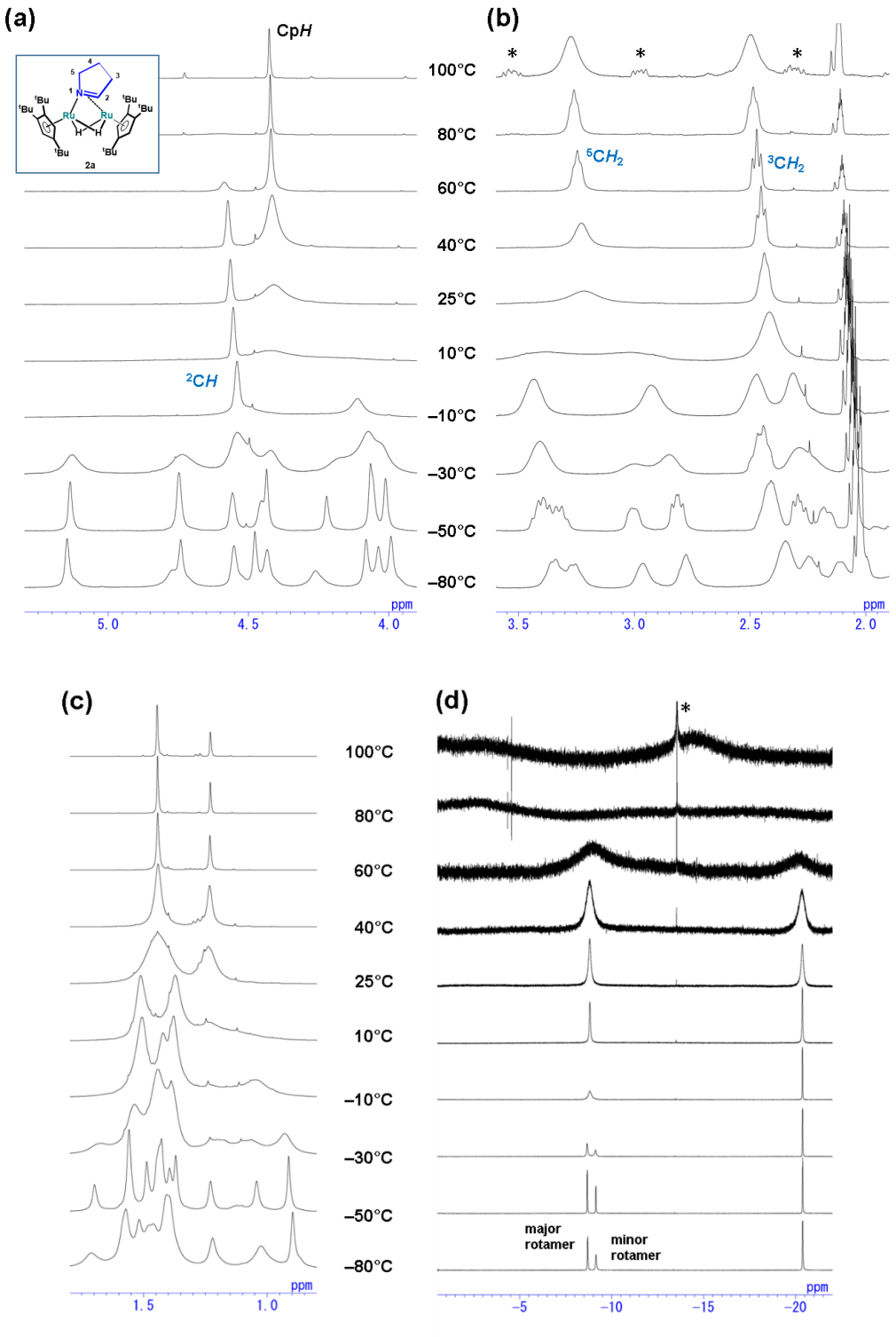

Figure S3. Variable temperature ^{1}H NMR spectra of **2a** showing (a) CpH and methine, (b) methylene, (c) ^{t}Bu, and (d) hydride regions. Signals marked with an asterisk derived from **5a** and **1** formed from thermal decomposition of **2a**. (400 MHz, toluene-d_8).

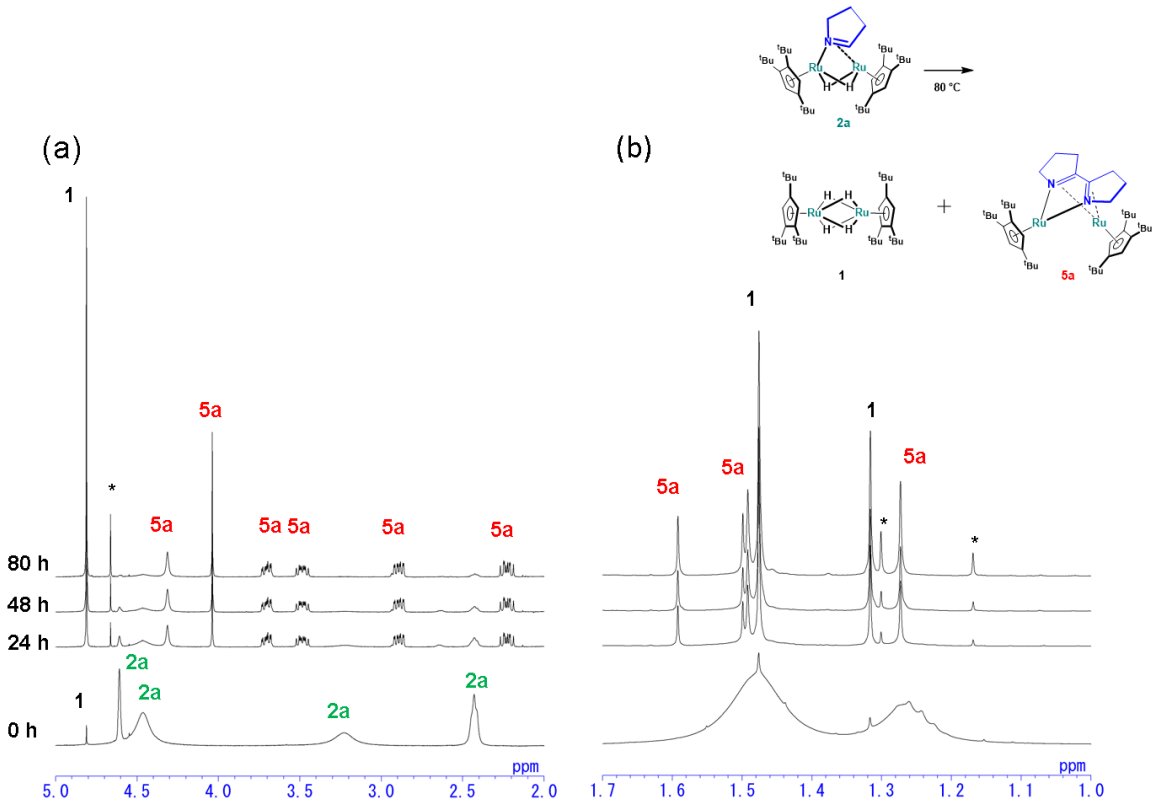

Figure S4. ^{1}H NMR spectra of a mixture obtained from the thermolysis of **2a** at 80 °C recorded after 0, 24, 48, and 80 h, showing (a) CpH and methylene and (b) ^{t}Bu regions. Signals marked with an asterisk were derived from unidentified byproducts (400 MHz, C_6D_6, 25 °C).

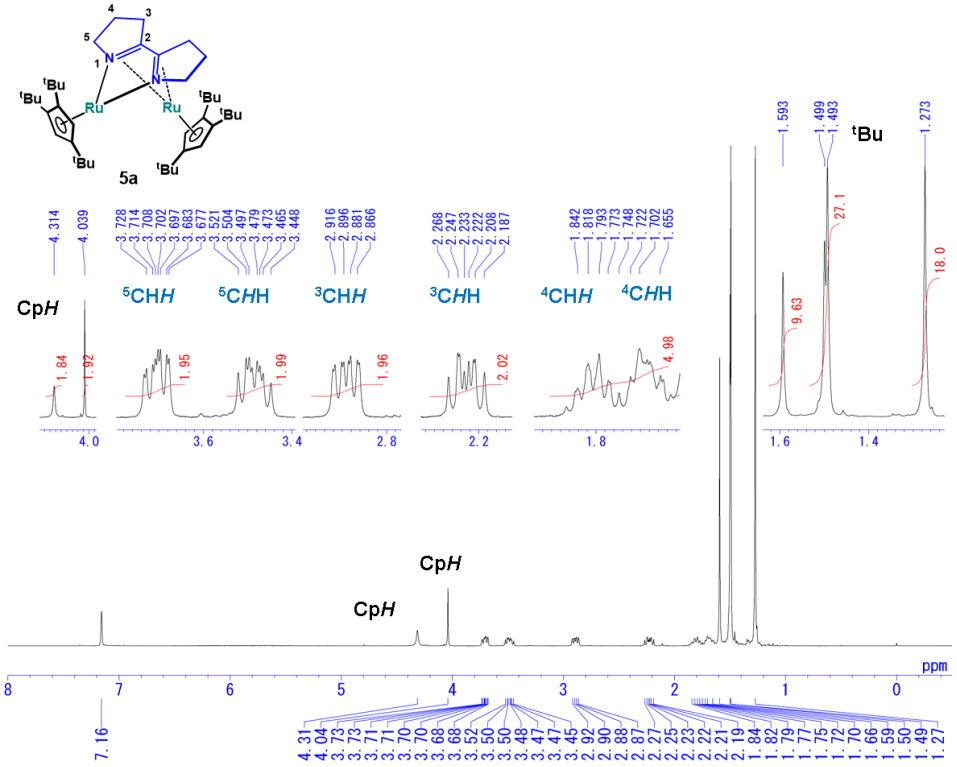

Figure S5. ^{1}H NMR spectrum of **5a** (400 MHz, C_6D_6, 25 °C).)

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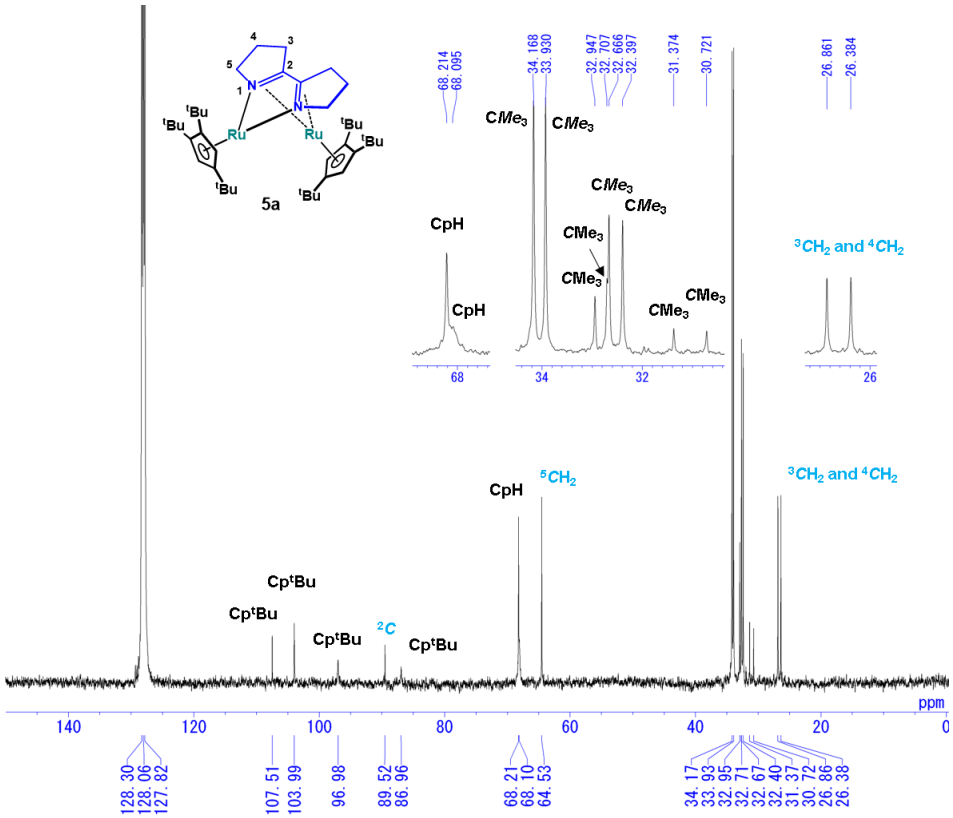


Figure S6. ^{13}C{^{1}H} NMR spectrum of the mixture of **5a** (100 MHz, C_6D_6, 25 °C).

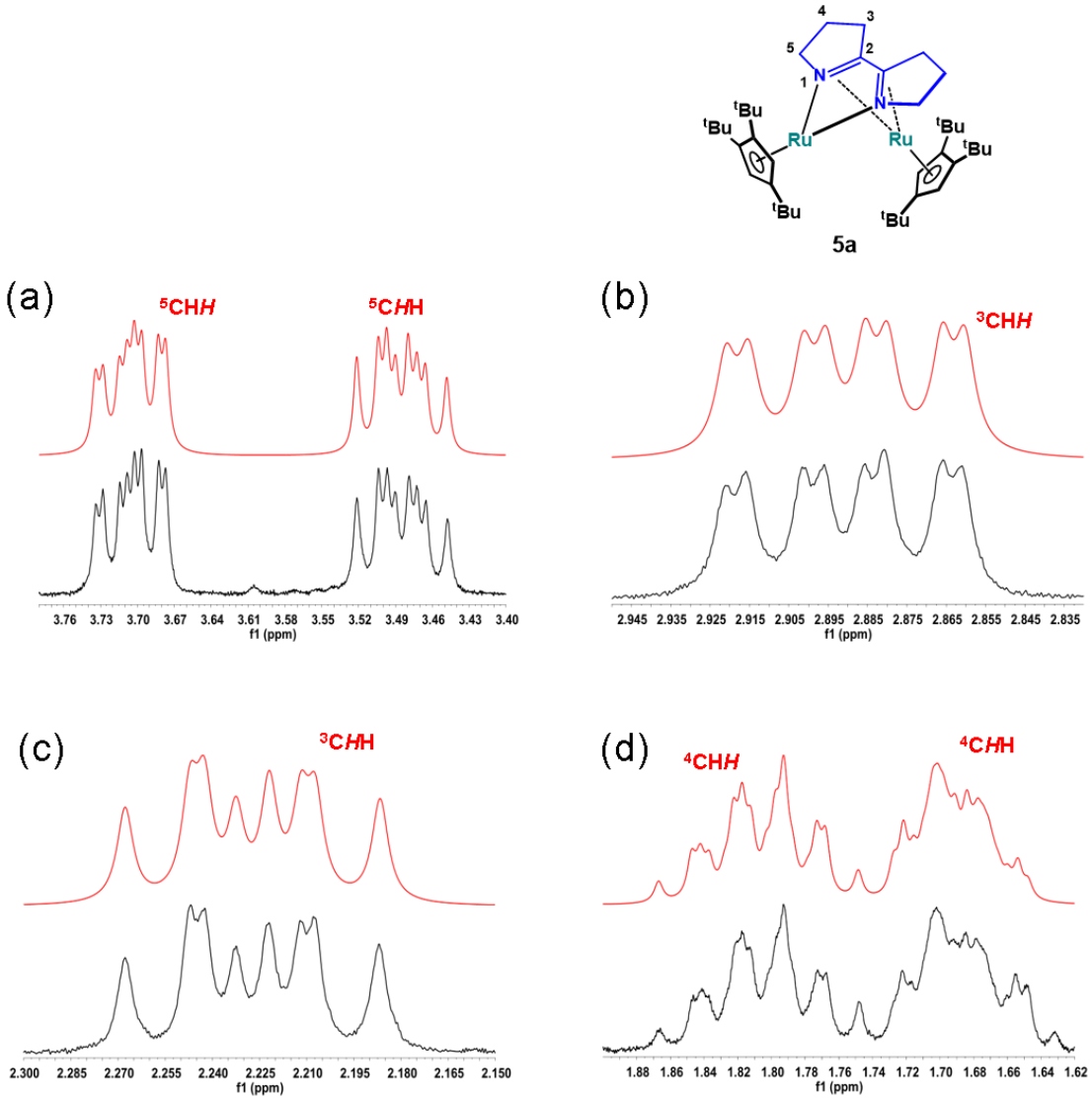


Figure S7. Shapes of ^{1}H NMR signals derived from the methylene protons of the μ-η^4-α-diimine moiety of **5a** (black) and their simulated signals (red) (400 MHz, C_6D_6, 25 °C).

Table S1. Estimate coupling parameters for the simulation of **5a**.

	Shift/ppm	Width	Coupling constant / Hz				
			3.704 (C^5)	3.486 (C^5)	2.890 (C^3)	2.227 (C^3)	1.806 (C^4)
C^5H*H*	3.704	2.60					
C^5*H*H	3.486	2.50	–12.60				
C^3H*H*	2.890	2.50	0.00	0.00			
C^3*H*H	2.227	2.50	0.00	0.00	–14.02		
C^4H*H*	1.806	2.50	7.80	9.80	7.90	10.10	
C^4*H*H	1.690	2.50	2.40	6.90	2.20	8.10	–12.00

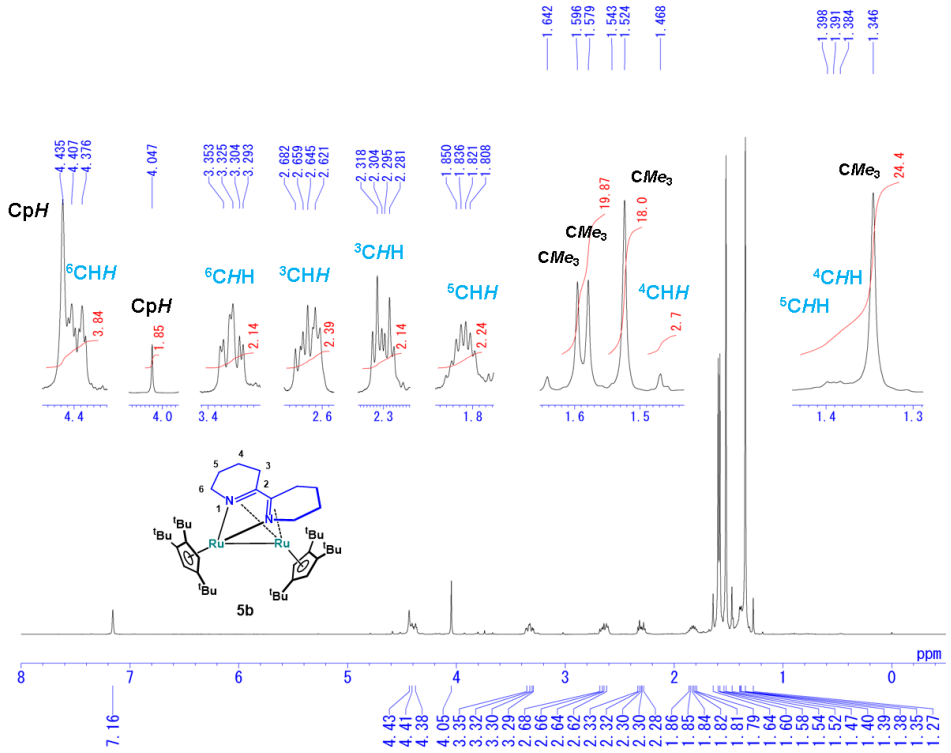


Figure S8. ^{1}H NMR spectrum of **5b** (400 MHz, C_6D_6, 25 °C).

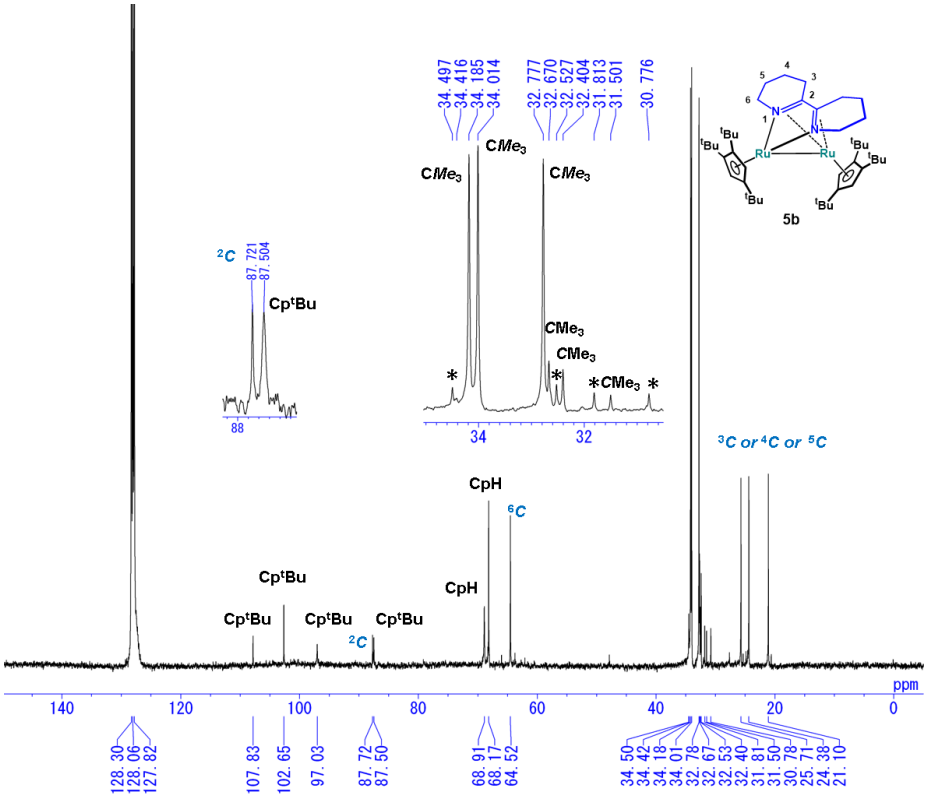


Figure S9. ^{13}C{^{1}H} NMR spectrum of **5b**. Signals marked with an asterisk are derived from unidentified impurities (100 MHz, C_6D_6, 25 °C).

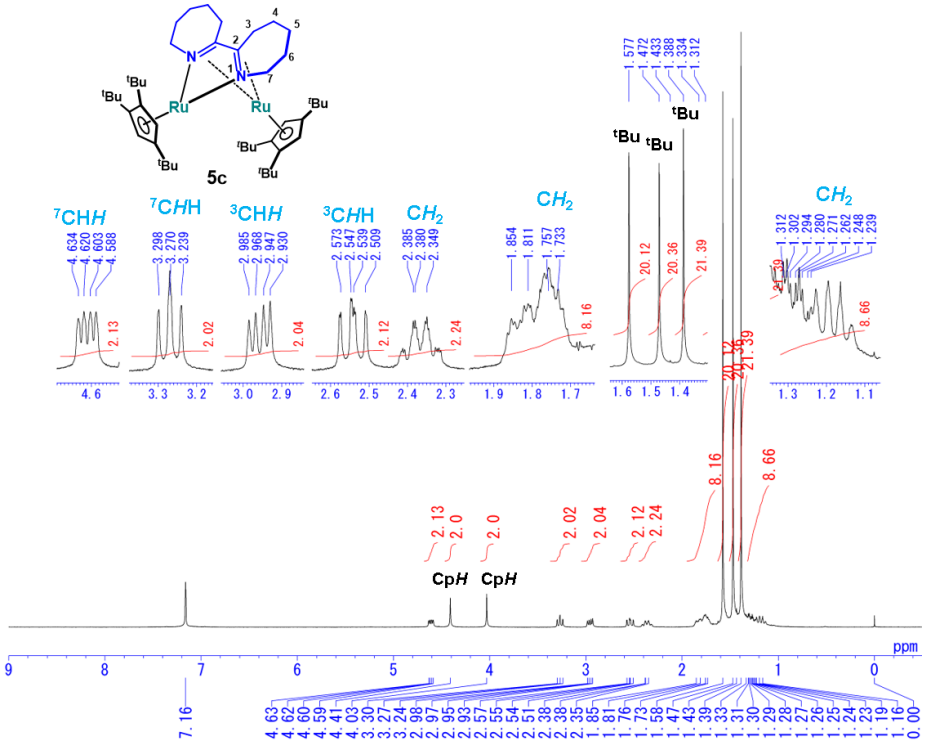


Figure S10. ^{1}H NMR spectrum of **5c** (400 MHz, C_6D_6, 80 °C).

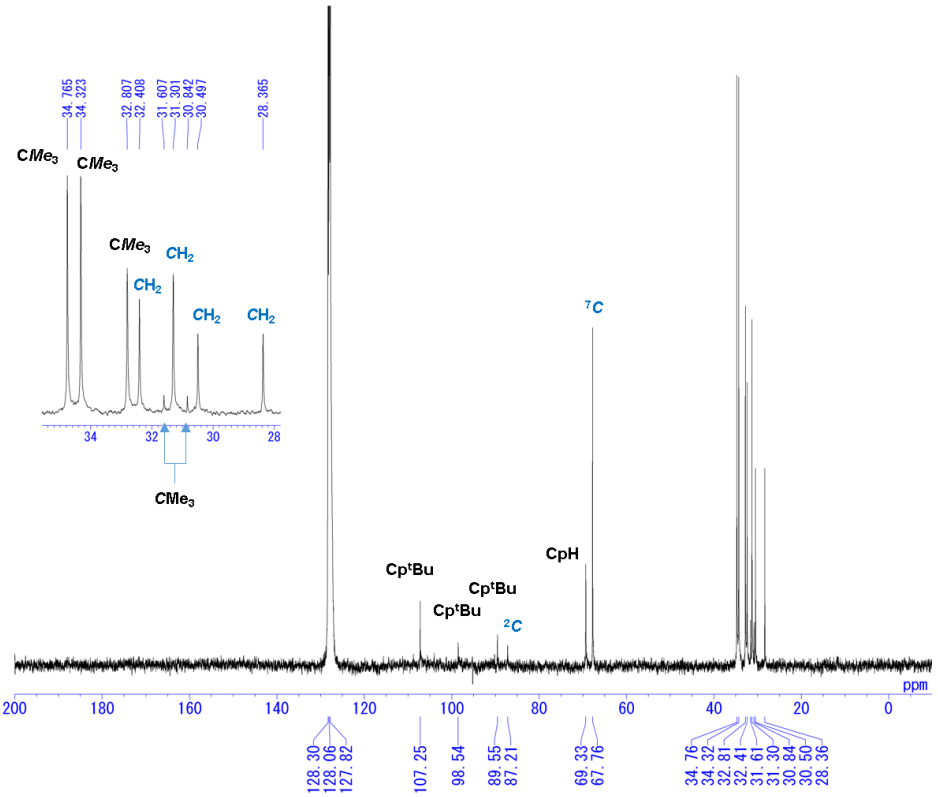


Figure S11. ^{13}C{^{1}H} NMR spectrum of **5c**. One quaternary carbon signal of the ^{t}Bu groups could not be found, presumably due to the overlap with the methylene or methyl signals (100 MHz, C_6D_6, 80 °C).

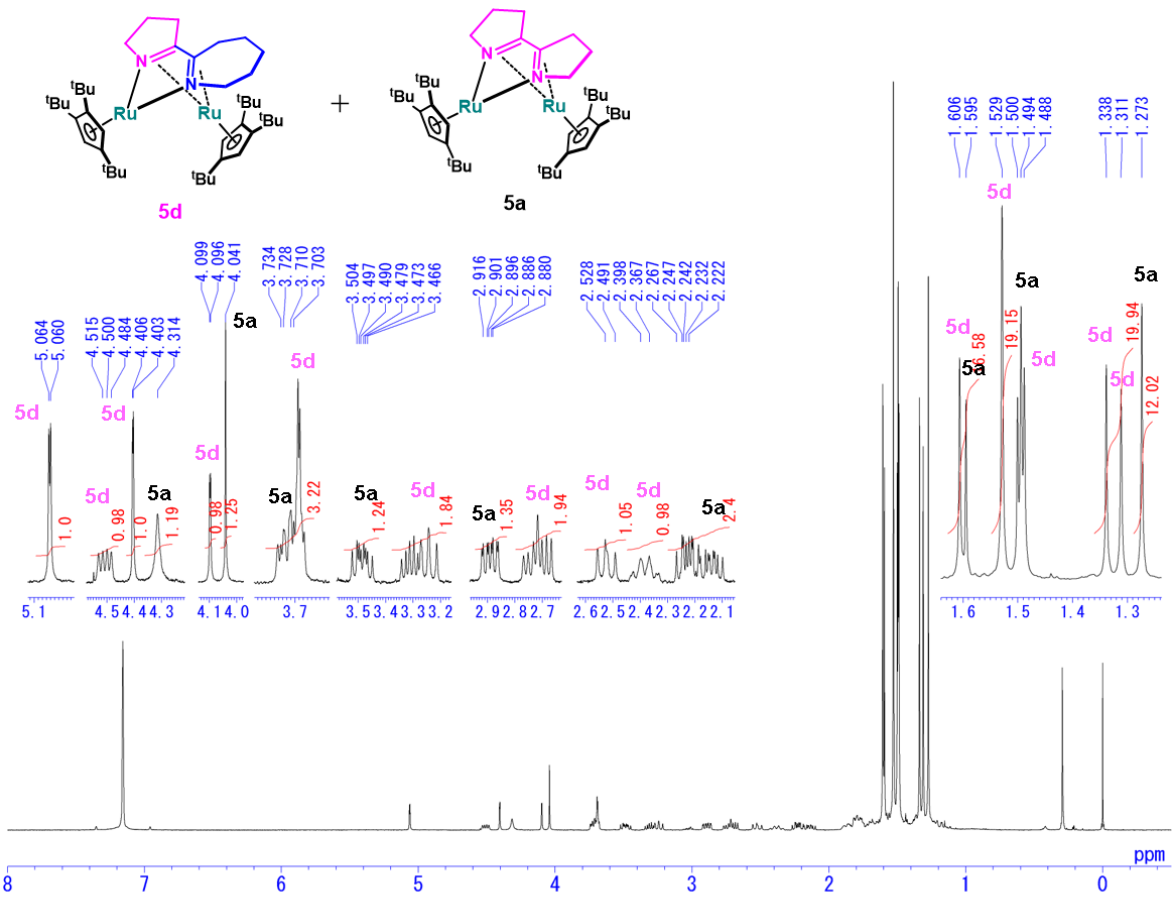


Figure S12. ^{1}H NMR spectrum of a mixture of **5a** and **5d** in a molar ratio of 38:62 obtained from the reaction of **3c** with 1-pyrroline (400 MHz, C_6D_6, 25 °C)

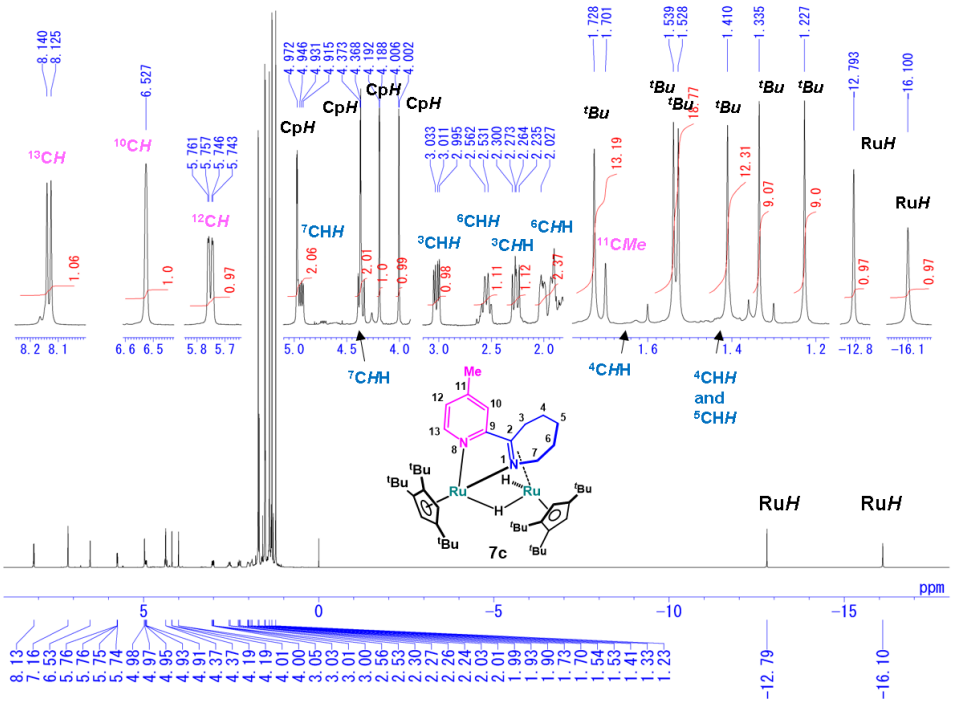


Figure S13. ^{1}H NMR spectrum of **7c** (400 MHz, C_6D_6, 25 °C).

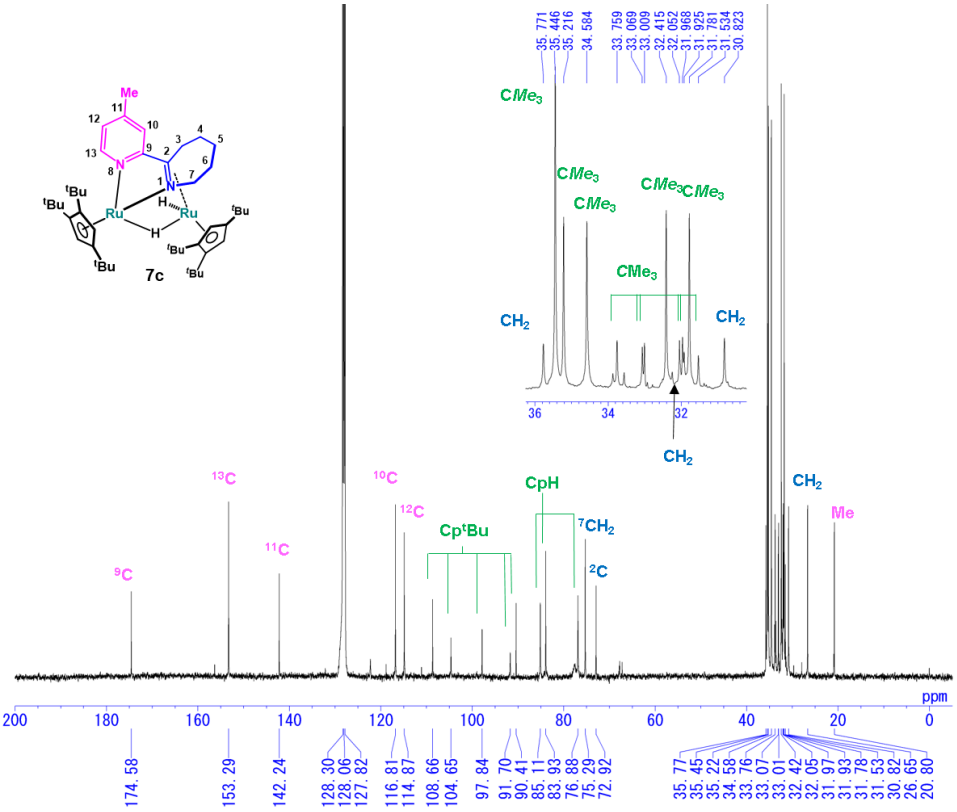


Figure S14. ^{13}C{^{1}H} NMR spectrum of **7c** (100 MHz, C_6D_6, 25 °C).

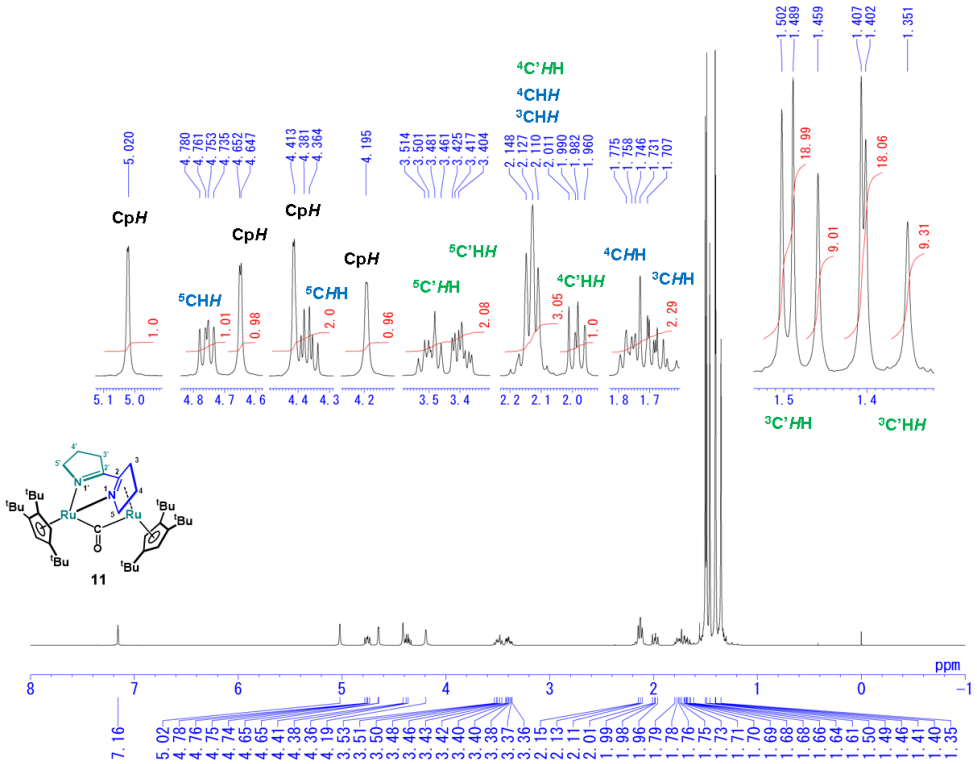


Figure S15. ^{1}H NMR spectrum of **11** (400 MHz, C_6D_6, 25 °C).

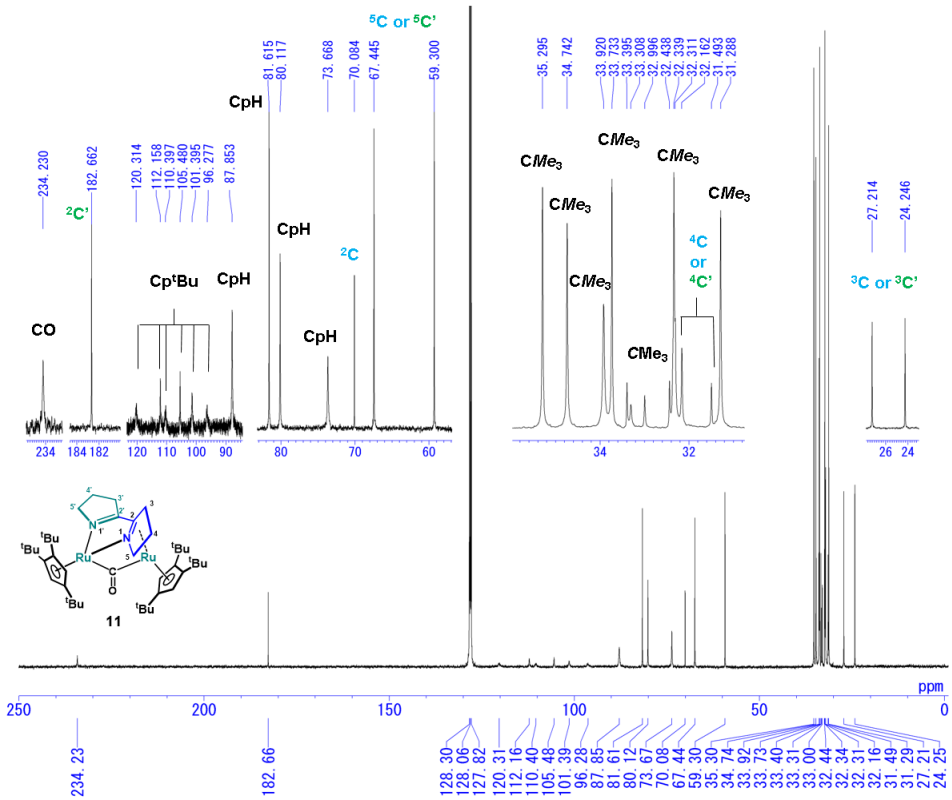
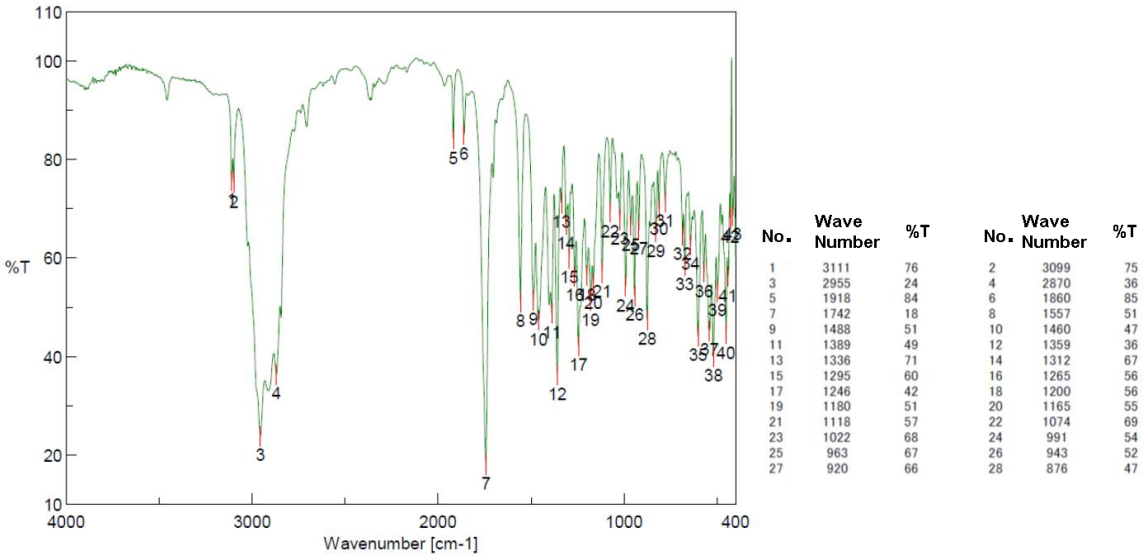


Figure S16. $^{13}C\{^{1}H\}$ NMR spectrum of **11** (100 MHz, C_6D_6, 25 °C).



No.	Wave Number	%T	No.	Wave Number	%T
1	3111	76	2	3099	75
3	2955	24	4	2870	36
5	1918	84	6	1860	85
7	1742	18	8	1557	51
9	1488	51	10	1460	47
11	1389	49	12	1359	36
13	1336	71	14	1312	67
15	1295	60	16	1265	56
17	1246	42	18	1200	56
19	1180	51	20	1165	55
21	1118	57	22	1074	69
23	1022	68	24	991	54
25	963	67	26	943	52
27	920	66	28	876	47

Figure S17. IR spectrum of **11** (KBr).

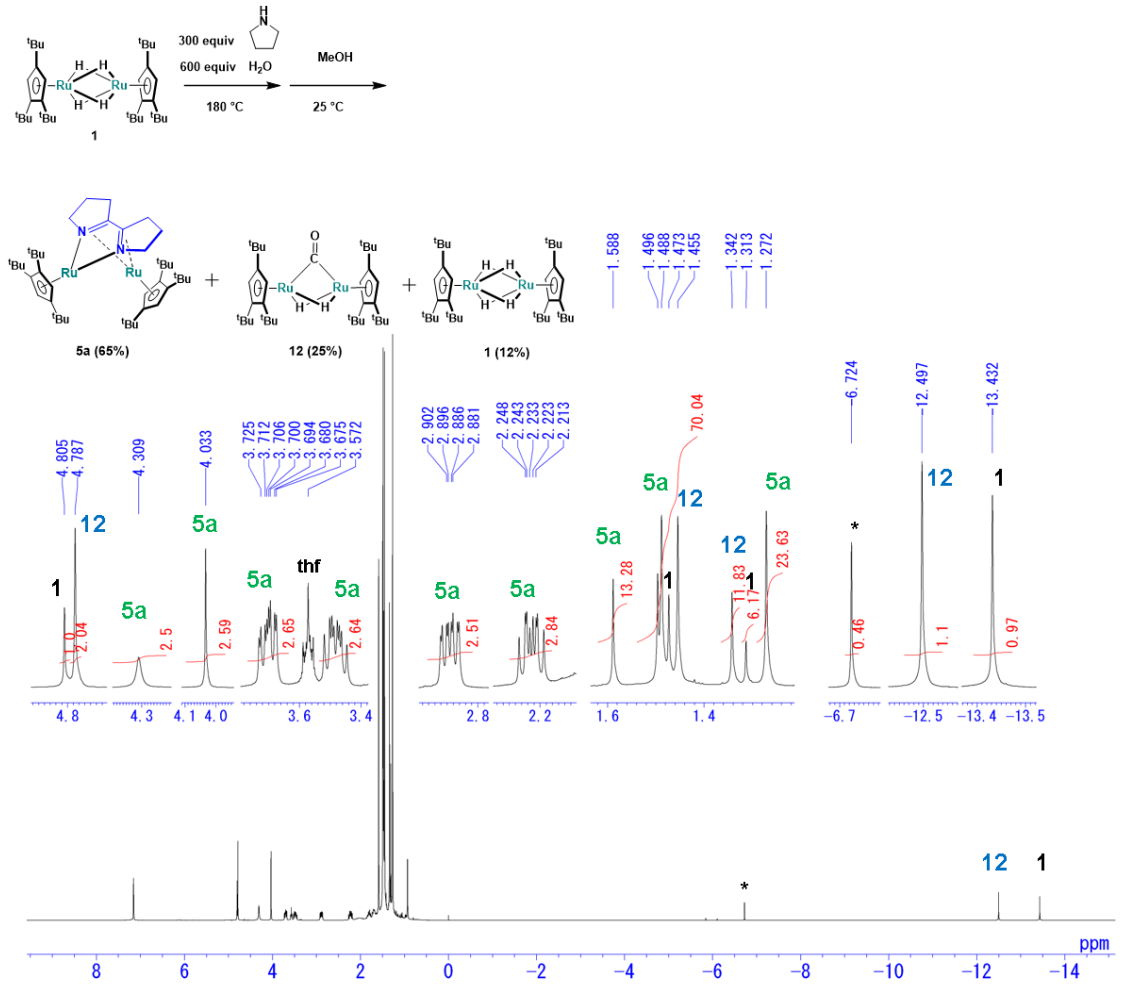


Figure S18. ^{1}H NMR spectrum of the mixture formed after the catalytic reaction of **1** with pyrrolidine. A hydrido signal marked with an asterisk is derived from an unidentified byproduct. (400 MHz, C_6D_6, 25 °C).

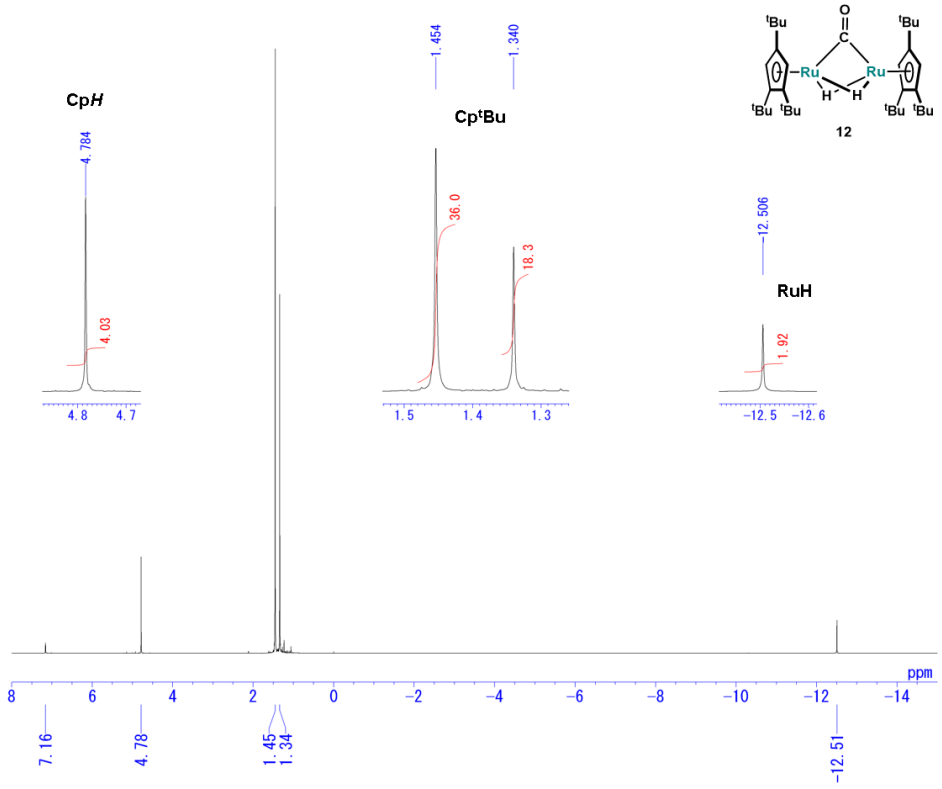


Figure S19. ^{1}H NMR spectrum of **12** (400 MHz, C_6D_6, 25 °C).

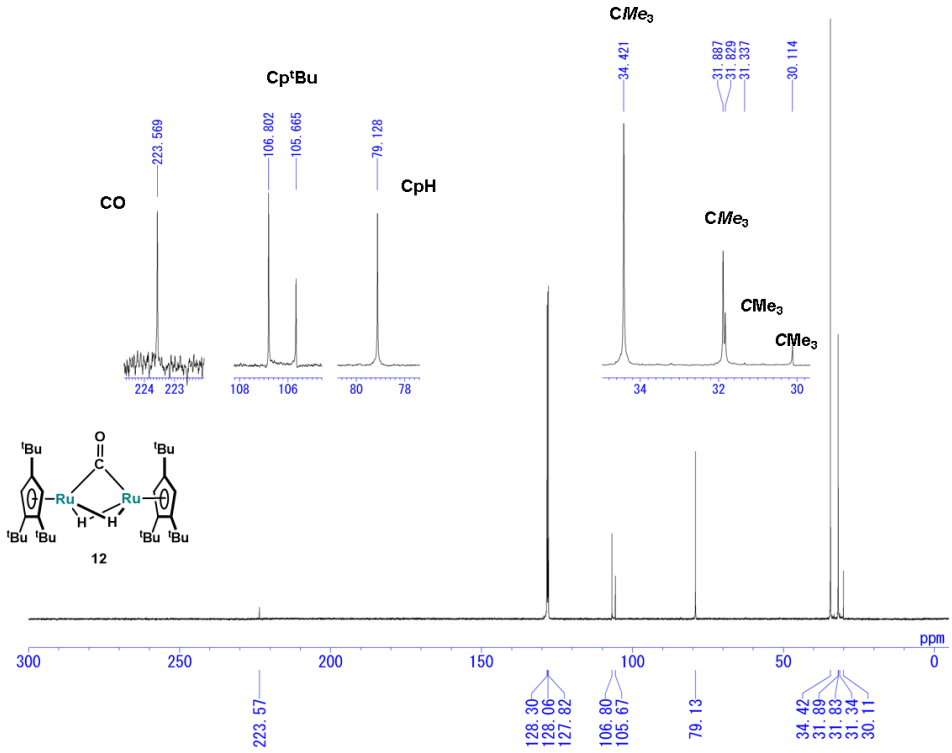
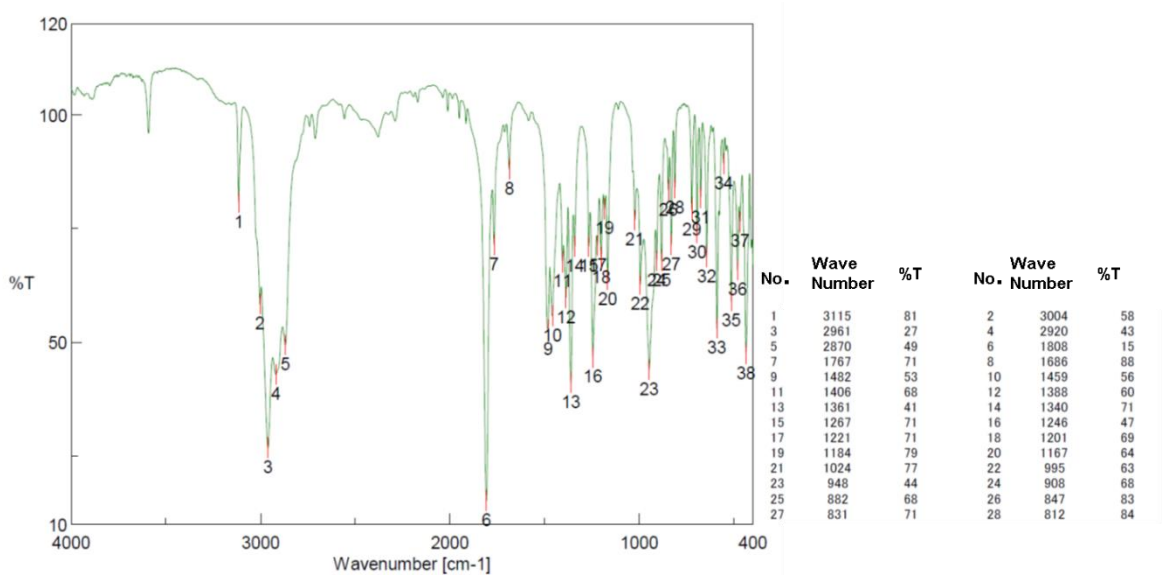


Figure S20. ^{13}C{^{1}H} NMR spectrum of **12** (100 MHz, C_6D_6, 25 °C).



No.	Wave Number	%T	No.	Wave Number	%T
1	3115	81	2	3004	58
3	2961	27	4	2920	43
5	2870	49	6	1808	15
7	1767	71	8	1686	88
9	1482	53	10	1459	56
11	1406	68	12	1388	60
13	1361	41	14	1340	71
15	1267	71	16	1246	47
17	1221	71	18	1201	69
19	1184	79	20	1167	64
21	1024	77	22	995	63
23	948	44	24	908	68
25	882	68	26	847	83
27	831	71	28	812	84

Figure S21. IR spectrum of **12** (KBr).

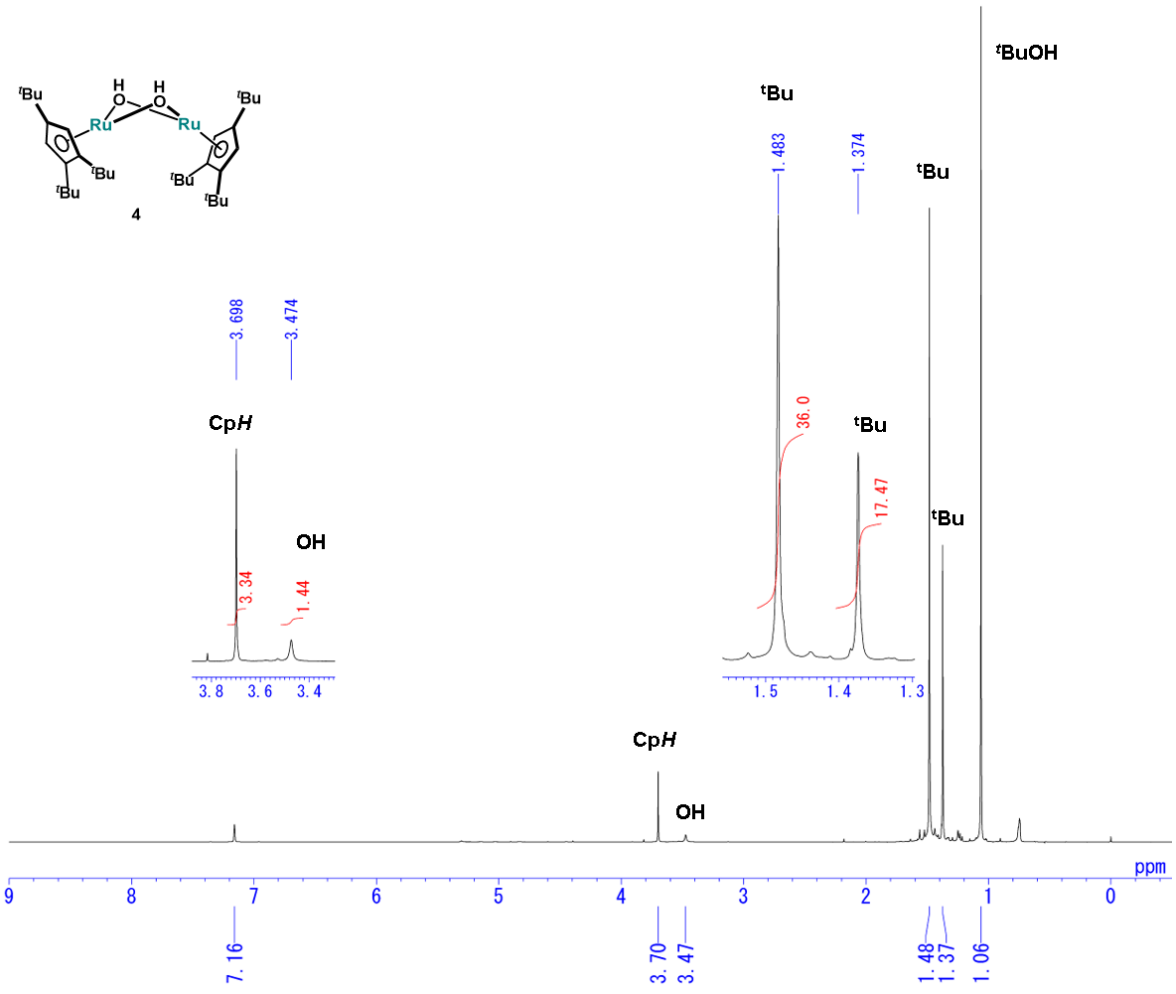


Figure S22. ^{1}H NMR spectrum of **4** (400 MHz, C_6D_6, 25 °C).

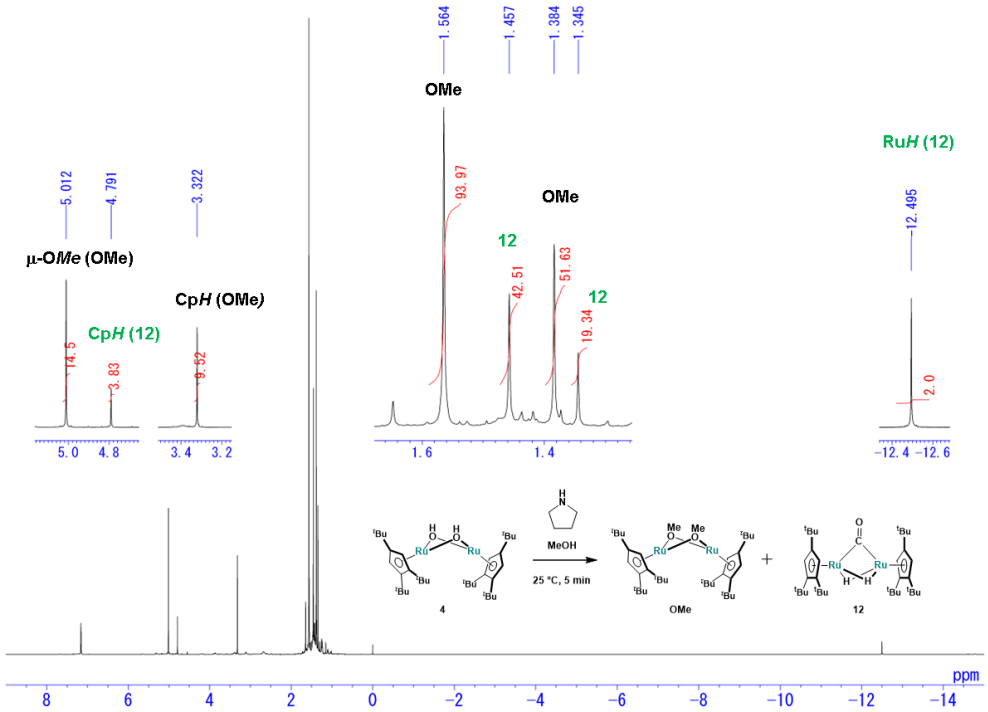


Figure S23. ^{1}H NMR spectrum of the mixture obtained from the reaction of **4** with MeOH min in the presence of pyrrolidine (400 MHz, C_6D_6, 25 °C).

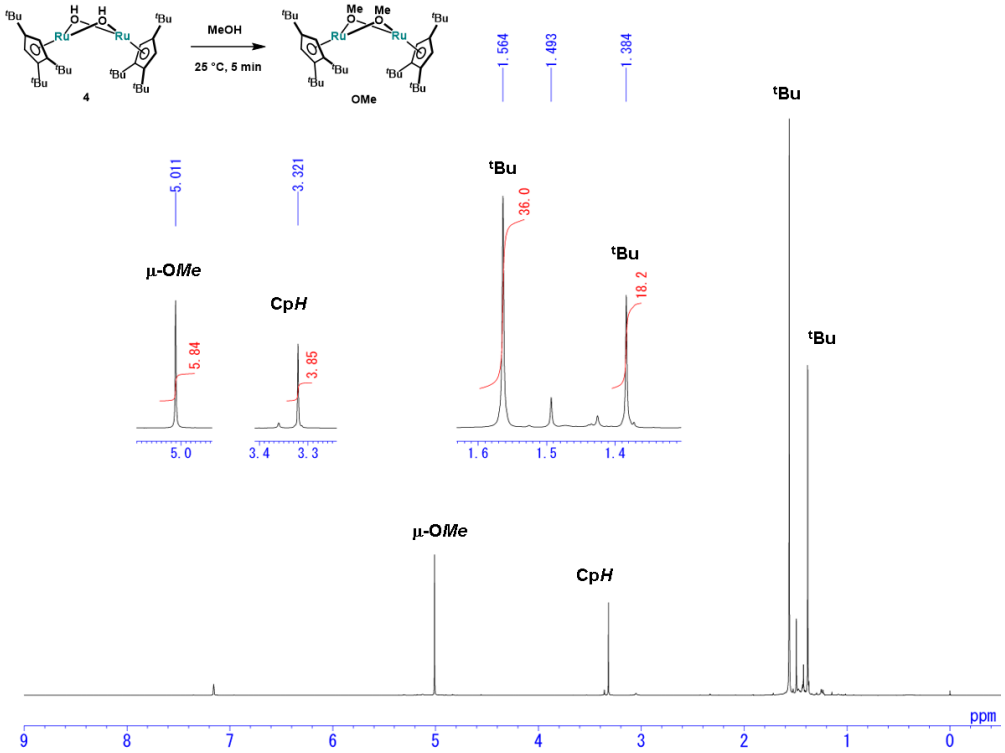


Figure S24. ^{1}H NMR spectrum of the mixture obtained from the reaction of **4** with MeOH (400 MHz, C_6D_6, 25 °C).

2. Crystal data and results of XRD studies

Table S2. Crystallographic Data for **2a**, **5a**, **5b**, **5c**, **5d**, **7c**, **11**, and **12**.

	2a	**5a**	**5b**	**5c**
(a) Crystal data				
Empirical formula	$C_{38}H_{67}NRu_2$	$C_{42}H_{70}N_2Ru_2$	$C_{44}H_{74}N_2Ru_2$	$C_{46}H_{78}N_2Ru_2$
Formula weight	740.06	805.14	833.19	861.24
Crystal description	Block	Block	Block	Block
Crystal color	Purple	Orange	Orange	Red
Crystal size (mm)	0.176×0.149×0.109	0.173×0.159×0.106	0.321×0.171×0.125	0.274×0.149× 0.115
Crystalizing solution	*n*-hexane (–30 °C)	THF (25 °C)	*n*-hexane (–30 °C)	*n*-hexane (0 °C)
Crystal system	Triclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	*P*-1(#2)	$P2_1$/n (#14)	*P*bca (#61)	*C*2/c (#15)
a (Å)	10.7174(4)	10.5579(5)	16.9579(4)	14.6002(9)
b (Å)	11.7914(6)	33.9623(12)	17.0098(5)	16.8492(11)
c (Å)	15.5572(6)	11.0622(5)	28.8179(8)	18.1756(10)
α (°)	106.892(2)			
β (°)	90.1440(10)	97.3520(10)		99.985(2)
γ (°)	100.581(2)			
Volume (Å^3)	1845.93(14)	3934.0(3)	8312.5(4)	4403.5(5)
Z value	2	4	8	4
D_{calc} (g/cm^3)	1.331	1.359	1.332	1.299
Measurement temp. (°C)	–150	–150	–130	–150
μ(MoKα) (mm^{-1})	0.843	0.798	0.758	0.717
(b) Intensity measurements				
Diffractometer	Rigaku R-AXIS RAPID	Rigaku R-AXIS RAPID	Rigaku R-AXIS RAPID	Rigaku R-AXIS RAPID
Radiation	MoKα (λ = 0.71069 Å)	MoKα (λ = 0.71069 Å)	MoKα (λ = 0.71069 Å)	MoKα (λ = 0.71069 Å)
Monochromator	Graphite	Graphite	Graphite	Graphite
2θmax (°)	55	55	55	55
Reflections collected	18552	38688	78815	21769
Independent reflections	8412 (R_{int} = 0.0371)	9009 (R_{int} = 0.0661)	9473 (R_{int} = 0.0623)	5033 (R_{int} = 0.0826)
Reflections observed (>2σ)	7232	7227	7749	3623
Abs. Correction type	Empirical	Empirical	Empirical	Numerical
Abs. Transmission	0.5642 (min) 1.0000 (max)	0.5729 (min) 1.0000 (max)	0.5701 (min) 1.0000 (max)	0.8612 (min) 1.0000 (max)
(c) Refinement (Shelxl-2018/3)				
R_1 ($I > 2\sigma(I)$)	0.0283	0.0499	0.0358	0.0519
wR_2 ($I > 2\sigma(I)$)	0.0607	0.0913	0.0819	0.1131
R_1 (all data)	0.0350	0.0672	0.0487	0.0789
wR_2 (all data)	0.0639	0.0987	0.0870	0.1503
Data/Restraints/Parameters	8412 / 0 / 424	9009 / 0 / 433	9473 / 0 / 483	5033 / 0 / 275
GOF	1.054	1.048	1.022	1.108
Largest diff. Peak and hole (e. Å^{-3})	0.975 and –0.575	3.070 and –1.694	1.201 and –0.926	1.139 and –1.401
CCDC deposition number	2296342	2296343	2296344	2296345

Table S2. Crystallographic Data for **2a**, **5a**, **5b**, **5c**, **5d**, **7c**, **11**, and **12**. (continued)

	5d	**7c**	**11**	**12**
(a) Crystal data				
Empirical formula	$C_{44}H_{74}N_2Ru_2$	$C_{46}H_{76}N_2Ru_2$	$C_{43}H_{70}N_2ORu_2$	$C_{35}H_{60}ORu_2$
Formula weight	833.19	859.22	833.15	698.97
Crystal description	Block	Block	Platelet	Block
Crystal color	Orange	Orange	Brown	Brown
Crystal size (mm)	0.108×0.075×0.061	0.176×0.162×0.150	0.238×0.225×0.097	0.344×0.294×0.152
Crystalizing solution	acetone (0 °C)	acetone (25 °C)	acetone (25 °C)	acetone (25 °C)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$ (#14)	$P2_1/n$ (#14)	$P2_1/n$ (#14)	$P2_1/n$ (#14)
a (Å)	10.7555(3)	18.4357(8)	12.2704(5)	11.7256(3)
b (Å)	35.2527(11)	11.3913(6)	16.9468(7)	10.3388(4)
c (Å)	11.1031(4)	20.9382(10)	20.4301(9)	28.2062(9)
α (°)				
β (°)	97.6250(10)	102.3070(10)	104.068(2)	91.8140(10)
γ (°)				
Volume (Å^3)	4172.6(2)	4296.1(4)	4120.9(3)	3417.69(19)
Z value	4	4	4	4
D_{calc} (g/cm^3)	1.328	1.328	1.343	1.358
Measurement temp. (°C)	–130	–150	–150	–150
μ(MoKα) (mm^{-1})	0.755	0.735	0.766	0.907
(b) Intensity measurements				
Diffractometer	Rigaku R-AXIS RAPID	Rigaku R-AXIS RAPID	Rigaku R-AXIS RAPID	Rigaku R-AXIS RAPID
Radiation	MoKα (λ = 0.71069 Å)	MoKα (λ = 0.71069 Å)	MoKα (λ = 0.71069 Å)	MoKα (λ = 0.71069 Å)
Monochromator	Graphite	Graphite	Graphite	Graphite
2θmax (°)	55	55	55	55
Reflections collected	65797	41821	65343	26962
Independent reflections	9526 (R_{int} = 0.0911)	9764 (R_{int} = 0.1012)	9419 (R_{int} = 0.0736)	6210 (R_{int} = 0.0383)
Reflections observed (>2σ)	7430	6804	7627	5930
Abs. Correction type	Empirical	Empirical	Numerical	Empirical
Abs. Transmission	0.7578 (min) 1.0000 (max)	0.5772 (min) 1.0000 (max)	0.7885 (min) 1.0000 (max)	0.7203 (min) 1.0000 (max)
(c) Refinement (Shelxl-2018/3)				
R_1 ($I > 2\sigma(I)$)	0.0457	0.0466	0.0350	0.0205
wR_2 ($I > 2\sigma(I)$)	0.0950	0.0910	0.0818	0.0524
R_1 (all data)	0.0657	0.0753	0.0472	0.0216
wR_2 (all data)	0.1041	0.1021	0.0866	0.0532
Data/Restraints/Parameters	9526 / 0 / 451	9764 / 0 / 478	9419 / 0 / 487	6210 / 0 / 416
GOF	1.068	1.040	1.056	0.963
Largest diff. Peak and hole (e. Å^{-3})	1.538 and –1.258	0.858 and –0.928	1.180 and –0.954	0.387 and –0.310
CCDC deposition number	2296346	2296347	2296348	2296349

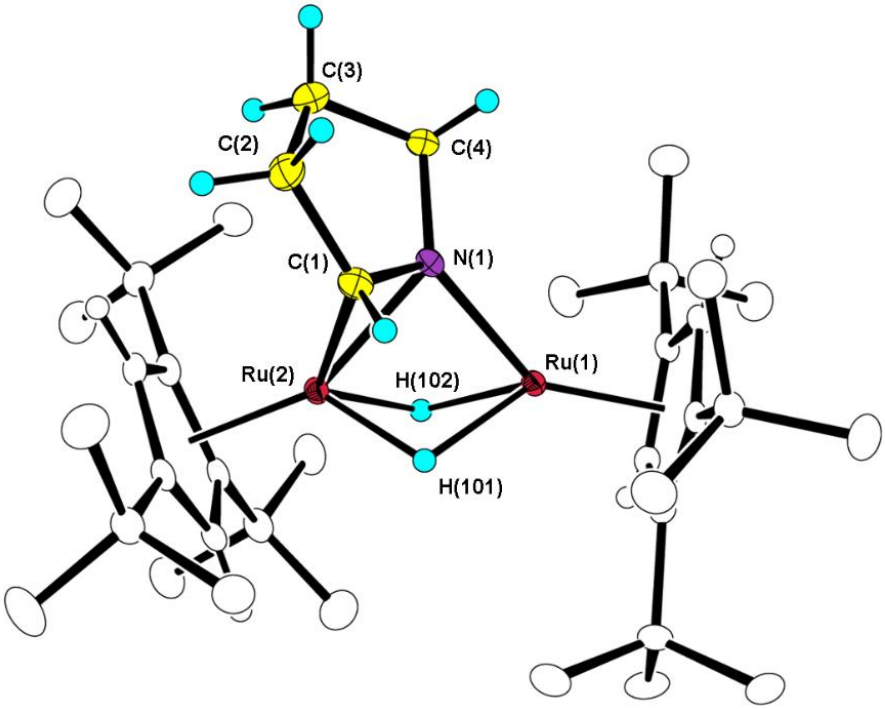


Figure S25. Molecular structures of **2a** with thermal ellipsoids at 30% probability. Hydrogen atoms in the ^{t}Bu groups were omitted for clarity.

Table S3. Selected bond lengths [Å] and angles [°] of **2a**.

Ru1 N1 2.0554(17)	C2 C3 1.534(3)	C1 Ru2 Ru1 77.79(6)	C1 N1 Ru2 71.49(11)
Ru1 Ru2 2.6290(3)	C3 C4 1.522(3)	N1 Ru2 H101 74.6(8)	C4 N1 Ru2 125.92(14)
Ru1 H101 1.81(2)		C1 Ru2 H101 77.5(8)	Ru1 N1 Ru2 77.71(6)
Ru1 H102 1.69(3)	N1 Ru1 Ru2 52.48(5)	Ru1 Ru2 H101 42.8(8)	N1 C1 C2 109.92(18)
Ru2 N1 2.1342(17)	N1 Ru1 H101 74.3(7)	N1 Ru2 H102 79.4(9)	N1 C1 Ru2 70.67(11)
Ru2 C1 2.145(2)	Ru2 Ru1 H101 39.2(7)	C1 Ru2 H102 114.4(9)	C2 C1 Ru2 123.61(15)
Ru2 H101 1.68(2)	N1 Ru1 H102 81.6(9)	Ru1 Ru2 H102 38.8(9)	C1 C2 C3 103.68(18)
Ru2 H102 1.68(3)	Ru2 Ru1 H102 38.6(9)	H101 Ru2 H102 66.9(12)	C4 C3 C2 103.53(19)
N1 C1 1.387(3)	H101 Ru1 H102 63.9(12)	C1 N1 C4 109.52(17)	N1 C4 C3 105.63(18)
N1 C4 1.477(3)	N1 Ru2 C1 37.84(7)	C1 N1 Ru1 121.47(14)	
C1 C2 1.520(3)	N1 Ru2 Ru1 49.81(5)	C4 N1 Ru1 128.82(14)	

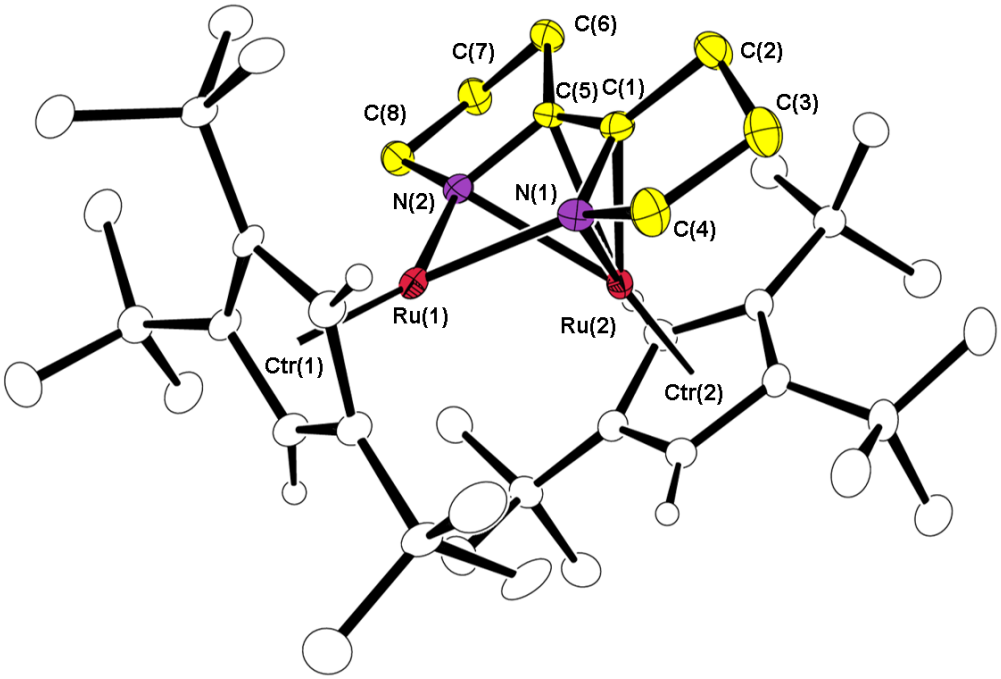


Figure S26. Molecular structures of **5a** with thermal ellipsoids at 30% probability. Hydrogen atoms in the ^{t}Bu groups and α-diimine moiety were omitted for clarity.

Table S4. Selected bond lengths [Å] and angles [°] of **5a**.

Ru1 N1 2.015(3)	C6 C7 1.532(6)	C1 N1 C4 107.6(3)	C5 C1 Ru2 71.0(2)
Ru1 N2 2.058(3)	C7 C8 1.518(6)	C1 N1 Ru1 120.2(3)	C2 C1 Ru2 133.1(3)
Ru1 Ru2 2.9274(4)		C4 N1 Ru1 128.4(3)	C1 C2 C3 101.6(3)
Ru2 C5 2.178(4)	N1 Ru1 N2 74.03(13)	C1 N1 Ru2 69.7(2)	C2 C3 C4 103.8(3)
Ru2 C1 2.189(4)	N1 Ru1 Ru2 49.81(9)	C4 N1 Ru2 129.8(3)	N1 C4 C3 106.1(3)
Ru2 N2 2.235(3)	N2 Ru1 Ru2 49.59(9)	Ru1 N1 Ru2 86.78(12)	C1 C5 N2 112.4(3)
Ru2 N1 2.240(3)	C5 Ru2 C1 37.19(14)	C5 N2 C8 105.9(3)	C1 C5 C6 134.5(4)
N1 C1 1.387(5)	C5 Ru2 N2 36.82(13)	C5 N2 Ru1 118.5(2)	N2 C5 C6 112.8(3)
N1 C4 1.474(5)	C1 Ru2 N2 63.13(13)	C8 N2 Ru1 133.0(3)	C1 C5 Ru2 71.8(2)
N2 C5 1.395(5)	C5 Ru2 N1 63.04(13)	C5 N2 Ru2 69.4(2)	N2 C5 Ru2 73.8(2)
N2 C8 1.479(5)	C1 Ru2 N1 36.50(13)	C8 N2 Ru2 126.0(3)	C6 C5 Ru2 127.3(3)
C1 C5 1.392(5)	N2 Ru2 N1 66.45(12)	Ru1 N2 Ru2 85.89(12)	C5 C6 C7 101.2(3)
C1 C2 1.502(5)	C5 Ru2 Ru1 69.82(10)	N1 C1 C5 112.4(3)	C8 C7 C6 102.6(3)
C2 C3 1.530(6)	C1 Ru2 Ru1 69.16(11)	N1 C1 C2 112.4(3)	N2 C8 C7 106.5(3)
C3 C4 1.530(6)	N2 Ru2 Ru1 44.52(8)	C5 C1 C2 133.8(4)	
C5 C6 1.500(5)	N1 Ru2 Ru1 43.40(9)	N1 C1 Ru2 73.8(2)	

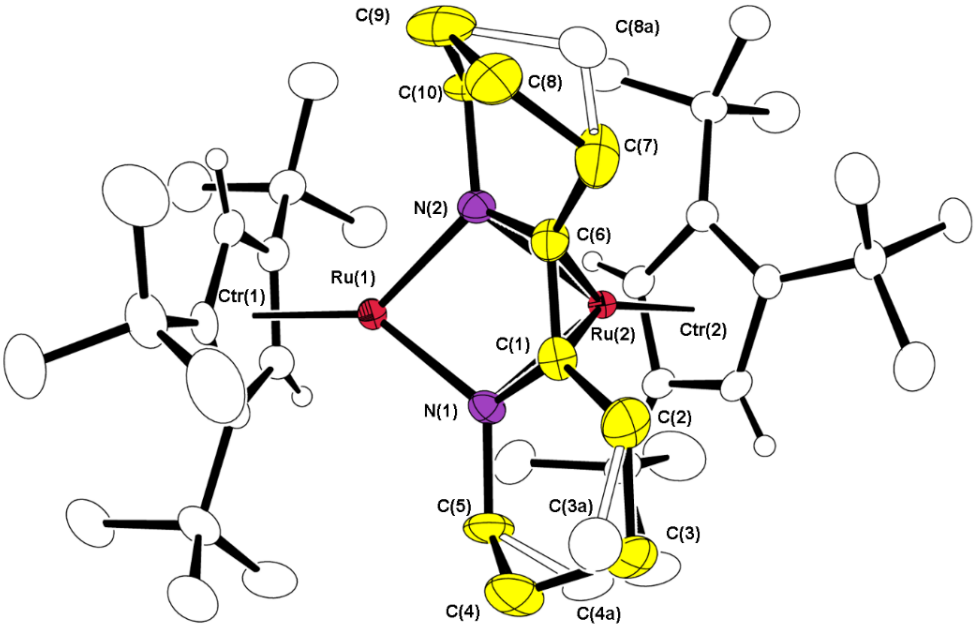


Figure S27. Molecular structures of **5b** with thermal ellipsoids at 30% probability. Hydrogen atoms in the ^{t}Bu groups and α-diimine moiety were omitted for clarity.

Table S5. Selected bond lengths [Å] and angles [°] of **5b**.

Ru1 N2 2.050(2)	C7 C8A 1.267(11)	C1 N1 C5 117.2(2)	C4 C3 C2 108.9(6)
Ru1 N1 2.070(2)	C7 C8 1.529(6)	C1 N1 Ru1 118.19(19)	C5 C4 C3 109.5(6)
Ru1 Ru2 2.9259(3)	C8 C8A 1.194(12)	C5 N1 Ru1 123.41(19)	C2 C3A C4A 107.7(10)
Ru2 C1 2.177(3)	C8 C9 1.487(7)	C1 N1 Ru2 70.24(15)	C3A C4A C5 111.9(10)
Ru2 C6 2.189(3)	C8A C9 1.806(12)	C5 N1 Ru2 123.2(2)	C4 C5 N1 115.4(4)
Ru2 N1 2.211(2)	C9 C10 1.523(4)	Ru1 N1 Ru2 86.17(8)	N1 C5 C4A 112.2(4)
Ru2 N2 2.220(2)		C6 N2 C10 113.0(2)	N2 C6 C1 112.9(3)
N1 C1 1.389(4)	N2 Ru1 N1 73.93(9)	C6 N2 Ru1 119.22(19)	N2 C6 C7 120.7(3)
N1 C5 1.487(4)	N2 Ru1 Ru2 49.23(6)	C10 N2 Ru1 125.64(19)	C1 C6 C7 124.7(3)
N2 C6 1.374(4)	N1 Ru1 Ru2 48.93(6)	C6 N2 Ru2 70.58(15)	N2 C6 Ru2 73.10(16)
N2 C10 1.479(3)	C1 Ru2 C6 37.78(11)	C10 N2 Ru2 125.88(19)	C1 C6 Ru2 70.68(17)
C1 C6 1.414(4)	C1 Ru2 N1 36.90(10)	Ru1 N2 Ru2 86.41(8)	C7 C6 Ru2 136.7(2)
C1 C2 1.522(4)	C6 Ru2 N1 63.94(10)	N1 C1 C6 112.4(3)	C8A C7 C6 123.7(6)
C2 C3A 1.400(13)	C1 Ru2 N2 63.77(10)	N1 C1 C2 124.1(3)	C8A C7 C8 49.5(5)
C2 C3 1.574(8)	C6 Ru2 N2 36.32(10)	C6 C1 C2 122.7(3)	C6 C7 C8 106.4(3)
C3 C4 1.533(11)	N1 Ru2 N2 67.99(9)	N1 C1 Ru2 72.86(16)	C9 C8 C7 112.2(4)
C4 C5 1.465(6)	C1 Ru2 Ru1 69.94(8)	C6 C1 Ru2 71.54(17)	C7 C8A C9 107.8(7)
C3A C4A 1.503(18)	C6 Ru2 Ru1 69.38(8)	C2 C1 Ru2 131.3(2)	C8 C9 C10 114.4(3)
C4A C5 1.568(11)	N1 Ru2 Ru1 44.90(6)	C3A C2 C1 115.4(6)	C10 C9 C8A 95.0(4)
C6 C7 1.517(4)	N2 Ru2 Ru1 44.36(6)	C1 C2 C3 112.2(4)	N2 C10 C9 112.6(3)

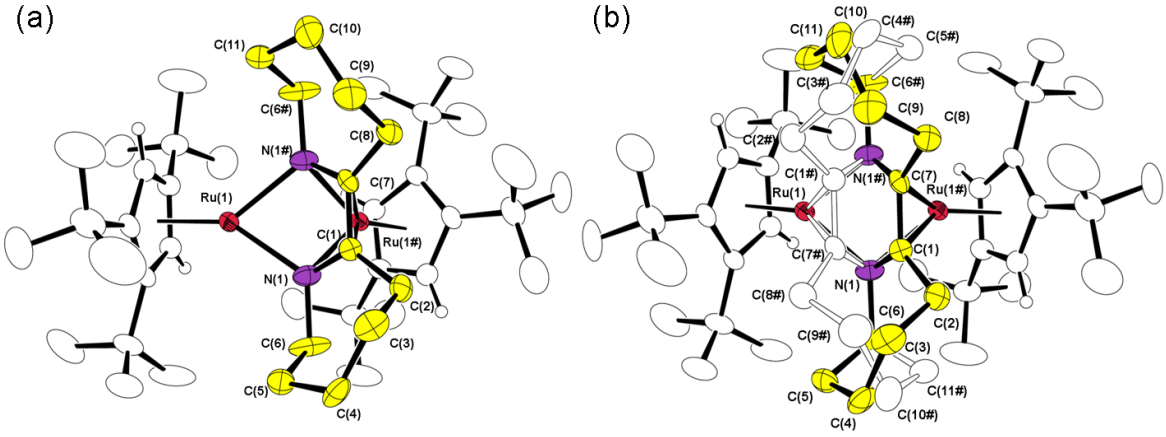


Figure S28. Molecular structures of **5c** with thermal ellipsoids at 30% probability. (a) Disordered atoms were omitted for clarity, (b) Disordered atoms were drawn in white lines. Hydrogen atoms in the ^{t}Bu groups and α-diimine moiety were omitted for clarity.

Table S6. Selected bond lengths [Å] and angles [°] of **5c**.

Ru1 N1# 2.137(4)	C5 C6 1.658(12)	C1 N1 Ru1# 75.7(5)	C5 C4 C3 114.5(15)
Ru1 N1 2.137(4)	C7 C8 1.468(12)	C6 N1 Ru1# 122.9(4)	C4 C5 C6 108.7(9)
Ru1 Ru1# 2.9173(7)	C8 C9 1.548(17)	C1 N1 Ru1 119.1(5)	N1 C6 C5 111.7(5)
N1 C1 1.267(10)	C9 C10 1.50(4)	C6 N1 Ru1 124.5(4)	C1 C7 C8 129.1(8)
N1 C6 1.496(6)	C10 C11 1.54(3)	Ru1 N1 Ru1# 86.11(14)	C7 C8 C9 113.2(9)
C1 C7 1.421(12)		N1 C1 C7 114.5(8)	C10 C9 C8 113.4(16)
C1 C2 1.521(12)	N1 Ru1 N1# 70.12(18)	N1 C1 C2 123.7(8)	C9 C10 C11 116.0(19)
C2 C3 1.536(18)	N1# Ru1 Ru1# 46.95(10)	C7 C1 C2 121.8(8)	
C3 C4 1.51(3)	N1 Ru1 Ru1# 46.95(11)	C1 C2 C3 113.9(9)	
C4 C5 1.48(2)	C1 N1 C6 113.8(5)	C2 C3 C4 111.1(14)	

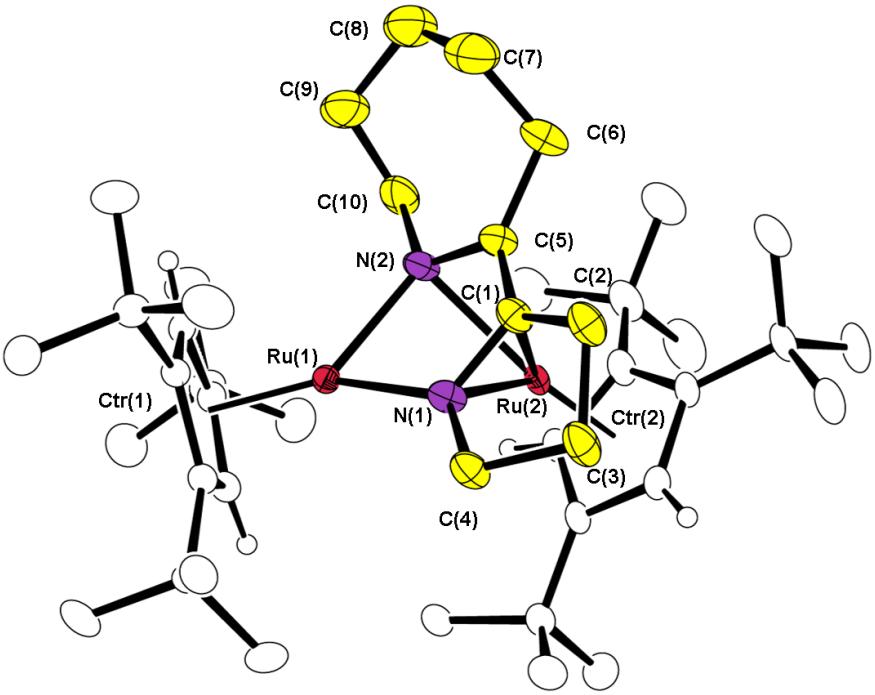


Figure S29. Molecular structures of **5d** with thermal ellipsoids at 30% probability. Hydrogen atoms in the ^{t}Bu groups and α-diimine moiety were omitted for clarity.

Table S7. Selected bond lengths [Å] and angles [°] of **5d**.

Ru1 N1 2.037(3)	C7 C8 1.526(8)	C1 N1 C4 106.4(3)	C2 C1 Ru2 126.8(3)
Ru1 N2 2.059(3)	C8 C9 1.519(7)	C1 N1 Ru1 118.6(2)	C1 C2 C3 101.5(3)
Ru1 Ru2 2.9346(4)	C9 C10 1.483(7)	C4 N1 Ru1 132.3(2)	C4 C3 C2 102.1(3)
Ru2 C1 2.188(4)		C1 N1 Ru2 69.7(2)	N1 C4 C3 106.4(3)
Ru2 C5 2.195(4)	N1 Ru1 N2 73.96(12)	C4 N1 Ru2 125.5(2)	N2 C5 C1 111.5(3)
Ru2 N2 2.218(3)	N1 Ru1 Ru2 49.63(9)	Ru1 N1 Ru2 86.51(11)	N2 C5 C6 122.4(3)
Ru2 N1 2.240(3)	N2 Ru1 Ru2 48.98(9)	C5 N2 C10 115.7(3)	C1 C5 C6 125.0(4)
N1 C1 1.386(5)	C1 Ru2 C5 37.52(14)	C5 N2 Ru1 119.3(2)	N2 C5 Ru2 72.8(2)
N1 C4 1.483(4)	C1 Ru2 N2 62.99(13)	C10 N2 Ru1 123.1(3)	C1 C5 Ru2 71.0(2)
N2 C5 1.376(5)	C5 Ru2 N2 36.32(13)	C5 N2 Ru2 70.9(2)	C6 C5 Ru2 133.3(3)
N2 C10 1.467(5)	C1 Ru2 N1 36.46(12)	C10 N2 Ru2 125.2(3)	C7 C6 C5 113.8(4)
C1 C5 1.409(5)	C5 Ru2 N1 63.58(13)	Ru1 N2 Ru2 86.56(11)	C6 C7 C8 112.7(4)
C1 C2 1.503(5)	N2 Ru2 N1 67.11(11)	N1 C1 C5 113.4(3)	C9 C8 C7 112.6(4)
C2 C3 1.541(6)	C1 Ru2 Ru1 68.91(10)	N1 C1 C2 112.7(3)	C10 C9 C8 113.1(5)
C3 C4 1.525(5)	C5 Ru2 Ru1 69.44(10)	C5 C1 C2 133.7(4)	N2 C10 C9 112.7(4)
C5 C6 1.505(5)	N2 Ru2 Ru1 44.46(8)	N1 C1 Ru2 73.8(2)	
C6 C7 1.498(7)	N1 Ru2 Ru1 43.86(8)	C5 C1 Ru2 71.5(2)	

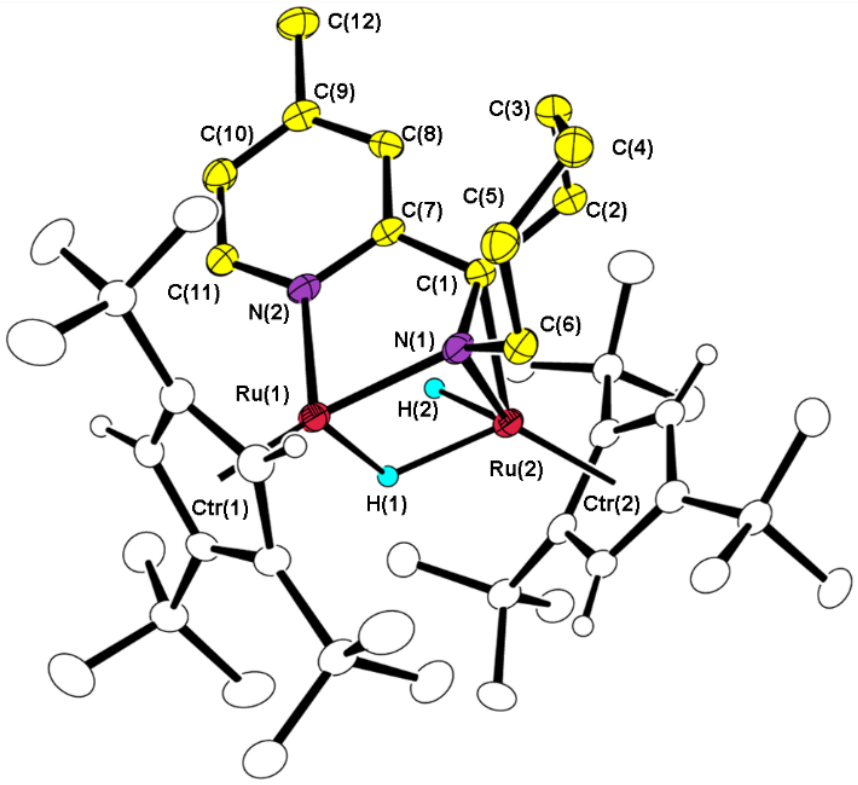


Figure S30. Molecular structures of **7c** with thermal ellipsoids at 30% probability. Hydrogen atoms in the ^{t}Bu groups and α-diimine moiety were omitted for clarity.

Table S8. Selected bond lengths [Å] and angles [°] of **7c**.

Ru1 N1 2.065(3)	C7 C8 1.388(5)	N1 Ru2 H2 102.9(13)	C3 C4 C5 114.6(3)
Ru1 N2 2.107(3)	C8 C9 1.386(5)	C1 Ru2 H2 81.5(14)	C6 C5 C4 113.6(3)
Ru1 Ru2 2.9524(4)	C9 C10 1.388(5)	Ru1 Ru2 H2 78.1(13)	N1 C6 C5 113.0(3)
Ru1 H1 1.80(3)	C9 C12 1.508(5)	H1 Ru2 H2 67.3(16)	C11 N2 C7 117.6(3)
Ru2 N1 2.097(3)	C10 C11 1.373(5)	C1 N1 C6 118.1(3)	C11 N2 Ru1 126.0(2)
Ru2 C1 2.150(3)		C1 N1 Ru1 114.7(2)	C7 N2 Ru1 116.4(2)
Ru2 H1 1.77(4)	N1 Ru1 N2 78.01(11)	C6 N1 Ru1 123.7(2)	N2 C7 C8 121.4(3)
Ru2 H2 1.52(4)	N1 Ru1 Ru2 45.26(7)	C1 N1 Ru2 72.55(17)	N2 C7 C1 113.9(3)
N1 C1 1.415(4)	N2 Ru1 Ru2 78.39(8)	C6 N1 Ru2 122.7(2)	C8 C7 C1 124.7(3)
N1 C6 1.483(4)	N1 Ru1 H1 78.6(11)	Ru1 N1 Ru2 90.36(10)	C9 C8 C7 120.8(3)
C1 C7 1.487(5)	N2 Ru1 H1 88.6(11)	N1 C1 C7 113.1(3)	C8 C9 C10 117.0(3)
C1 C2 1.529(5)	Ru2 Ru1 H1 33.7(11)	N1 C1 C2 119.8(3)	C8 C9 C12 121.4(3)
C2 C3 1.543(5)	N1 Ru2 C1 38.90(11)	C7 C1 C2 116.2(3)	C10 C9 C12 121.6(3)
C3 C4 1.524(5)	N1 Ru2 Ru1 44.39(8)	N1 C1 Ru2 68.55(17)	C11 C10 C9 120.2(3)
C4 C5 1.537(5)	C1 Ru2 Ru1 68.63(9)	C7 C1 Ru2 110.8(2)	N2 C11 C10 122.8(3)
C5 C6 1.526(5)	N1 Ru2 H1 78.4(11)	C2 C1 Ru2 119.5(2)	
N2 C11 1.351(4)	C1 Ru2 H1 99.5(12)	C1 C2 C3 114.1(3)	
N2 C7 1.360(4)	Ru1 Ru2 H1 34.3(11)	C4 C3 C2 112.7(3)	

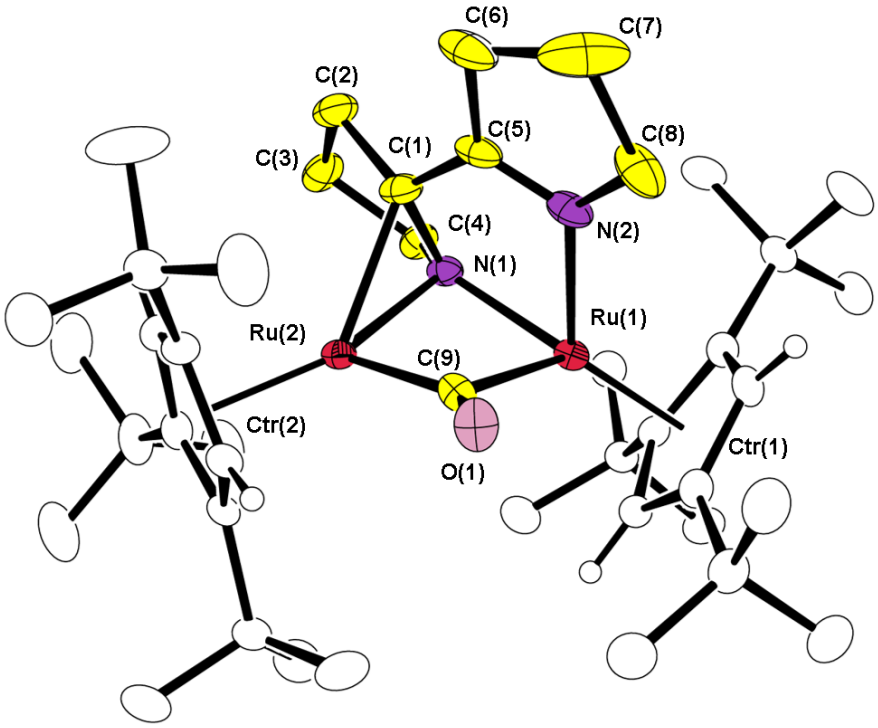


Figure S31. Molecular structures of **11** with thermal ellipsoids at 30% probability. Hydrogen atoms in the ^{t}Bu groups were omitted for clarity.

Table S9. Selected bond lengths [Å] and angles [°] of **11**.

Ru1 N1 2.059(2)	C3 C4 1.523(4)	N1 Ru2 Ru1 46.28(6)	C5 C1 Ru2 111.42(19)
Ru1 N2 2.082(2)	C5 C6 1.511(4)	C1 Ru2 Ru1 69.01(7)	C2 C1 Ru2 120.7(2)
Ru1 C9 2.173(3)	C6 C7 1.527(6)	C1 N1 C4 107.9(2)	C1 C2 C3 102.9(2)
Ru1 Ru2 2.8455(3)	C7 C8 1.518(5)	C1 N1 Ru1 110.89(17)	C4 C3 C2 103.7(3)
Ru2 C9 1.944(3)		C4 N1 Ru1 135.49(17)	N1 C4 C3 104.9(2)
Ru2 N1 2.062(2)	N1 Ru1 N2 78.37(9)	C1 N1 Ru2 74.49(14)	N2 C5 C1 117.9(2)
Ru2 C1 2.173(3)	N1 Ru1 C9 86.35(9)	C4 N1 Ru2 123.96(18)	N2 C5 C6 113.3(3)
O1 C9 1.179(3)	N2 Ru1 C9 74.49(9)	Ru1 N1 Ru2 87.34(8)	C1 C5 C6 128.7(3)
N1 C1 1.431(3)	N1 Ru1 Ru2 46.38(6)	C5 N2 C8 111.6(2)	C5 C6 C7 102.7(3)
N1 C4 1.475(3)	N2 Ru1 Ru2 84.08(7)	C5 N2 Ru1 114.45(19)	C8 C7 C6 105.8(3)
N2 C5 1.286(4)	C9 Ru1 Ru2 43.03(7)	C8 N2 Ru1 131.6(2)	N2 C8 C7 105.4(3)
N2 C8 1.468(4)	C9 Ru2 N1 92.56(10)	N1 C1 C5 112.9(2)	O1 C9 Ru2 143.2(2)
C1 C5 1.440(4)	C9 Ru2 C1 93.48(11)	N1 C1 C2 109.7(2)	O1 C9 Ru1 129.5(2)
C1 C2 1.520(4)	N1 Ru2 C1 39.40(9)	C5 C1 C2 122.2(3)	Ru2 C9 Ru1 87.27(10)
C2 C3 1.530(5)	C9 Ru2 Ru1 49.70(7)	N1 C1 Ru2 66.11(13)	

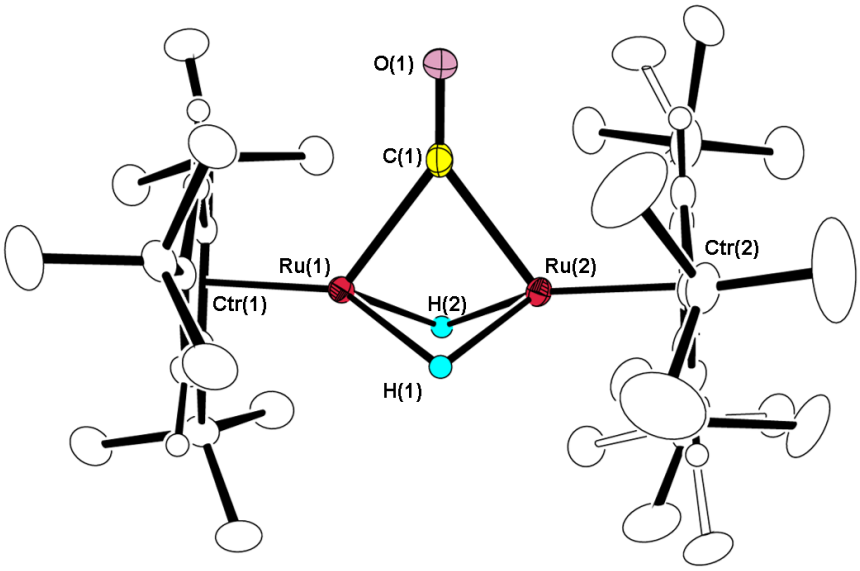


Figure S32. Molecular structures of **12** with thermal ellipsoids at 30% probability. Hydrogen atoms in the ^{t}Bu groups were omitted for clarity.

Table S10. Selected bond lengths [Å] and angles [°] of **12**.

Ru1 C1 2.0187(19)		C1 Ru2 H1 86.8(9)
Ru1 Ru2 2.43300(19)	C1 Ru1 Ru2 53.35(5)	Ru1 Ru2 H1 46.9(9)
Ru1 H1 1.78(3)	C1 Ru1 H1 85.3(9)	C1 Ru2 H2 82.1(8)
Ru1 H2 1.71(2)	Ru2 Ru1 H1 44.4(9)	Ru1 Ru2 H2 44.7(8)
Ru2 C1 2.0325(18)	C1 Ru1 H2 83.2(8)	H1 Ru2 H2 72.3(12)
Ru2 H1 1.70(3)	Ru2 Ru1 H2 45.6(8)	O1 C1 Ru1 143.50(15)
Ru2 H2 1.74(2)	H1 Ru1 H2 71.1(12)	O1 C1 Ru2 142.66(15)
O1 C1 1.173(2)	C1 Ru2 Ru1 52.83(5)	Ru1 C1 Ru2 73.82(6)

Table S11. Comparison of selected metrical parameters of **11** with those of [{Cp*Ru(μ-H)}$_2$(CO)].[#]

	11	**[{Cp*Ru(μ-H)}$_2$(CO)]$^{\#}$**		**11**	**[{Cp*Ru(μ-H)}$_2$(CO)]$^{\#}$**
Ru(1)–Ru(2)	2.43300(19)	2.444(1)	Ru(1)–C(1)–Ru(2)	73.82(6)	74.1(2)
Ru(1)–C(1)	2.0187(19)	2.004(6)	Ru(1)–C(1)–O(1)	143.50(15)	147.1(5)
Ru(2)–C(1)	2.0325(18)	2.052(6)	Ru(2)–C(1)–O(1)	142.66(15)	138.7(5)
C(1)–O(1)	1.173(2)	1.183(8)			

[#]Kang, B.-S.; Koellw, U.; Thewalt, U. *Organometallics* **1991**, *10*, 2560-2573.

3. Results of DFT calculations

(a) [{Cp‡Ru(μ-H)}$_2$(μ-η^2-C_4H_7N)] (**2a**) and [{CpRu(μ-H)}$_2$(μ-η^2-C_4H_7N)] (**2a-m**)

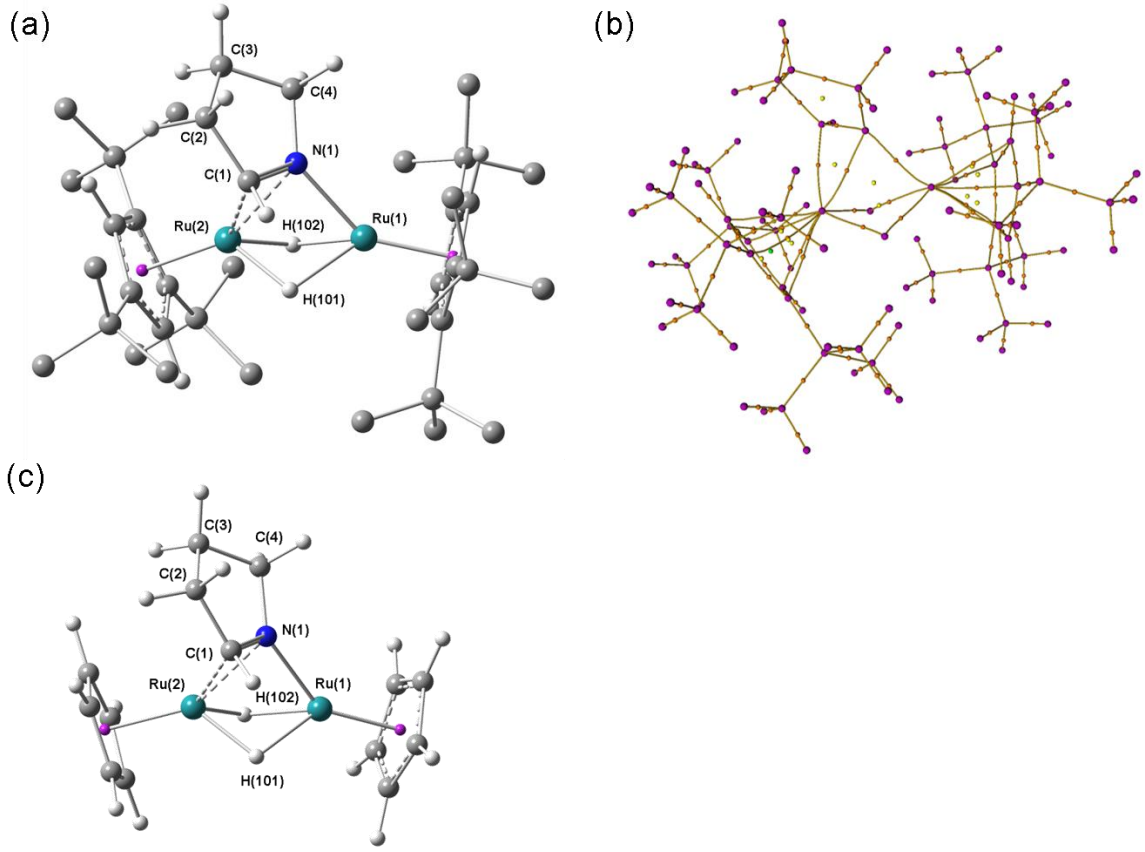


Figure S33. (a) Optimized structure of [{Cp‡Ru(μ-H)}$_2$(μ-η^2-C_4H_7N)] (**2a**) by DFT calculations (ωB97X-D / SDD (Ru), 6-31G(d,p) (C, H, and N)). Hydrogen atoms in the ^{t}Bu groups were omitted for clarity. (b) Bond paths (orange lines) and bond critical points (small orange circles), ring critical points (small yellow circles), and cage critical points (small green circles) in **2a**. (c) Optimized structure of [{CpRu(μ-H)}$_2$(μ-η^2-C_4H_7N)] (**2a-m**) by DFT calculations (B3LYP / SDD (Ru), 6-31G(d,p) (C, H, and N).

Table S12. Selected bond lengths [Å] and angles [°] of the optimized structure of **2a** and **2a-m**. The observed data of **2a** were listed for comparison.

Lengths	**obsd.**	**2a**	**2a-m**		Angles	**obsd.**	**2a**	**2a-m**
Ru(1)–Ru(2)	2.6290(3)	2.6277	2.6453		Ru(2)–Ru(1)–N(1)	52.48(5)	52.265	52.445
Ru(1)–H(101)	1.81(2)	1.8784	1.8900		Ru(1)–Ru(2)–N(1)	49.81(5)	50.634	50.620
Ru(1)–H(102)	1.69(3)	1.8261	1.7993		Ru(1)–Ru(2)–C(1)	77.79(6)	77.950	77.837
Ru(2)–H(101)	1.68(2)	1.7053	1.7217		Ru(1)–N(1)–Ru(2)	77.71(6)	77.102	76.934
Ru(2)–H(102)	1.68(3)	1.7171	1.7411		Ru(1)–N(1)–C(1)	121.47(14)	119.962	120.644
Ru(1)–N(1)	2.0554(17)	2.0840	2.0991		Ru(1)–N(1)–C(4)	128.82(14)	129.566	129.334
Ru(2)–N(1)	2.1342(17)	2.1319	2.1529		C(1)–N(1)–C(4)	109.52(17)	110.358	110.011
Ru(2)–C(1)	2.145(2)	2.1390	2.1676		N(1)–C(1)–C(2)	109.92(18)	109.653	109.985
C(1)–N(1)	1.387(3)	1.3826	1.3834					

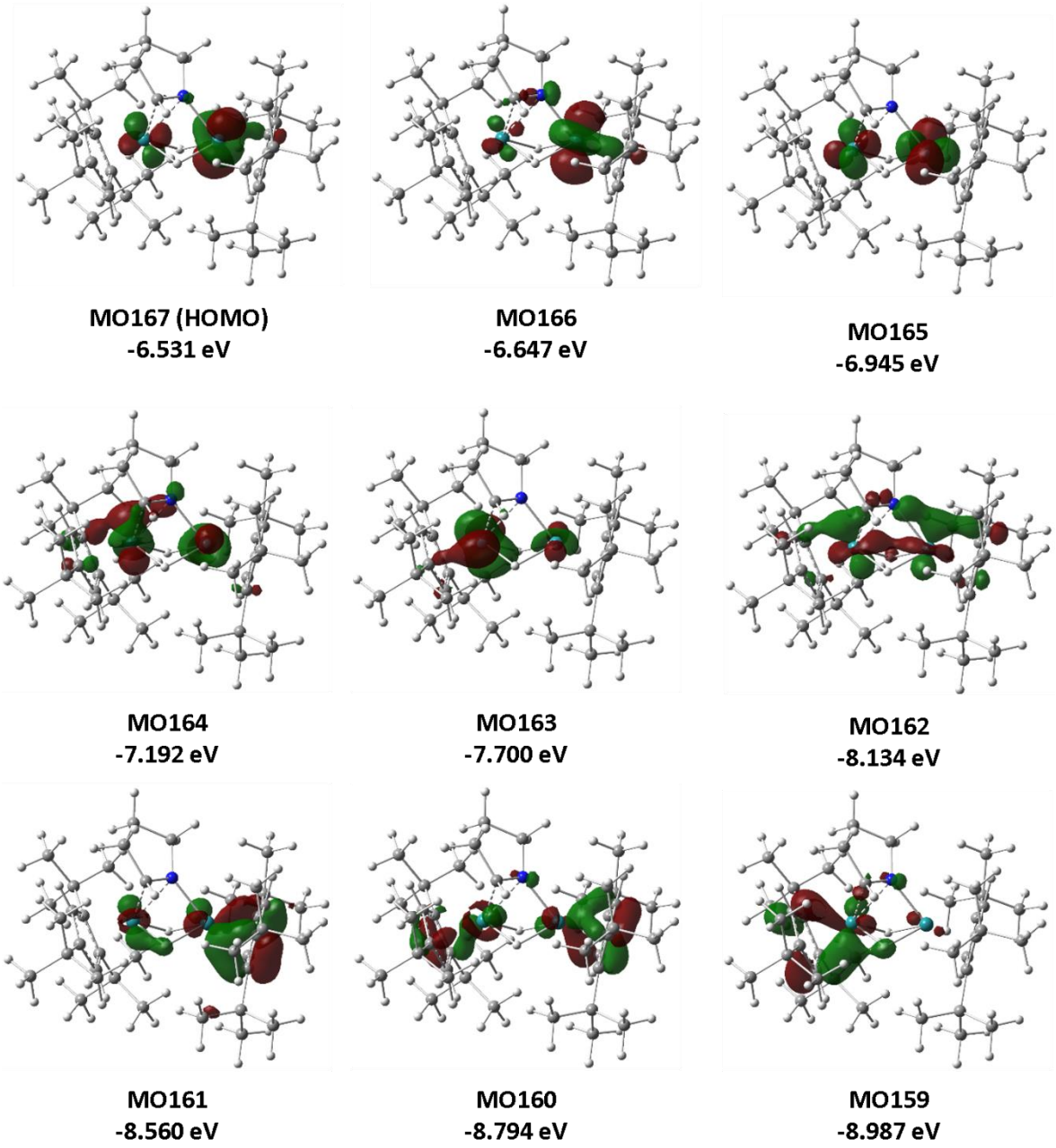


Figure S34. Shapes of selected molecular orbitals of **2a** with their Eigenvalues (eV) (ωB97X-D / SDD (Ru), 6-31G(d,p) (C, H, and N)), isovalue 0.06).

(b) [(Cp‡Ru)$_2$(μ-η^1:η^1 η^4-$C_8H_{12}N_2$)] (**5a**) and [(CpRu)$_2$(μ-η^1:η^1 η^4-$C_8H_{12}N_2$)] (**5a-m**)

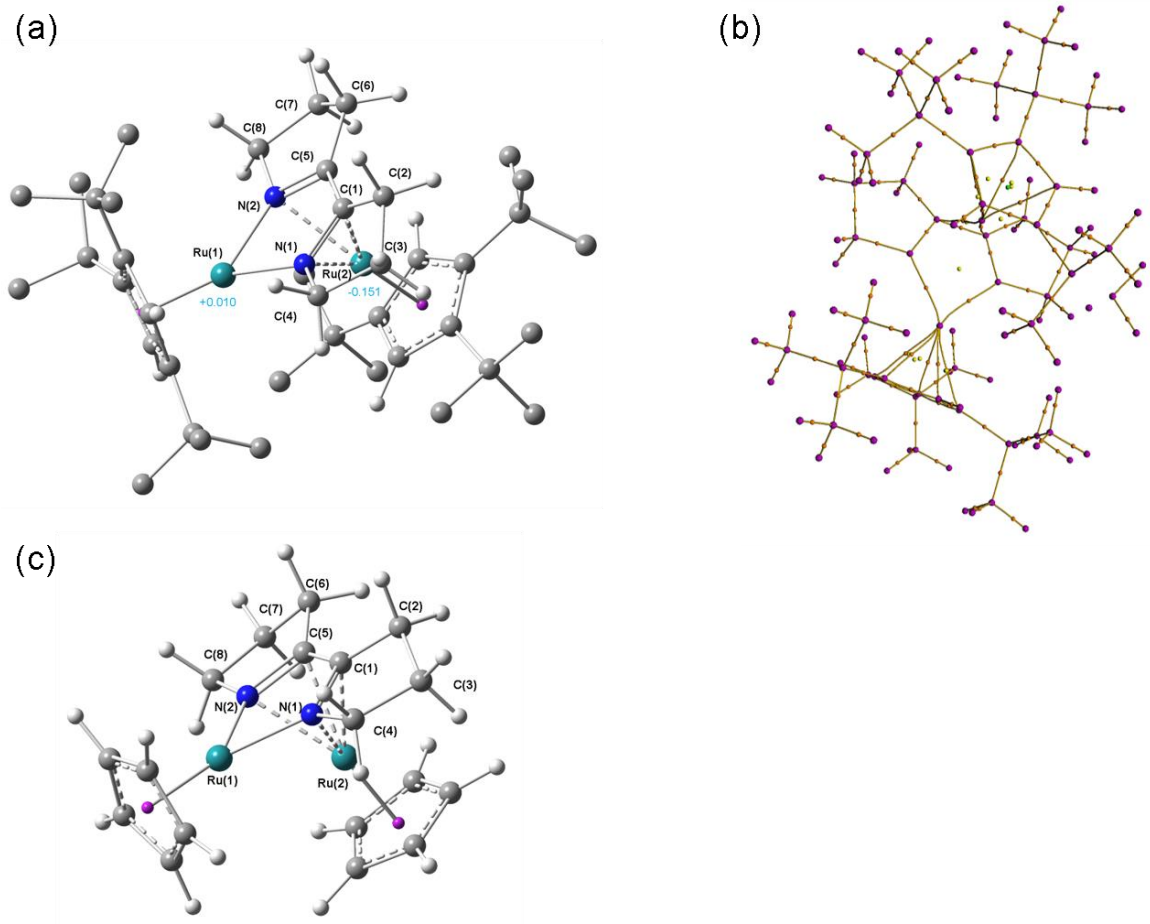


Figure S35. (a) Optimized structure of [(Cp‡Ru)$_2$(μ-η^1:η^1 η^4-$C_8H_{12}N_2$)] (**5a**) by DFT calculations (ωB97X-D / SDD (Ru), 6-31G(d,p) (C, H, and N)). Hydrogen atoms in the ^{t}Bu groups were omitted for clarity. The NBO charges at the Ru atoms were shown in a blue letter. (b) Bond paths (orange lines) and bond critical points (small orange circles), ring critical points (small yellow circles), and cage critical points (small green circles) in **5a**. (c) Optimized structure of [(CpRu)$_2$(μ-η^1:η^1 η^4-$C_8H_{12}N_2$)] (**5a-m**) by DFT calculations (B3LYP / SDD (Ru), 6-31G(d,p) (C, H, and N).

Table S13. Selected bond lengths [Å] and angles [°] of the optimized structure of **5a** and **5a-m**. The observed data of **5a** were listed for comparison.

Lengths	**obsd.**	**5a**	**5a-m**		Angles	**obsd.**	**5a**	**5a-m**
Ru(1)–Ru(2)	2.9274(4)	2.9498	2.8281		Ru(2)–Ru(1)–N(1)	49.81(9)	50.013	51.469
Ru(1)–N(1)	2.015(3)	2.0390	2.0649		Ru(2)–Ru(1)–N(2)	49.59(9)	49.410	51.4536
Ru(1)–N(2)	2.058(3)	2.0700	2.0648		N(1)–Ru(1)–N(2)	74.03(13)	73.756	74.286
Ru(2)–N(1)	2.240(3)	2.2647	2.2330		Ru(1)–Ru(2)–N(1)	43.40(9)	43.618	46.333
Ru(2)–N(2)	2.235(3)	2.2451	2.2324		Ru(1)–Ru(2)–N(2)	44.52(8)	44.439	46.332
Ru(2)–C(1)	2.189(4)	2.1782	2.1797		N(1)–Ru(2)–N(2)	66.45(12)	66.296	67.890
Ru(2)–C(5)	2.178(4)	2.1572	2.1794		Ru(1)–N(1)–C(1)	120.2(3)	120.490	119.586
N(1)–C(1)	1.387(5)	1.3889	1.3971		N(1)–C(1)–C(5)	112.4(3)	112.303	112.837
N(2)–C(5)	1.395(5)	1.3951	1.3971		C(1)–C(5)–N(2)	112.4(3)	112.671	112.830
C(1)–C(5)	1.392(5)	1.4012	1.4092		Ru(1)–N(2)–C(5)	118.5(2)	118.943	119.593

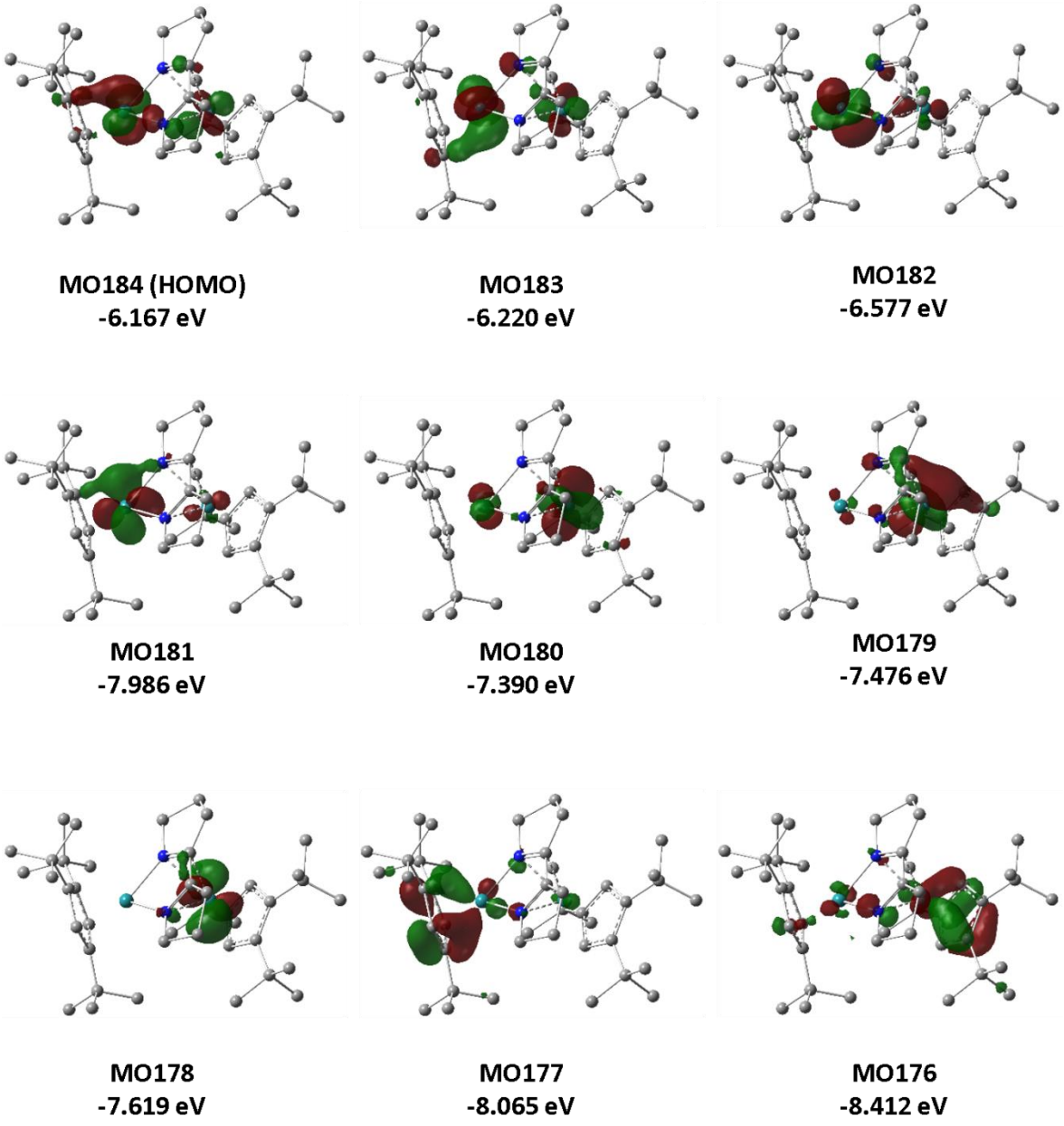


Figure S36. Shapes of selected molecular orbitals of **5a** with their Eigenvalues (eV) (ωB97X-D / SDD (Ru), 6-31G(d,p) (C, H, and N)), isovalue 0.06).

(c) $[(Cp^{‡}Ru)_2(H)(\mu\text{-}H)\}_2(\mu\text{-}\eta^1\text{:}\eta^2\text{-4-Me-}C_5H_3N\text{-}C_6H_{10}N)]$ (**7c**)

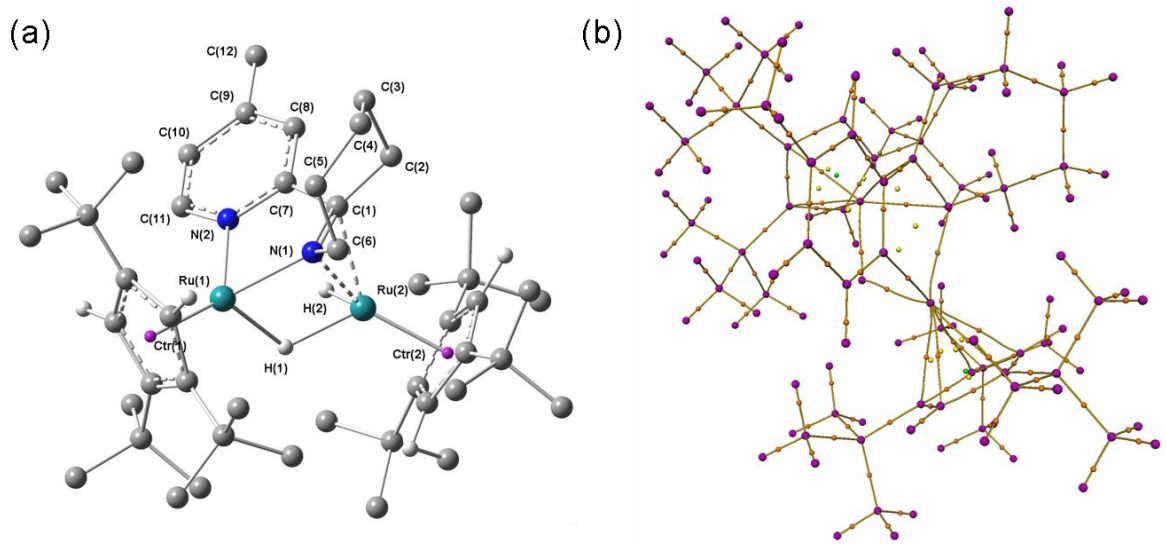


Figure S37. (a) $[(Cp^{‡}Ru)_2(H)(\mu\text{-}H)(\mu\text{-}\eta^1\text{:}\eta^2\text{-4-Me-}C_5H_3N\text{-}C_6H_{10}N)]$ (**7c**) by DFT calculations (ωB97X-D / SDD (Ru), 6-311++G(2d,p) (N(1), N(2), C(1), C(7), H(1), and H(2)), 6-31G(d,p) (other C, H)). Hydrogen atoms in the ^{t}Bu and diimine moieties were omitted for clarity. (b) Bond paths (orange lines) and bond critical points (small orange circles), ring critical points (small yellow circles), and cage critical points (small green circles) in **7c**.

Table S14. Selected bond lengths [Å] and angles [°] of the optimized structure of **7c**. The observed data of **7c** were listed for comparison.

Lengths	**obsd.**	**Opt.**		Angles	**obsd.**	**Opt.**
Ru(1)–Ru(2)	2.9524(4)	2.9399		Ru(2)–Ru(1)–N(1)	45.26(7)	45.030
Ru(1)–N(1)	2.065(3)	2.0660		Ru(2)–Ru(1)–N(2)	78.39(8)	77.560
Ru(1)–N(2)	2.107(3)	2.1168		N(1)–Ru(1)–N(2)	78.01(11)	78.064
Ru(1)–H(1)	1.80(3)	1.8530		Ru(1)–Ru(2)–N(1)	44.39(8)	44.647
Ru(2)–N(1)	2.097(3)	2.0799		Ru(1)–Ru(2)–C(1)	68.63(9)	68.764
Ru(2)–C(1)	2.150(3)	2.1338		Ru(1)–N(1)–Ru(2)	90.36(10)	90.323
Ru(2)–H(1)	1.77(4)	1.7227		Ru(1)–N(1)–C(1)	114.7(2)	114.777
Ru(2)–H(2)	1.52(4)	1.5622		N(1)–C(1)–C(7)	113.1(3)	113.696
N(1)–C(1)	1.415(4)	1.3998		C(1)–C(7)–N(2)	113.9(3)	115.343
N(2)–C(7)	1.360(4)	1.3477		Ru(1)–N(2)–C(7)	116.4(2)	115.230
C(1)–C(7)	1.487(5)	1.4730				

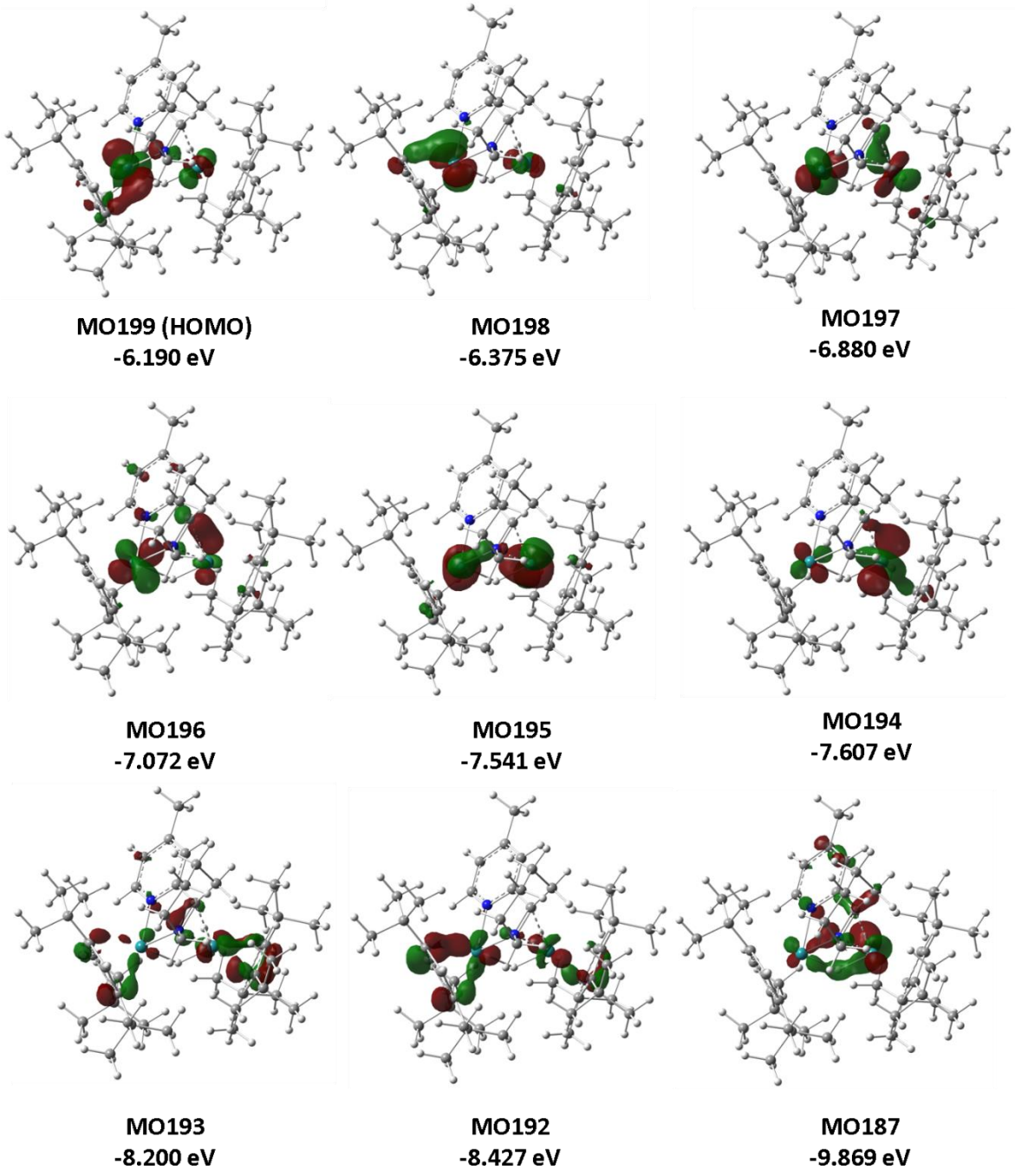


Figure S38. Shapes of selected molecular orbitals of **7c** with their Eigenvalues (eV) (ωB97X-D / SDD (Ru), 6-311++G(2d,p) (N(1), N(2), C(1), C(7), H(1), and H(2)), 6-31G(d,p) (other C, H), isovalue 0.06).

(d) [(Cp‡Ru)$_2$(μ-η^1:η^1:η^2-$C_8H_{12}N_2$)(μ-H)(H)] (**7a**)

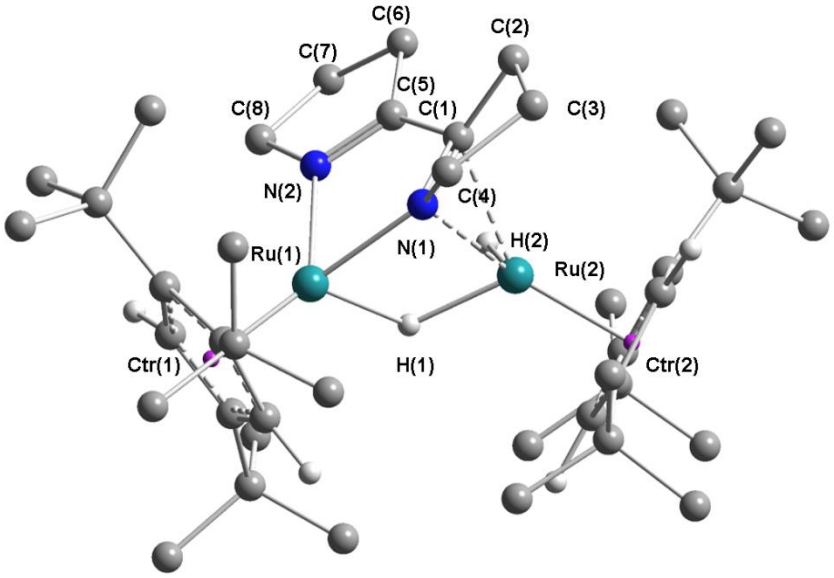


Figure S39. Optimized structure of [(Cp‡Ru)$_2$(μ-η^1:η^1:η^2-$C_8H_{12}N_2$)(μ-H)CO)] (**7a**) by DFT calculations (ωB97X-D / SDD (Ru), 6-31G(d,p) (C, H, and N)). Hydrogen atoms on the ^{t}Bu groups and diimine moiety were omitted for clarity.

Table S15. Selected bond lengths [Å] and angles [°] of the optimized structure of **7a**. The observed data of **7c** were listed for comparison.

Lengths	**7a**		Angles	**7a**
Ru(1)–Ru(2)	2.9447		Ru(2)–Ru(1)–N(1)	45.707
Ru(1)–N(1)	2.0763		Ru(2)–Ru(1)–N(2)	79.382
Ru(1)–N(2)	2.1131		N(1)–Ru(1)–N(2)	77.046
Ru(1)–H(1)	1.8313		Ru(1)–Ru(2)–N(1)	44.836
Ru(2)–N(1)	2.1078		Ru(1)–Ru(2)–C(1)	68.452
Ru(2)–C(1)	2.1387		Ru(1)–N(1)–Ru(2)	89.457
Ru(2)–H(1)	1.7194		Ru(1)–N(1)–C(1)	113.295
Ru(2)–H(2)	1.5747		N(1)–C(1)–C(5)	112.930
N(1)–C(1)	1.4110		C(1)–C(5)–N(2)	117.580
N(2)–C(5)	1.2910		Ru(1)–N(2)–C(5)	115.158
C(1)–C(5)	1.4515			
			5a + H_2	**7a**
Sum of electronic and zero-point Energies (Hartree)			–1941.836965	–1941.843161
Sum of electronic and thermal Energies (Hartree)			–1941.783122	–1941.791132
Sum of electronic and thermal Enthalpies (Hartree)			–1941.781233	–1941.790188
Sum of electronic and thermal Free Energies (Hartree)			–1941.924596	–1941.920112
Relative energy to **5a** + H_2 at 298.15 K (kcal mol^{-1})			0.00	+2.82
Relative energy to **5a** + H_2 at 353 K (kcal mol^{-1})			0.00	+4.27

(e) [(Cp‡Ru)$_2$(μ-η^1:η^1:η^2-$C_8H_{12}N_2$)(μ-CO)] (**11**)

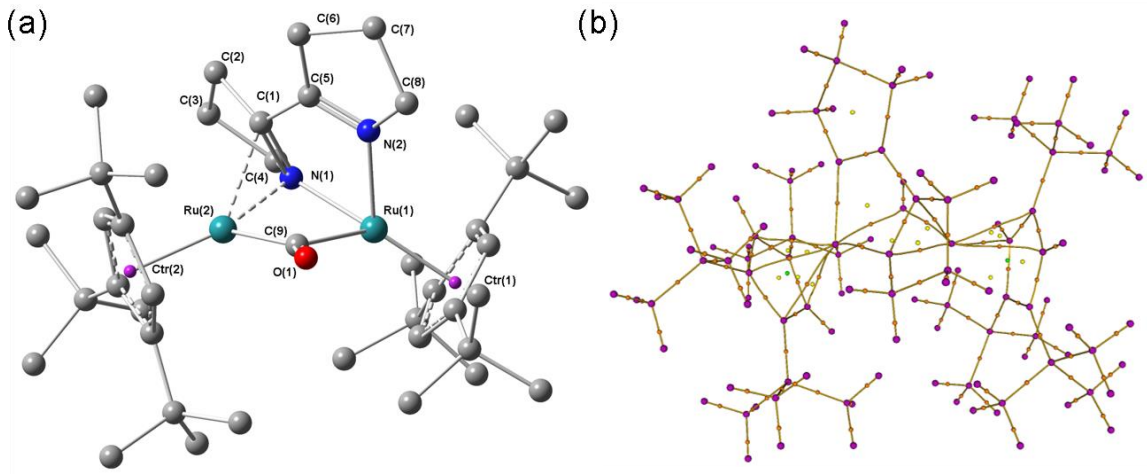


Figure S40. (a) Optimized structure of [(Cp‡Ru)$_2$(μ-η^1:η^1:η^2-$C_8H_{12}N_2$)(μ-CO)] (**11**) by DFT calculations (ωB97X-D / SDD (Ru), 6-311++G(2d,p) (N(1), N(2), C(1), C(5), C(9), and O(1)), 6-31G(d,p) (other C, H)). Hydrogen atoms were omitted for clarity. (b) Bond paths (orange lines) and bond critical points (small orange circles), ring critical points (small yellow circles), and cage critical points (small green circles) in **11**.

Table S16. Selected bond lengths [Å] and angles [°] of the optimized structure of **11**. The observed data of **11** were listed for comparison.

Lengths	**obsd.**	**Opt.**		Angles	**obsd.**	**Opt.**
Ru(1)–Ru(2)	2.8455(3)	2.8173		Ru(2)–Ru(1)–N(1)	46.38(6)	46.252
Ru(1)–N(1)	2.059(2)	2.0686		Ru(2)–Ru(1)–N(2)	84.08(7)	84.754
Ru(1)–N(2)	2.082(2)	2.0869		Ru(2)–Ru(1)–C(9)	43.03(7)	43.349
Ru(1)–C(9)	2.173(3)	2.1667		N(1)–Ru(1)–N(2)	78.37(9)	78.088
Ru(2)–N(1)	2.062(2)	2.0388		Ru(1)–Ru(2)–N(1)	46.28(6)	47.133
Ru(2)–C(1)	2.173(3)	2.1514		Ru(1)–Ru(2)–C(1)	69.01(7)	69.620
Ru(2)–C(9)	1.944(3)	1.9375		Ru(1)–Ru(2)–C(9)	49.70(7)	50.141
N(1)–C(1)	1.431(3)	1.4243		Ru(1)–N(1)–Ru(2)	87.34(8)	86.614
N(2)–C(5)	1.286(4)	1.2907		Ru(1)–N(1)–C(1)	110.89(17)	110.223
C(1)–C(5)	1.440(4)	1.4343		N(1)–C(1)–C(5)	112.9(2)	113.601
C(9)–O(1)	1.179(3)	1.1773		C(1)–C(5)–N(2)	117.9(2)	117.558
				Ru(1)–N(2)–C(5)	114.45(19)	114.188
				Ru(1)–C(9)–Ru(2)	87.27(10)	86.510

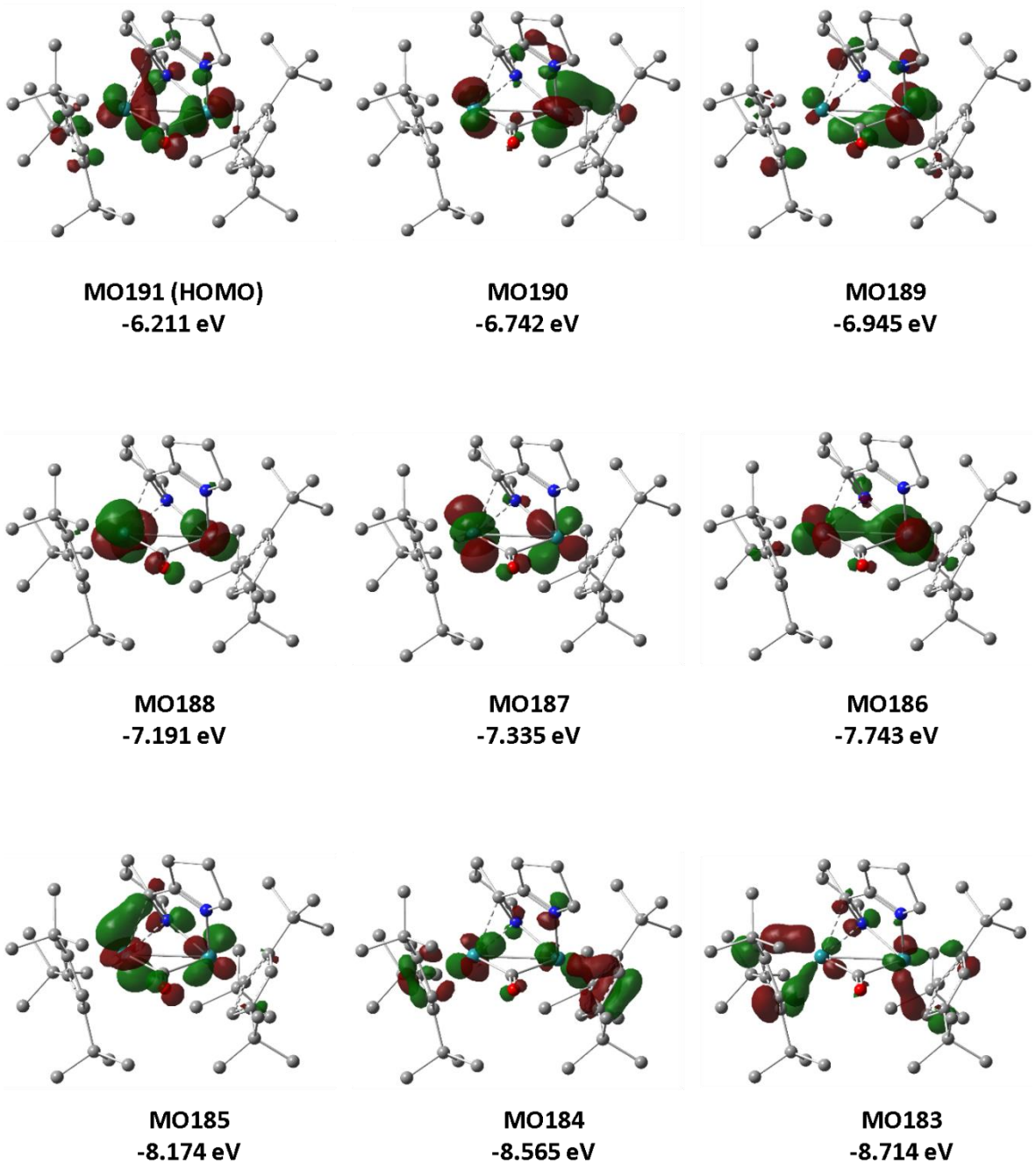


Figure S41. Shapes of selected molecular orbitals of **11** with their Eigenvalues (eV) (ωB97X-D / SDD (Ru), -311++G(2d,p) (N(1), N(2), C(1), C(5), C(9), and O(1)), 6-31G(d,p) (other C, H), isovalue 0.06).

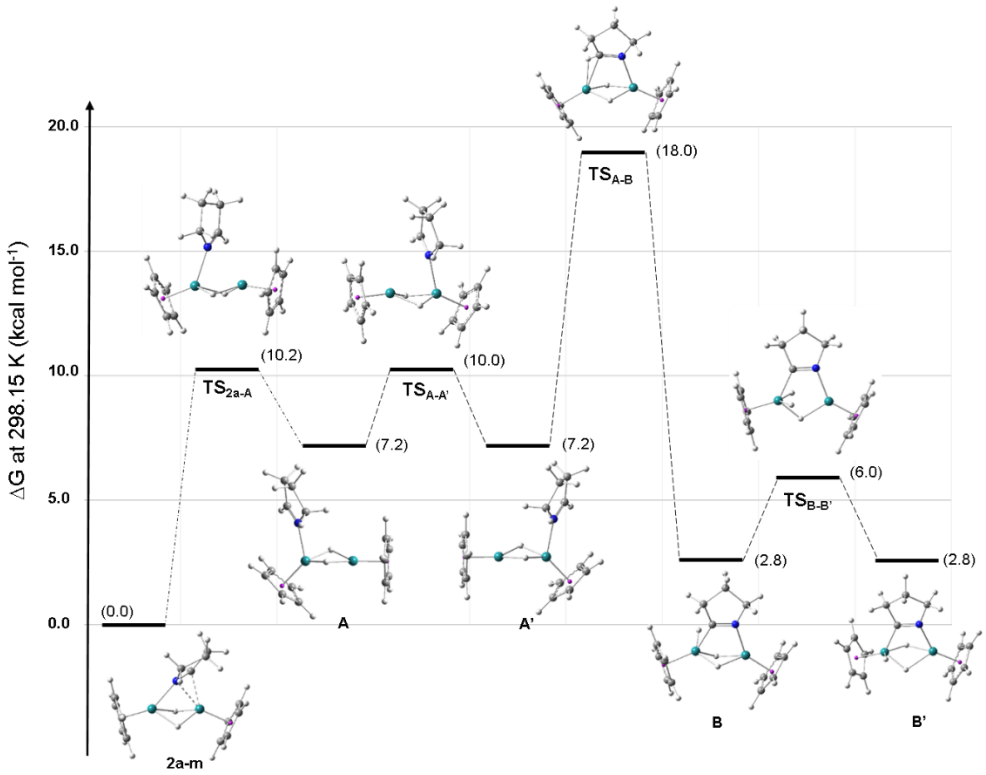


Figure S42. Computed free energy profile (kcal mol^{-1}, 298.15 K) for the isomerization of [(CpRu)$_2$(μ-η^2-C$_4$H$_7$N)(μ-H)$_2$] (**2a-m**) to [(CpRu)$_2$(μ-C$_4$H$_6$N)(μ-H)$_2$(H)] (**B**) (B3LYP / SDD (Ru), 6-31G(d,p) (C, H, N)).

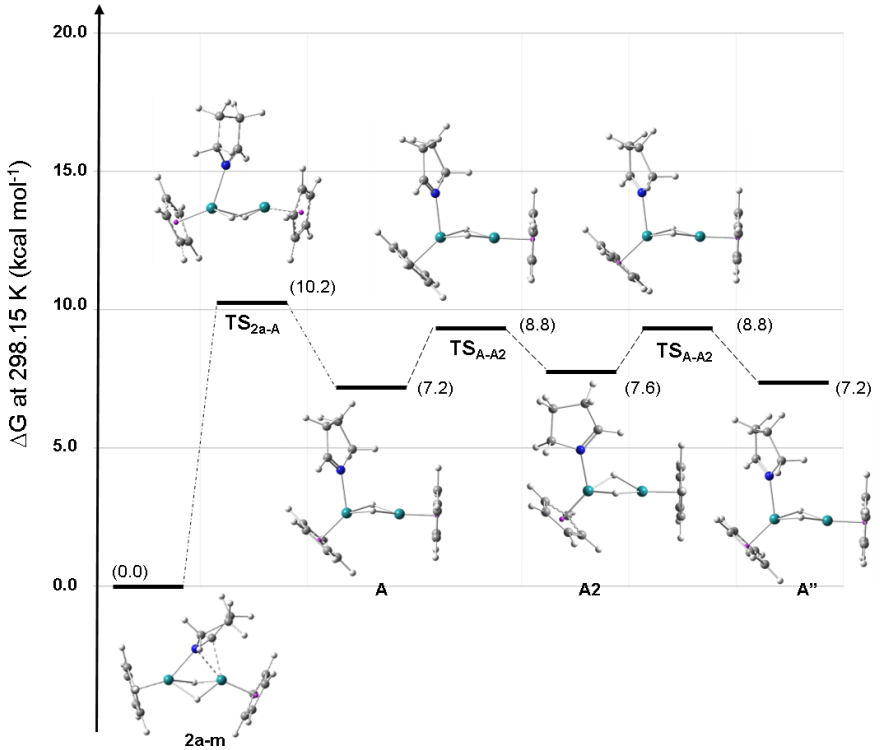
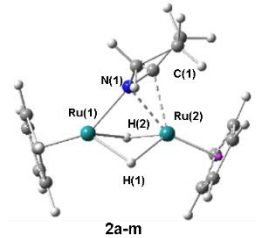
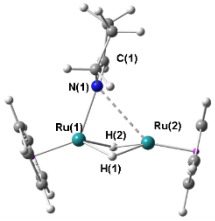
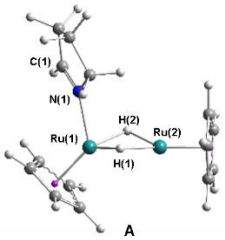


Figure S43. Computed free energy profile (kcal mol^{-1}, 298.15 K) for the rotation of κ(*N*)-coordinated 1-pyrroline ligand in [(CpRu)$_2$(κ(*N*)-C$_4$H$_7$N)(μ-H)$_2$] (**A**) (B3LYP / SDD (Ru), 6-31G(d,p) (C, H, N)).

Table S17. Selected bond lengths [Å] and results of frequency calculations for the optimized structures **2a-m**, **TS$_{2a-A}$**, **A**, **TS$_{A-A'}$**, **A2**, **TS$_{A-A2}$**, **TS$_{A-B}$**, **B**, and **TS$_{B-B'}$**.

	 2a-m	 Ts_{2a-A}	 A
Ru(1)–Ru(2)	2.6453	2.5711	2.5370
Ru(1)–N(1)	2.0991	2.1290	2.1015
Ru(1)–H(1)	1.8900	1.7842	1.7706
Ru(1)–H(2)	1.7993	1.7788	1.7743
Ru(2)–N(1)	2.1529	2.7308	3.5381
Ru(2)–C(1)	2.1676		
Ru(2)–H(1)	1.7217	1.7729	1.8125
Ru(2)–H(2)	1.7411	1.7882	1.8113
C(1)–N(1)	1.3834	1.2916	1.2847
Sum of electronic and zero-point Energies (Hartree)	–789.273746	–789.25543	–789.257433
Sum of electronic and thermal Energies (Hartree)	–789.257355	–789.238618	–789.239801
Sum of electronic and thermal Enthalpies (Hartree)	–789.256411	–789.237674	–789.238856
Sum of electronic and thermal Free Energies (Hartree)	–789.319481	–789.303256	–789.307975
Relative energy to **2a-m** at 298.15 K (kcal mol^{-1})	0.00	+10.18	+7.22

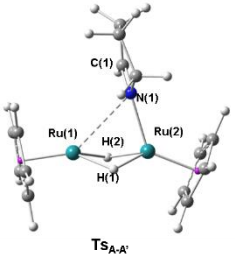
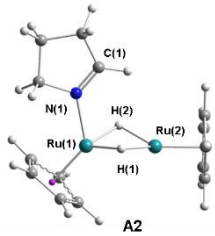
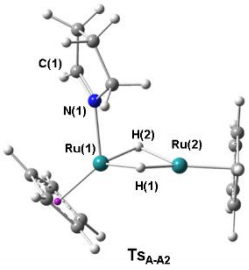
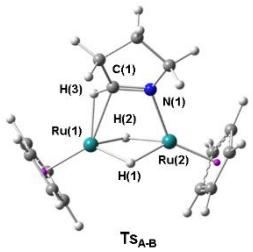
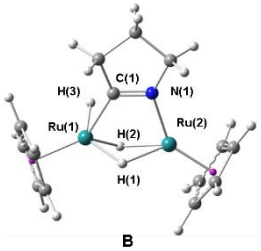
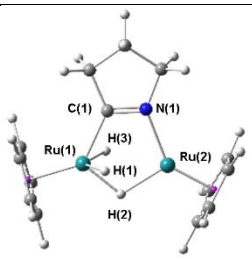
	 $Ts_{A-A'}$	 A2	 Ts_{A-A2}
Ru(1)–Ru(2)	2.5674	2.52863	2.5342
Ru(1)–N(1)	2.8397	2.10065	2.1050
Ru(1)–H(1)	1.7900	1.77403	1.7671
Ru(1)–H(2)	1.7773	1.77339	1.7703
Ru(2)–N(1)	2.1188	3.58768	3.4993
Ru(2)–C(1)			
Ru(2)–H(1)	1.7753	1.80785	1.8153
Ru(2)–H(2)	1.7827	1.80793	1.8121
C(1)–N(1)	1.2901	1.28760	1.2841
Sum of electronic and zero-point Energies (Hartree)	–789.255665	–789.257645	–789.257095
Sum of electronic and thermal Energies (Hartree)	–789.238866	–789.240169	–789.240343
Sum of electronic and thermal Enthalpies (Hartree)	–789.237922	–789.240169	–789.239398
Sum of electronic and thermal Free Energies (Hartree)	–789.303537	–789.307299	–789.305537
Relative energy to **2a-m** at 298.15 K (kcal mol^{-1})	+10.01	+7.64	+8.75

Table S17 (continued)**.** Selected bond lengths [Å] and results of frequency calculations for the optimized structures **2a-m**, **TS$_{2a-A}$**, **A**, **TS$_{A-A'}$**, **A2**, **TS$_{A-A2}$**, **TS$_{A-B}$**, **B**, and **TS$_{B-B'}$**.

	 TS_{A-B}	 B	 $TS_{B-B'}$
Ru(1)–Ru(2)	2.7084	2.8273	2.8646
Ru(1)–N(1)	2.3105	2.0168	2.0091
Ru(1)–H(1)	1.7258	1.6793	1.6006
Ru(1)–H(2)	1.7316	1.6645	1.6602
Ru(2)–N(1)	1.7650	1.5883	1.6019
Ru(2)–C(1)	2.1322	2.0869	2.0772
Ru(2)–H(1)	1.8174	1.8882	2.5402
Ru(2)–H(2)	1.8567	1.9526	1.8761
C(1)–N(1)	1.2960	1.3032	1.3064
C(1)–H(3)	1.1809	2.1865	
Sum of electronic and zero-point Energies (Hartree)	–789.244139	–789.267646	–789.263334
Sum of electronic and thermal Energies (Hartree)	–789.227673	–789.250484	–789.246700
Sum of electronic and thermal Enthalpies (Hartree)	–789.226729	–789.24954	–789.245756
Sum of electronic and thermal Free Energies (Hartree)	–789.290799	–789.315006	– 789. 309981
Relative energy to **2a-m** at 298.15 K (kcal mol^{-1})	+18.00	+2.81	+5.96

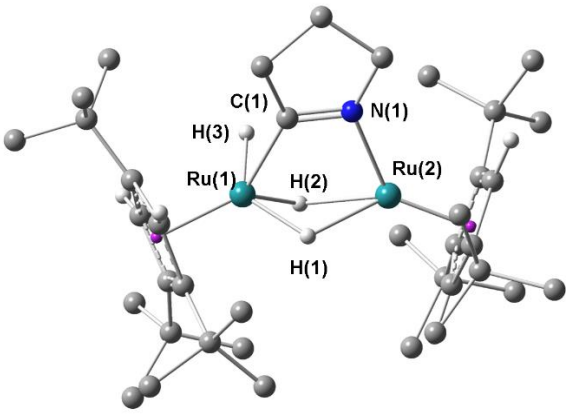


Figure S44. Optimized structure of [(Cp‡Ru)$_2$(μ-C$_4$H$_6$N)(μ-H)$_2$(H)] (**B‡**) (ωB97X-D / SDD (Ru), 6-31G(d,p) (C, H, N)). Hydrogen atoms in the imidoyl and Cp‡ groups were omitted for clarity.

Table S18. Selected bond lengths [Å] in **B‡** and **B'**, which were optimized at a *ω*B97X-D level**.** Corresponding data of **B** was also shown for comparison

	B‡ (*ω*B97X-D)	**B** (B3LYP)	**B'** (*ω*B97X-D)
Ru(1)–Ru(2)	2.8915	2.8273	2.8122
Ru(1)–C(1)	2.0155	2.0168	2.0073
Ru(1)–H(1)	1.6630	1.6793	1.6619
Ru(1)–H(2)	1.65459	1.6645	1.6512
Ru(1)–H(3)	1.5871	1.5883	1.5840
Ru(2)–N(1)	2.0660	2.0869	2.0813
Ru(2)–H(1)	1.9485	1.8882	1.9175
Ru(2)–H(2)	2.0416	1.9526	1.9775
C(1)–N(1)	1.2973	1.3032	1.2970
C(1)–H(3)	2.1997	2.1865	2.1595

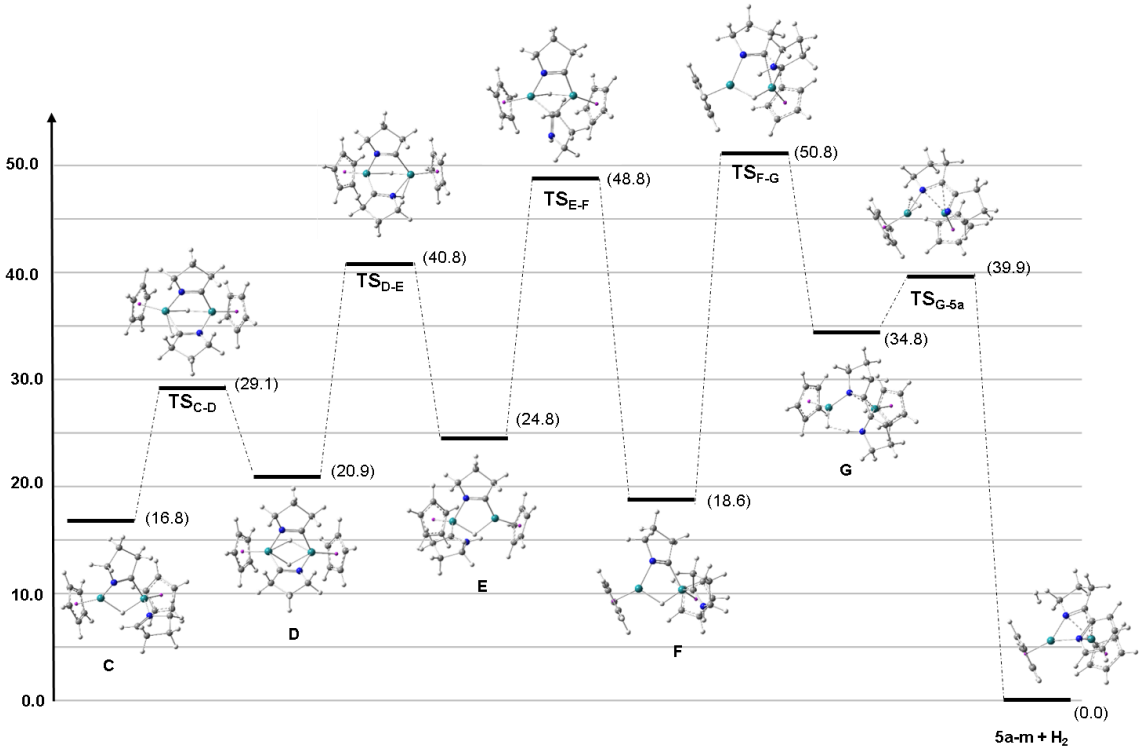


Figure S45. Computed free energy profile (kcal mol^{-1}, 298.15 K) for the reaction of **3a-m** with 1-pyrroline yielding **5a-m** (B3LYP / SDD (Ru), 6-31G(d,p) (C, H, N))

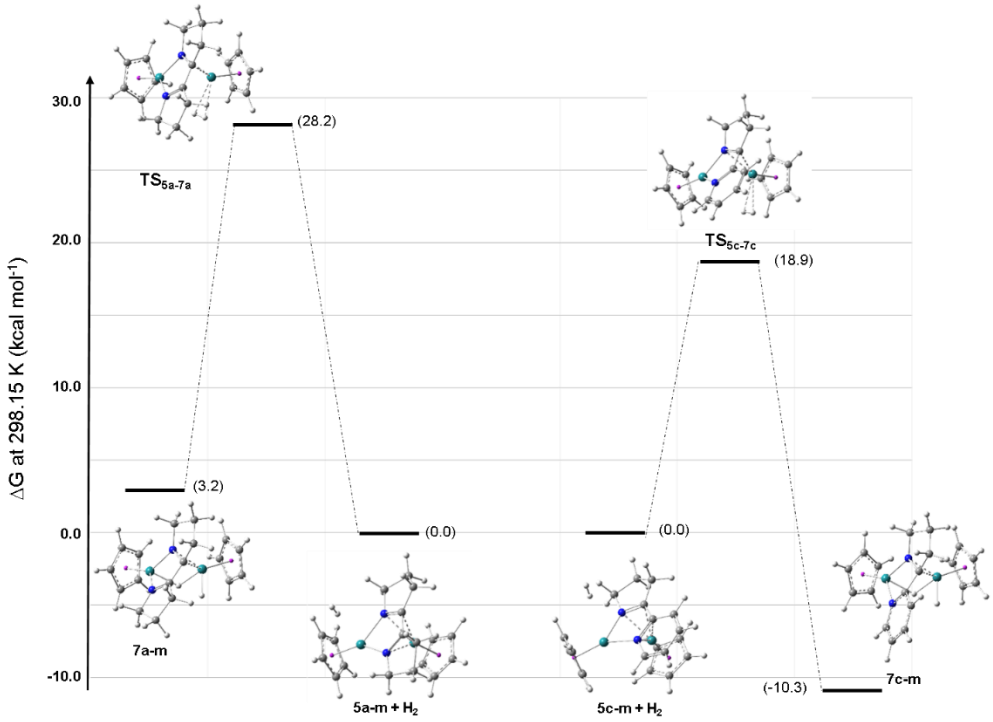


Figure S46. Computed free energy profile (kcal mol^{-1}, 298.15 K) for the reaction of **5a-m** and **5c-m** with dihydrogen yielding **7a-m** and **7c-m** (B3LYP / SDD (Ru), 6-31G(d,p) (C, H, N))

Table S19. Selected bond lengths [Å] and results of frequency calculations for the optimized structures **3a-m**, **1-pyrroline**, **C**, **TS$_{C-D}$**, **D**, **TS$_{D-E}$**, **E**, **TS$_{E-F}$**, **F**, **TS$_{F-G}$**, **G**, **TS$_{G-5a}$**, **5a-m**, **TS$_{5a-7a}$**, **7a-m**, and **C'**.

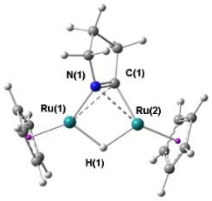
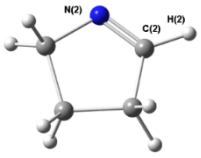
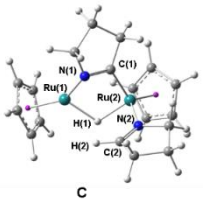
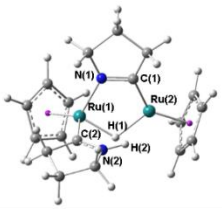
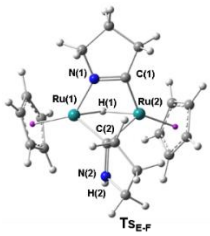
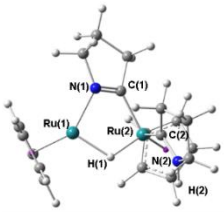
	 3a-m		 C
Ru(1)–Ru(2)	2.8106		2.8927
Ru(1)–N(1)	2.0097		2.0329
Ru(1)–C(1)	2.4696		2.5692
Ru(1)–H(1)	1.7696		1.7861
Ru(2)–N(1)	2.5622		2.8946
Ru(2)–N(2)			2.1009
Ru(2)–C(1)	1.9592		1.9942
Ru(2)–H(1)	1.7255		1.7088
C(1)–N(1)	1.3398		1.3282
C(2)–N(2)		1.2741	1.2877
C(2)–H(2)		1.0912	1.0849
Sum of electronic and zero-point Energies (Hartree)	–788.071278	–211.276478	–999.380756
Sum of electronic and thermal Energies (Hartree)	–788.054629	–211.271924	–999.358517
Sum of electronic and thermal Enthalpies (Hartree)	–788.053685	–211.27098	–999.357573
Sum of electronic and thermal Free Energies (Hartree)	–788.119414	–211.303961	–999.435568
Relative energy to [**5a-m** + H_2] at 298.15 K (kcal mol^{-1})	[**3a-m** + 1-pyrroline] +24.48		+16.83
	 E	 TS_{E-F}	 F
Ru(1)–Ru(2)	2.8906	2.8001	2.9073
Ru(1)–N(1)	2.0947	1.9701	2.0294
Ru(1)–C(2)	1.9635	2.0183	
Ru(1)–H(1)	1.7212	1.7362	1.7960
Ru(2)–C(1)	2.0158	1.9528	1.9793
Ru(2)–C(2)		2.2019	1.9671
Ru(2)–H(1)	1.7674	1.7699	1.7015
C(1)–N(1)	1.3010	1.3469	1.3331
C(2)–N(2)	1.3380	1.4147	1.3449
N(2)– H(2)	1.0158	1.0096	1.0109
Sum of electronic and zero-point Energies (Hartree)	–999.36858	–999.332972	–999.377463
Sum of electronic and thermal Energies (Hartree)	–999.346191	–999.332972	–999.355145
Sum of electronic and thermal Enthalpies (Hartree)	–999.345247	–999.332972	–999.354201
Sum of electronic and thermal Free Energies (Hartree)	–999.422881	–999.384548	–999.432696
Relative energy to [**5a-m** + H_2] at 298.15 K (kcal mol^{-1})	+24.79	+48.84	+18.63

Table S19 (continued)**.** Selected bond lengths [Å] and results of frequency calculations for the optimized structures **3a-m**, **1-pyrroline**, **C**, **TS$_{C-D}$**, **D**, **TS$_{D-E}$**, **E**, **TS$_{E-F}$**, **F**, **TS$_{F-G}$**, **G**, **TS$_{G-5a}$**, **5a-m**, **TS$_{5a-7a}$**, **7a-m**, and **C'**.

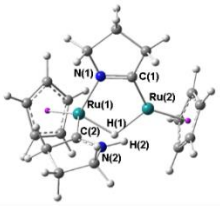
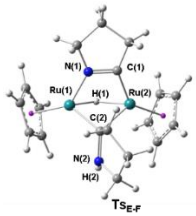
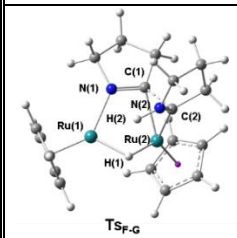
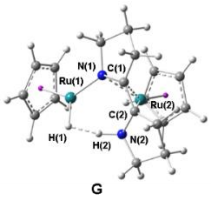
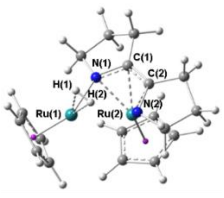
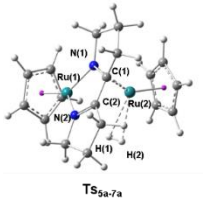
	 E	 TS$_{E-F}$	 F
Ru(1)–Ru(2)	2.8906	2.8001	2.9073
Ru(1)–N(1)	2.0947	1.9701	2.0294
Ru(1)–C(2)	1.9635	2.0183	
Ru(1)–H(1)	1.7212	1.7362	1.7960
Ru(2)–C(1)	2.0158	1.9528	1.9793
Ru(2)–C(2)		2.2019	1.9671
Ru(2)–H(1)	1.7674	1.7699	1.7015
C(1)–N(1)	1.3010	1.3469	1.3331
C(2)–N(2)	1.3380	1.4147	1.3449
N(2)– H(2)	1.0158	1.0096	1.0109
Sum of electronic and zero-point Energies (Hartree)	–999.36858	–999.332972	–999.377463
Sum of electronic and thermal Energies (Hartree)	–999.346191	–999.332972	–999.355145
Sum of electronic and thermal Enthalpies (Hartree)	–999.345247	–999.332972	–999.354201
Sum of electronic and thermal Free Energies (Hartree)	–999.422881	–999.384548	–999.432696
Relative energy to [**5a-m** + H_2] at 298.15 K (kcal mol^{-1})	+24.79	+48.84	+18.63
	 TS$_{F-G}$	 G	 TS$_{G-5a}$
Ru(1)–Ru(2)	2.6916	3.1382	2.9047
Ru(1)–N(1)	2.0541	2.1000	2.0522
Ru(1)–N(2)			2.7879
Ru(1)–H(1)	1.7776	1.6584	2.0084
Ru(1)–H(2)			2.0562
Ru(2)–N(1)	2.7381	2.2520	2.1952
Ru(2)–N(2)	3.0315	2.1887	2.2081
Ru(2)–C(1)	2.1713	2.2091	2.1694
Ru(2)–C(2)	1.9909	2.1659	2.1862
Ru(2)–H(1)	1.7590		
C(1)–N(1)	1.3166	1.3916	1.4083
C(1)–C(2)	1.8071	1.4070	1.4182
C(2)–N(2)	1.3886	1.4130	1.3693
N(2)–H(2)	1.01039	1.0515	2.2438
H(1)–H(2)		1.4354	0.7764
Sum of electronic and zero-point Energies (Hartree)	–999.329206	–999.356303	–999.349246
Sum of electronic and thermal Energies (Hartree)	–999.307623	–999.335343	–999.327894
Sum of electronic and thermal Enthalpies (Hartree)	–999.306679	–999.334399	–999.326950
Sum of electronic and thermal Free Energies (Hartree)	–999.38144	–999.406858	–999.398850
Relative energy to [**5a-m** + H_2] at 298.15 K (kcal mol^{-1})	+50.79	+34.84	+39.87

Table S19 (continued)**.** Selected bond lengths [Å] and results of frequency calculations for the optimized structures **3a-m**, **1-pyrroline**, **C**, **TS$_{C-D}$**, **D**, **TS$_{D-E}$**, **E**, **TS$_{E-F}$**, **F**, **TS$_{F-G}$**, **G**, **TS$_{G-5a}$**, **5a-m**, **TS$_{5a-7a}$**, **7a-m**, and **C'**.

	 **5a-m**	H_2	 **TS_{5a-7a}**
Ru(1)–Ru(2)	2.8281		2.9382
Ru(1)–N(1)	2.0648		2.0436
Ru(1)–N(2)	2.0649		2.0345
Ru(2)–N(1)	2.2324		2.1526
Ru(2)–N(2)	2.2330		
Ru(2)–C(1)	2.1794		2.1898
Ru(2)–C(2)	2.1797		
Ru(2)–H(1)			2.3135
Ru(2)–H(2)			2.3145
C(1)–N(1)	1.3971		1.4132
C(1)–C(2)	1.4092		
C(2)–N(2)	1.3971		1.3395
H(1)–H(2)		0.7428	0.7667
Sum of electronic and zero-point Energies (Hartree)	–998.232732	–1.168366	–999.366682
Sum of electronic and thermal Energies (Hartree)	–998.212651	–1.166005	–999.345217
Sum of electronic and thermal Enthalpies (Hartree)	–998.212651	–1.166005	–999.344272
Sum of electronic and thermal Free Energies (Hartree)	–998.282529	–1.179853	–999.417431
Relative energy to [**5a-m** + H_2] at 298.15 K (kcal mol^{-1})	[**5a-m** + H_2] 0.00		+28.21

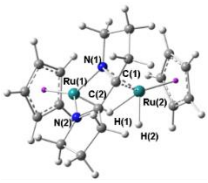
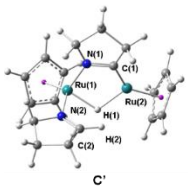
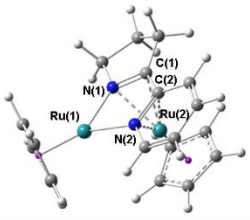
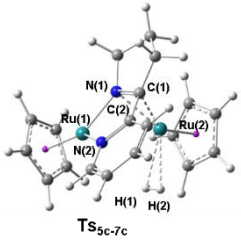
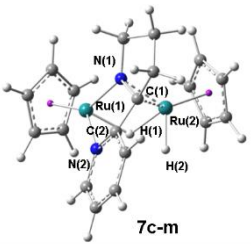
	 **7a-m**	 **C'**
Ru(1)–Ru(2)	2.89701	2.88617
Ru(1)–N(1)	2.05594	2.09556
Ru(1)–N(2)		2.10467
Ru(1)–H(1)	1.80466	1.74277
Ru(2)–N(1)	2.08885	
Ru(2)–C(1)	2.18602	2.01191
Ru(2)–H(1)	1.73112	1.76261
Ru(2)–H(2)	1.58119	
C(1)–N(1)	1.41500	1.30285
C(1)–C(2)	1.45587	
C(2)–N(2)	1.30013	1.28763
Sum of electronic and zero-point Energies (Hartree)	–999.407107	–999.36929
Sum of electronic and thermal Energies (Hartree)	–999.386333	–999.346808
Sum of electronic and thermal Enthalpies (Hartree)	–999.385389	–999.345864
Sum of electronic and thermal Free Energies (Hartree)	–999.457319	–999.423822
Relative energy to [**5a-m** + H_2] at 298.15 K (kcal mol^{-1})	+3.18	+24.20

Table S20. Selected bond lengths [Å] and results of frequency calculations for the optimized structures **5c-m**, **TS$_{5c-7c}$**, and **7c-m**.

	 **5c-m**	 **Ts$_{5c-7c}$**	 **7c-m**
Ru(1)–Ru(2)	2.8275	2.8823	2.8595
Ru(1)–N(1)	2.0413	2.0131	2.0445
Ru(1)–N(2)	2.1084	2.0837	2.0964
Ru(1)–H(1)			1.8113
Ru(2)–N(1)	2.2346	2.1716	2.0638
Ru(2)–N(2)	2.3097		
Ru(2)–C(1)	2.1710	2.1674	2.1456
Ru(2)–C(2)	2.2599		
Ru(2)–H(1)		2.3847	1.7208
Ru(2)–H(2)		2.6025	1.5826
C(1)–N(1)	1.3940	1.4095	1.4074
C(1)–C(2)	1.4209	1.4388	1.4555
C(2)–N(2)	1.3001	1.3841	1.3951
Sum of electronic and zero-point Energies (Hartree)	−1035.133143	−1036.282576	−1036.330359
Sum of electronic and thermal Energies (Hartree)	−1035.112717	−1036.260698	−1036.309823
Sum of electronic and thermal Enthalpies (Hartree)	−1035.111773	−1036.259754	−1036.308879
Sum of electronic and thermal Free Energies (Hartree)	−1035.183767	−1036.33358	−1036.379975
Relative energy to **7c-m** at 298.15 K (kcal mol^{-1})	[**5c-m** + H_2] +10.26	+29.11	0.00