Supporting Information

Synthesis of Ruthenium Polyhydride Clusters with 1,4,7-Triazacyclononane-type Ligands: Stereo and Electronic Effects of Ancillary Ligands

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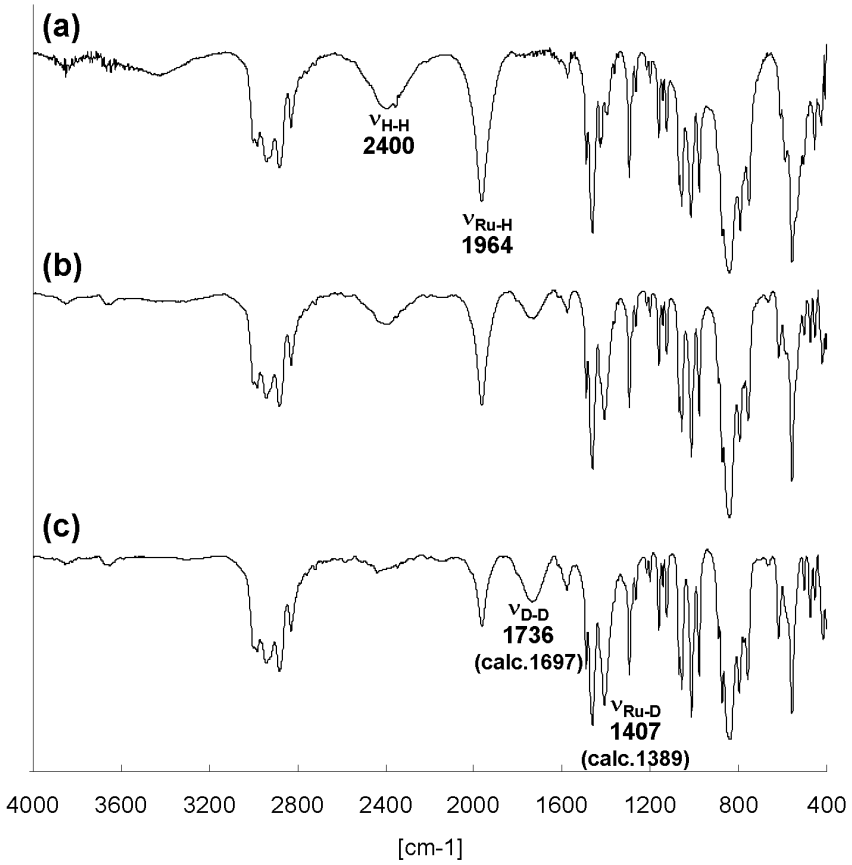
Contents

1. Infrared spectra of [Cn*RuH(H_2)$_2$](PF_6) (2b-PF_6) and its isotopomers.

To identify absorption bands, infrared spectra of complex **2b-PF_6** and partly deuterated **2b-PF_6** were recorded. (SFigure 1) The deuteration of **2b-PF_6** was carried out by methanol-d_4 and deuteration levels were confirmed by ^{1}H NMR spectroscopy.

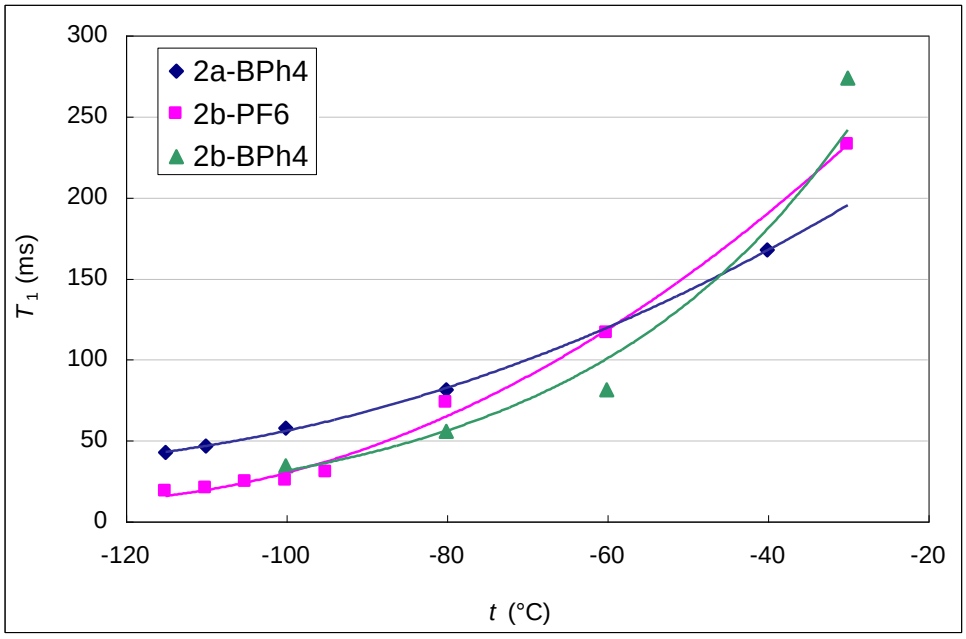


SFigure 1. Infrared spectra (KBr) of **2b-PF_6** at various deuteration levels:

(a) not deuterated; (b) 60% deuterated; (c) 80% deuterated.

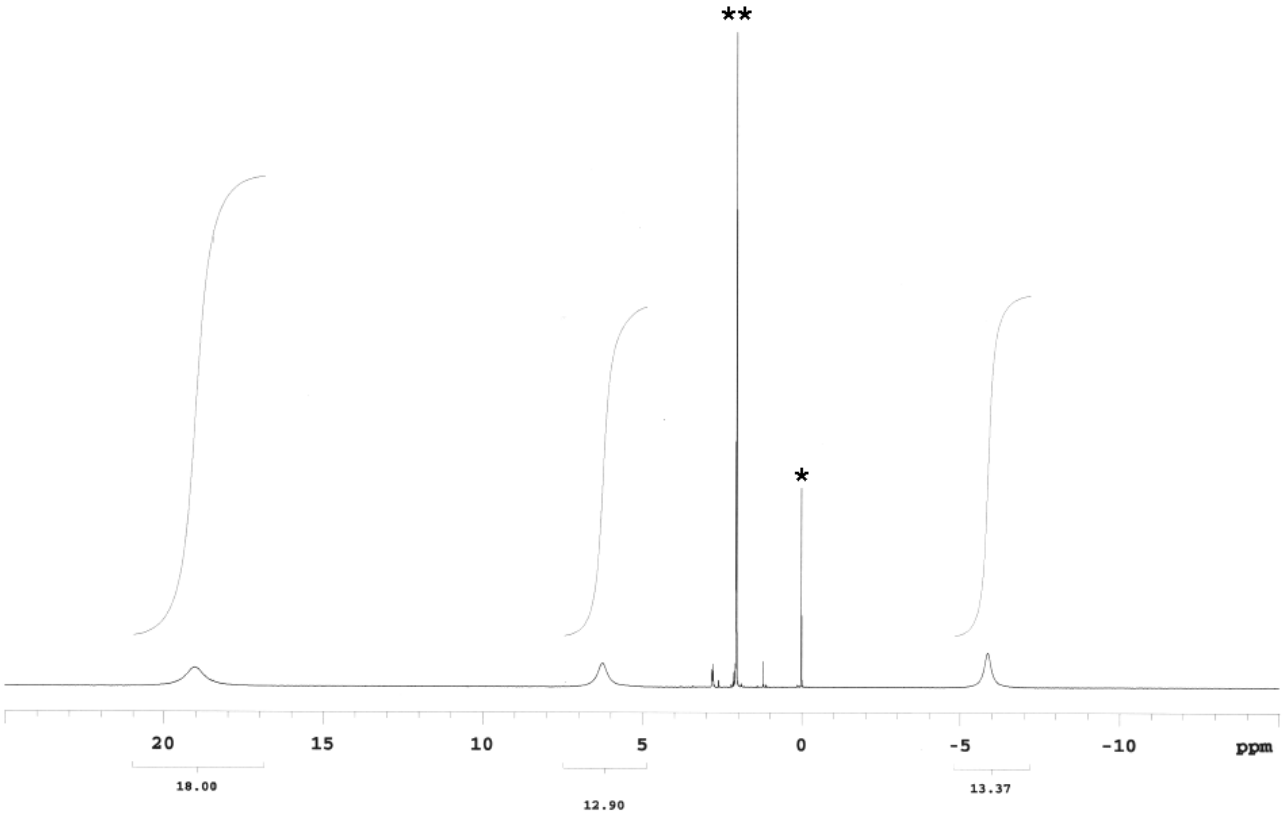
2. T_1 measurements of complexes 2a-BPh_4, 2b-PF_6 and 2b-BPh_4.

T_1 measurements of **2a-BPh_4**, **2b-PF_6** and **2b-BPh_4** were performed by the inversion recovery method. Measurements of **2a-BPh_4** and **2b-PF_6** were performed in THF-d_8 / toluene-d_8 = 5 / 1 mixed solvent and T_1 minima were 42 and 18 ms at –115 °C. Because of low solubility to the mixed solvent, measurement of **2b-BPh_4** were performed in THF-d_8 and T_1 minimum was 34 ms at –100 °C (SFigure 2).



SFigure 2. T_1 measurements of complex **2a-BPh_4, 2b-PF_6, and 2b-BPh_4**.

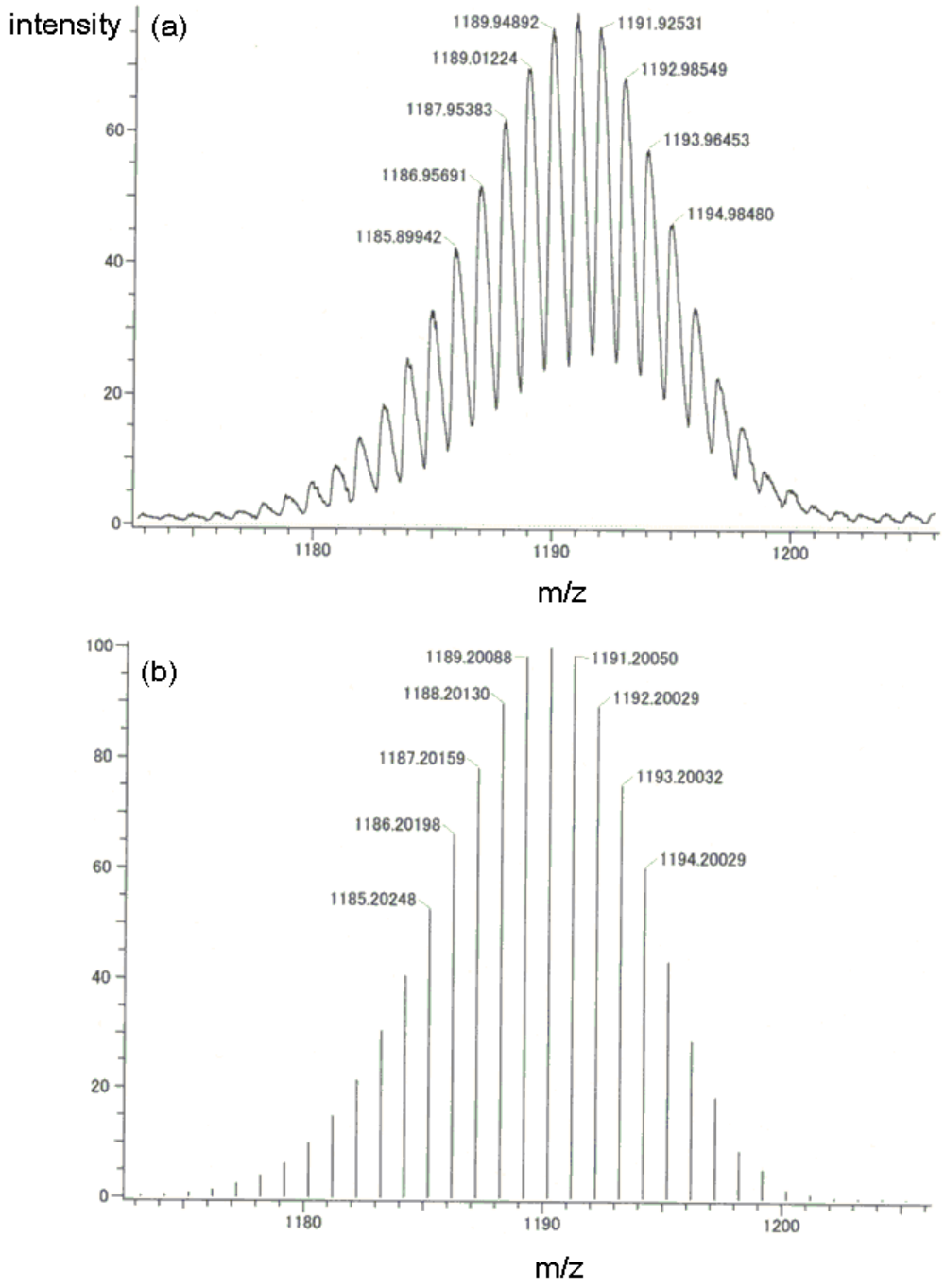
3. ^{1}H NMR spectrum of complex 4-PF_6.



SFigure 3. ^{1}H NMR spectrum of **4-PF_6** in acetone-d_6 at ambient temperature:

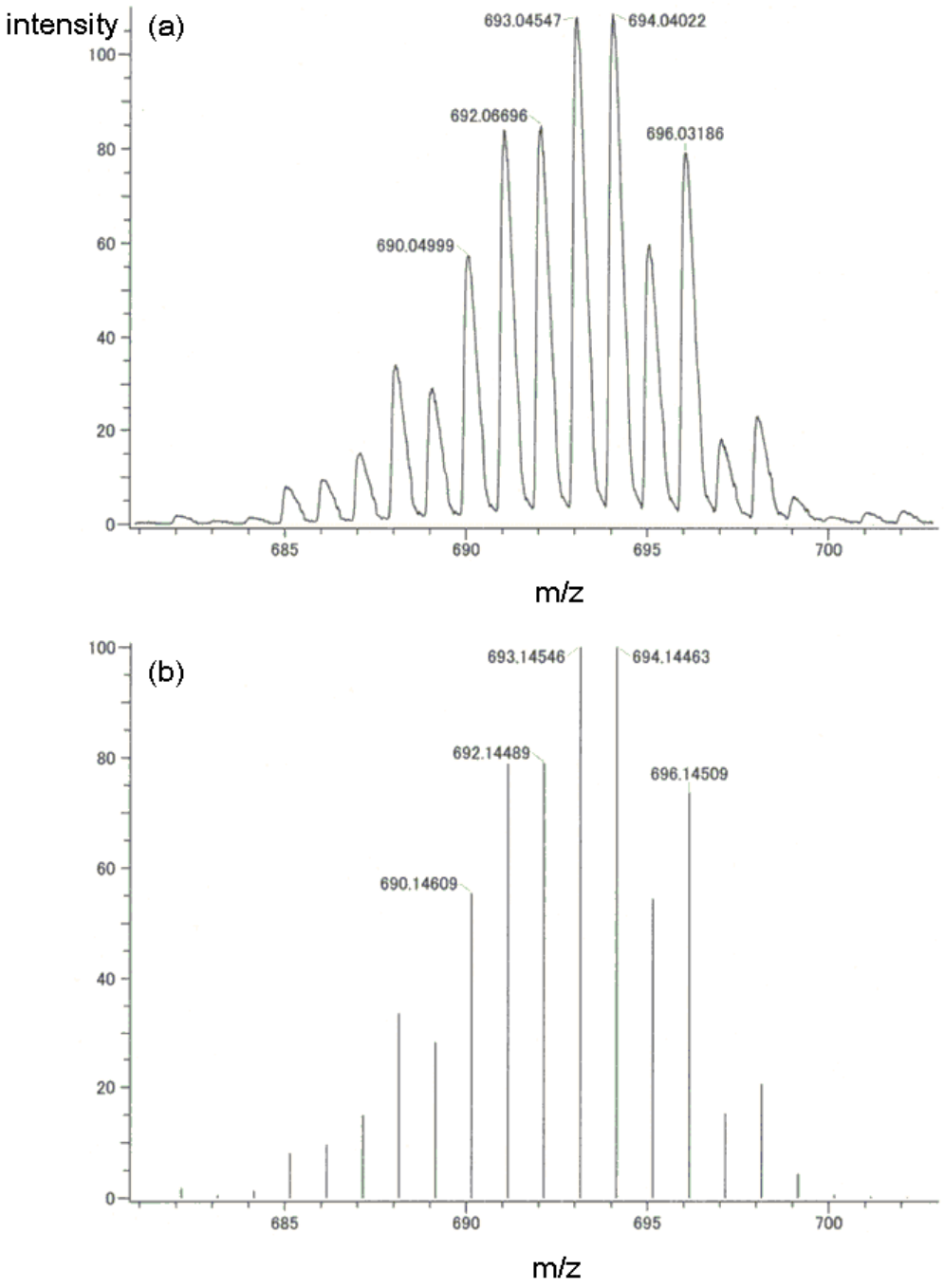
* TMS peak; ** solvent peak.

4. ESI-MS spectra of 3-BF_4 and 4-PF_6.



SFigure 4. ESI-MS spectrum of **3-BF_4**:

(a) observed spectrum; (b) simulation of $[C_{24}H_{68}N_{12}Ru_4 + (BF_4)_3]^+$.



SFigure 5. ESI-MS spectrum of **4-PF_6**:

(a) observed spectrum; (b) simulation of $[C_{18}H_{45}N_6Ru_2 + PF_6]^+$.

5. Density Functional Theory (DFT) calculations for the structures and natural charges of $[CnRuH(H_2)_2]^+$ ($2a^+$) and $[Cn^*RuH(H_2)_2]^+$ ($2b^+$).

Density functional theory (DFT) calculations were carried out at the B3PW91 level[i] in conjunction with the Stuttgart/Dresden ECP[ii] and associated with triple-ζ SDD basis sets for Ru. For N and H, 6-311G(d,p) basis sets were employed, and for C, 6-31G(d) was done. All calculations were performed by utilizing the Gaussian03 program.[iii] Molecular structures were drawn by using the *GaussView version 4.1.2* program.[iv] Frequency calculations at the same level of theory as geometry optimizations were performed on optimized structures to ensure that minima exhibit only positive frequency.

The optimized structures were reproduced the geometry, which was characterized by X-ray diffraction studies[v]. Selected bond lengths (Å) and angles (deg) shown in STable 1 and STable 2 correspond well with those of crystal structures. Natural population analyses[vi] at the same level of theory were performed on optimized structures. The optimized structures and natural charges displayed in SFigure 6.

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[i] (a) Becke, A. D. *Phys. Rev.* **1988**, *A38*, 3098. (b) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (c) Perdew, J. P.; Wang, Y. *Phys. Rev.* **1992**, *B45*, 13244.

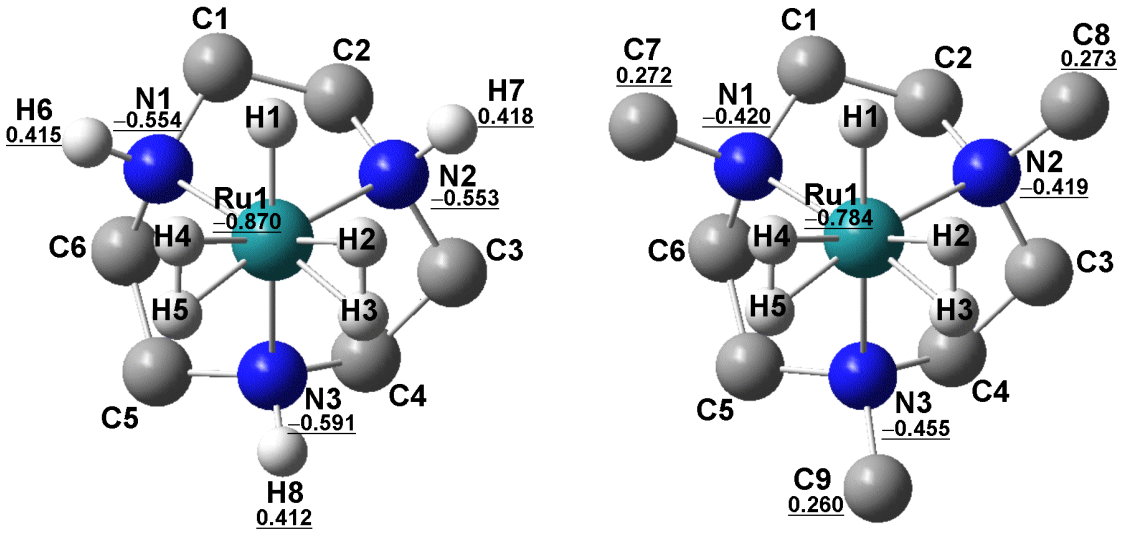
[ii] Andrae, D.; Haussermann, U.; Dolg, M.; Stoll, H.; Preuss, H. *Theor. Chim. Acta* **1990**, *77*, 123.

[iii] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.;Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.;Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.;Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03,Revision D.02*; Gaussian, Inc.: Wallingford, CT, 2004.

[iv] Dennington, R. II.; Keith, T.; Millam, J. *GaussView*, Version 4.1, Semichem, Inc., Shawnee Mission, KS, 2007.

[v] We reported X-ray diffraction study and DFT calculation for **2b** previously. For detail see: Shima, T.; Namura, K.; Kameo, H.; Suzuki, H. *Organometallics* **2010**, *29*, 337..

[vi] Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735−746.



SFigure 6. Optimized structures of **2a**$^+$ (left) and **2b**$^+$ (right).

Hydrogens on carbons are omitted for clarity.

Natural charges are underlined (Values of methyl groups are total charges of carbon and bonding hydrogens).

STable 1. Selected bond lengths (Å) and angles (deg) of **2a**$^+$

Ru(1)-N(1)	2.1576	N(1)-H(6)	1.0147	N(3)-H(8)	1.0135
Ru(1)-N(2)	2.1514	N(1)-C(6)	1.4945	N(3)-C(4)	1.4886
Ru(1)-N(3)	2.2452	N(1)-C(1)	1.4876	N(3)-C(5)	1.4810
Ru(1)-H(1)	1.5933	Ru(1)-H(5)	1.6635	H(2)-H(3)	0.9470
Ru(1)-H(2)	1.6415	H(1)-H(2)	1.8270	H(3)-H(5)	2.1957
Ru(1)-H(3)	1.6625	H(1)-H(4)	1.8293	H(4)-H(5)	0.9455
Ru(1)-H(4)	1.6418				
N(1)-Ru(1)-N(2)	80.27	H(6)-N(1)-Ru(1)	108.55	H(8)-N(3)-Ru(1)	109.42
N(1)-Ru(1)-N(3)	78.80	C(6)-N(1)-Ru(1)	113.08	C(4)-N(3)-Ru(1)	110.71
N(2)-Ru(1)-N(3)	78.67	C(1)-N(1)-Ru(1)	104.96	C(5)-N(3)-Ru(1)	104.97
H(1)-Ru(1)-N(3)	165.58	H(3)-Ru(1)-N(1)	167.94	H(5)-Ru(1)-N(2)	167.01
H(2)-Ru(1)-N(1)	158.02	H(4)-Ru(1)-N(2)	159.25		

STable 2. Selected bond lengths (Å) and angles (deg) of **2b**$^+$

Ru(1)-N(1)	2.1688	N(1)-C(7)	1.4824	N(3)-C(9)	1.4790
Ru(1)-N(2)	2.1670	N(1)-C(6)	1.4999	N(3)-C(4)	1.4934
Ru(1)-N(3)	2.2626	N(1)-C(1)	1.4906	N(3)-C(5)	1.4841
Ru(1)-H(1)	1.5943	Ru(1)-H(5)	1.6673	H(2)-H(3)	0.9360
Ru(1)-H(2)	1.6443	H(1)-H(2)	1.8348	H(3)-H(5)	2.2111
Ru(1)-H(3)	1.6678	H(1)-H(4)	1.8300	H(4)-H(5)	0.9375
Ru(1)-H(4)	1.6433				
N(1)-Ru(1)-N(2)	82.44	C(7)-N(1)-Ru(1)	113.53	C(9)-N(3)-Ru(1)	114.77
N(1)-Ru(1)-N(3)	80.95	C(6)-N(1)-Ru(1)	110.58	C(4)-N(3)-Ru(1)	108.33
N(2)-Ru(1)-N(3)	80.72	C(1)-N(1)-Ru(1)	102.84	C(5)-N(3)-Ru(1)	102.66
H(1)-Ru(1)-N(3)	167.59	H(3)-Ru(1)-N(1)	168.95	H(5)-Ru(1)-N(2)	167.68
H(2)-Ru(1)-N(1)	157.83	H(4)-Ru(1)-N(2)	159.24		

STable 3. Coordination of **2a**$^{+}$

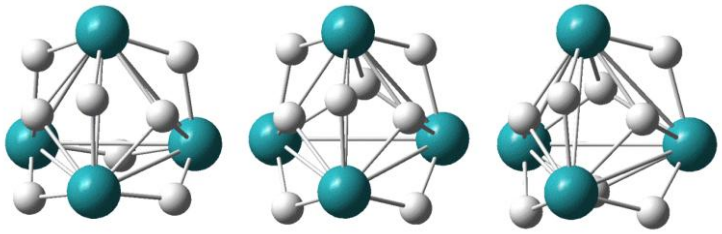
1	44	0	0.047226	0.004548	5.022887
2	7	0	-1.463014	0.055968	3.362301
3	1	0	-0.990568	-0.061528	2.473438
4	6	0	-2.467229	-1.029936	3.530269
5	6	0	-2.033684	1.421933	3.406476
6	1	0	-2.670915	-1.520132	2.573648
7	1	0	-3.412228	-0.582618	3.851007
8	1	0	-1.256945	2.103638	3.052119
9	1	0	-2.900545	1.523970	2.739501
10	7	0	-1.417783	1.367012	5.830849
11	1	0	-0.937093	2.193362	6.171057
12	6	0	-2.446328	1.782745	4.829425
13	6	0	-1.991319	0.660418	7.007596
14	1	0	-2.629879	2.858815	4.897287
15	1	0	-3.389884	1.293905	5.086995
16	1	0	-1.206721	0.619328	7.764784
17	1	0	-2.845836	1.208604	7.425230
18	7	0	-1.410851	-1.408882	5.733460
19	1	0	-0.919302	-2.111724	6.275810
20	6	0	-2.423361	-0.748064	6.614557
21	6	0	-2.002053	-2.072409	4.543639
22	1	0	-2.589849	-1.345400	7.515329
23	1	0	-3.377351	-0.722981	6.081454
24	1	0	-1.222639	-2.702652	4.109489
25	1	0	-2.841894	-2.721598	4.824127
26	1	0	0.791885	-0.021292	6.431166
27	1	0	1.287404	-1.070778	5.020130
28	1	0	0.950456	-1.072489	4.135085
29	1	0	1.284248	1.083404	5.058778
30	1	0	0.943248	1.122753	4.177826

STable 4. Coordination of **2b**$^{+}$

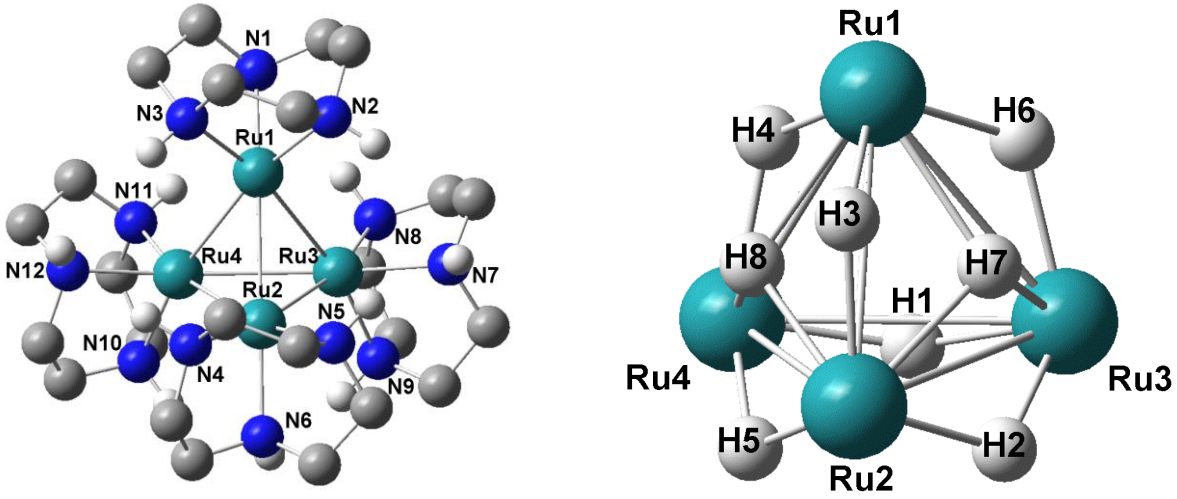
1	44	0	4.868127	-0.001076	5.063230
2	7	0	6.326611	0.066666	3.334711
3	6	0	5.712911	-0.098416	1.999230
4	6	0	7.362448	-0.986884	3.552514
5	6	0	6.901485	1.430297	3.447376
6	1	0	7.619706	-1.464386	2.601066
7	1	0	8.283117	-0.517799	3.907416
8	1	0	6.119996	2.129398	3.139096
9	1	0	7.750527	1.559191	2.758806
10	7	0	6.309239	1.394532	5.887338
11	6	0	5.695727	2.637510	6.412940
12	6	0	7.351463	1.740871	4.865882
13	6	0	6.904002	0.627321	7.018513
14	1	0	7.601428	2.804093	4.938997
15	1	0	8.270084	1.201045	5.105040
16	1	0	6.129095	0.544308	7.782615
17	1	0	7.752791	1.174815	7.453783
18	7	0	6.308885	-1.459909	5.764444
19	6	0	5.699846	-2.541479	6.576724
20	6	0	7.357494	-0.754643	6.575383
21	6	0	6.893645	-2.053671	4.529895
22	1	0	7.609498	-1.351195	7.457656
23	1	0	8.273657	-0.688436	5.984645
24	1	0	6.112352	-2.666312	4.073611
25	1	0	7.730158	-2.721174	4.783483
26	1	0	4.906856	0.625302	1.874471
27	1	0	6.457451	0.045698	1.204222
28	1	0	5.290791	-1.100529	1.913674
29	1	0	4.897447	2.381336	7.108932
30	1	0	6.447816	3.252584	6.923547
31	1	0	5.270939	3.208516	5.586489
32	1	0	4.900982	-3.018688	6.008877
33	1	0	6.454304	-3.292999	6.842526
34	1	0	5.272238	-2.116182	7.484040
35	1	0	3.965618	1.127155	4.231180
36	1	0	3.627066	1.075284	5.103900
37	1	0	4.125669	-0.031016	6.473743
38	1	0	3.625456	-1.077843	5.052265
39	1	0	3.959055	-1.083284	4.177741

6. Density Functional Theory (DFT) calculation for the structure of $[(CnRu)_4(\mu\text{-}H)_6(\mu_3\text{-}H)_2]^{4+}$ ($\mathbf{3}^{4+}$).

Density functional theory (DFT) calculations were carried out at the B3PW91 level[i] in conjunction with the Stuttgart/Dresden ECP[ii] and associated with triple-ζ SDD basis sets for Ru. For N and H, 6-311G(d,p) basis sets were employed, and for C, 6-31G(d) was done. All calculations were performed by utilizing the Gaussian03 program.[iii] The molecular structure was drawn by using the *GaussView version 4.1.2* program.[iv] Frequency calculations at the same level of theory as geometry optimizations were performed on optimized structure to ensure that minima exhibit only positive frequency. Calculations for three initial structures $[(CnRu)_4(\mu\text{-}H)_6(\mu_3\text{-}H)_2]^{4+}$ (**3A**), $[(CnRu)_4(\mu\text{-}H)_5(\mu_3\text{-}H)_3]^{4+}$ (**3B**) and $[(CnRu)_4(\mu\text{-}H)_4(\mu_3\text{-}H)_4]^{4+}$ (**3C**) (SFigure 7) converged to the same optimized structure displayed in SFigure 8. Selected bond lengths (Å) and angles (deg) are shown in STable 5.



SFigure 7. Initial structures of $\mathbf{3}^{4+}$; **3A** (left), **3B** (middle) and **3C** (right). Cn ligands are omitted for clarity. These structures afforded the same optimized structure shown in Sfigure 3.



SFigure 8. Optimized structures of $\mathbf{3}^{4+}$ (left), hydrogens on carbons and hydrido ligands are omitted for clarity, and Ru_4 core of $\mathbf{3}^{4+}$ (right).

STable 5. Selected bond lengths (Å) and angles (deg) of $\mathbf{3}^{4+}$

Ru(1)-Ru(2)	2.9915	Ru(1)-N(1)	2.1651	Ru(3)-N(7)	2.1874
Ru(1)-Ru(3)	3.0153	Ru(1)-N(2)	2.1663	Ru(3)-N(8)	2.1669
Ru(1)-Ru(4)	3.0204	Ru(1)-N(3)	2.1641	Ru(3)-N(9)	2.1717
Ru(2)-Ru(3)	3.0175	Ru(2)-N(4)	2.1678	Ru(4)-N(10)	2.1687
Ru(2)-Ru(4)	3.0176	Ru(2)-N(5)	2.1647	Ru(4)-N(11)	2.1723
Ru(3)-Ru(4)	3.0802	Ru(2)-N(6)	2.1663	Ru(4)-N(12)	2.1848
H(3)-H(7)	1.7742	H(2)-H(7)	1.7176	H(4)-H(8)	1.7210
H(3)-H(8)	1.7749	H(6)-H(7)	1.7272	H(5)-H(8)	1.7216
Ru(3)-Ru(1)-Ru(2)	60.31	Ru(1)-Ru(3)-Ru(2)	59.46	Ru(3)-Ru(4)-Ru(1)	59.23
Ru(3)-Ru(1)-Ru(4)	61.37	Ru(3)-Ru(2)-Ru(1)	60.24	Ru(2)-Ru(4)-Ru(1)	59.40
Ru(2)-Ru(1)-Ru(4)	60.25	Ru(3)-Ru(2)-Ru(4)	61.38	N(1)-Ru(1)-N(2)	78.87
Ru(4)-Ru(3)-Ru(1)	59.40	Ru(1)-Ru(2)-Ru(4)	59.40	N(2)-Ru(1)-N(3)	79.09
Ru(4)-Ru(3)-Ru(2)	59.31	Ru(3)-Ru(4)-Ru(2)	59.31	N(3)-Ru(1)-N(1)	78.88

STable 6. Coordination of $\mathbf{3}^{4+}$

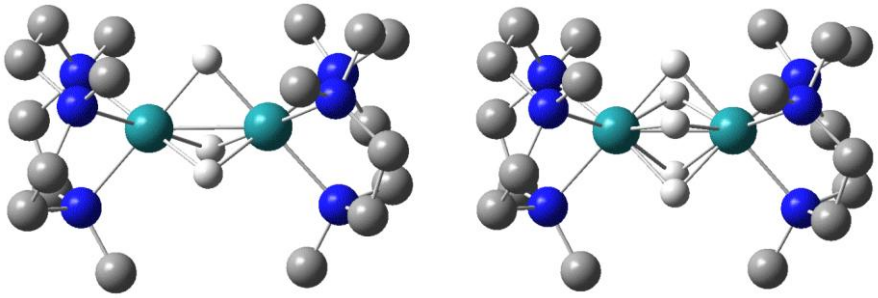
1	44	0	2.424166	-0.006429	5.015628
2	7	0	3.893085	1.376267	4.229474
3	7	0	3.895391	-0.010599	6.605720
4	7	0	3.895021	-1.373833	4.209399
5	1	0	3.427030	2.074109	3.660291
6	1	0	3.442422	0.131802	7.501836
7	1	0	3.444048	-2.223447	3.888025
8	6	0	4.494990	2.083714	5.392409
9	6	0	4.925513	1.070208	6.439846
10	6	0	4.507087	-1.368428	6.628651
11	6	0	4.933942	-1.762312	5.222908
12	6	0	4.487732	-0.714343	3.013900
13	6	0	4.922103	0.696971	3.373228
14	1	0	3.729055	2.751003	5.792226
15	1	0	5.350539	2.697928	5.086757
16	1	0	5.111868	1.569084	7.394683
17	1	0	5.871492	0.603800	6.156148
18	1	0	3.748799	-2.056090	7.008802
19	1	0	5.367360	-1.408722	7.307643
20	1	0	5.131027	-2.836705	5.175134
21	1	0	5.874088	-1.273886	4.957730
22	1	0	3.712774	-0.695072	2.245039
23	1	0	5.339321	-1.284291	2.623279
24	1	0	5.106716	1.278809	2.466145
25	1	0	5.868692	0.682627	3.917645
26	44	0	-0.010215	-1.519418	5.872292
27	7	0	0.264226	-2.269829	7.884175
28	7	0	-1.990529	-2.282143	6.307311
29	7	0	0.260897	-3.635409	5.486799
30	1	0	0.960939	-1.719179	8.373997
31	1	0	-2.680950	-1.575786	6.078088
32	1	0	0.709837	-3.772854	4.587885
33	6	0	-1.029580	-2.072862	8.594288

34	6	0	-2.162854	-2.639960	7.754669
35	6	0	-2.221751	-3.437386	5.398060
36	6	0	-1.038543	-4.388017	5.466406
37	6	0	1.190012	-4.150717	6.530635
38	6	0	0.715082	-3.703126	7.904337
39	1	0	-1.155364	-0.997083	8.733240
40	1	0	-1.019163	-2.545163	9.583996
41	1	0	-3.125884	-2.277983	8.124732
42	1	0	-2.198964	-3.728286	7.839447
43	1	0	-2.332762	-3.032520	4.390406
44	1	0	-3.147478	-3.967364	5.652768
45	1	0	-1.063121	-5.083489	4.623200
46	1	0	-1.092726	-5.005968	6.365300
47	1	0	2.177916	-3.740299	6.312106
48	1	0	1.264628	-5.244265	6.496462
49	1	0	1.508821	-3.843477	8.643102
50	1	0	-0.119806	-4.321588	8.240381
51	44	0	-0.025582	1.497541	5.926165
52	7	0	0.257307	2.221484	7.970844
53	7	0	0.218410	3.623696	5.586317
54	7	0	-2.013783	2.237926	6.389966
55	1	0	0.717242	1.526201	8.547710
56	1	0	0.906764	3.772418	4.857180
57	1	0	-2.701150	1.680605	5.895218
58	6	0	1.171938	3.391593	7.880528
59	6	0	0.676196	4.355975	6.813628
60	6	0	-1.082175	4.130706	5.070274
61	6	0	-2.205682	3.669213	5.983173
62	6	0	-2.230261	2.027979	7.846755
63	6	0	-1.044955	2.570545	8.630915
64	1	0	2.159953	3.005880	7.621866
65	1	0	1.257074	3.912582	8.842312
66	1	0	1.461547	5.073113	6.559486
67	1	0	-0.158816	4.948969	7.192637
68	1	0	-1.208400	3.720606	4.066511
69	1	0	-1.082245	5.224721	4.993062
70	1	0	-3.172482	3.799547	5.489493
71	1	0	-2.244570	4.282077	6.886539
72	1	0	-2.334044	0.952468	8.003198
73	1	0	-3.156195	2.507658	8.186538
74	1	0	-1.069203	2.190285	9.655860
75	1	0	-1.109022	3.657542	8.715715
76	44	0	-0.026057	-0.026930	3.249681
77	7	0	0.226439	1.341847	1.581832
78	7	0	0.255841	-1.421092	1.591275
79	7	0	-2.011933	-0.044738	2.378359
80	1	0	0.669992	2.192261	1.910309
81	1	0	0.953960	-2.120964	1.816224
82	1	0	-2.700924	-0.193625	3.106876
83	6	0	1.156565	0.693262	0.618291
84	6	0	0.696808	-0.728664	0.334787
85	6	0	-1.039091	-2.133196	1.419837
86	6	0	-2.178929	-1.128236	1.352870

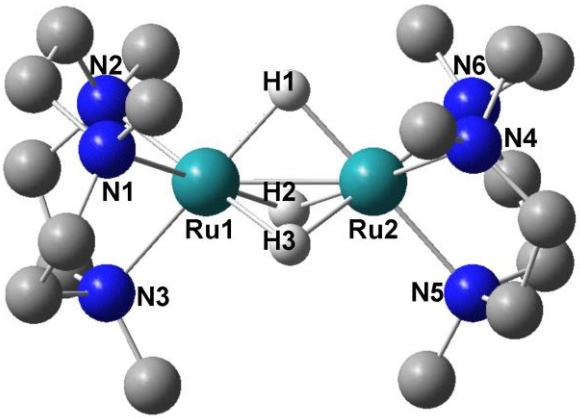
87	6	0	-2.252623	1.313361	1.820145
88	6	0	-1.078575	1.722132	0.946268
89	1	0	2.146436	0.693249	1.079328
90	1	0	1.222335	1.260827	-0.317888
91	1	0	1.498044	-1.291486	-0.152027
92	1	0	-0.136708	-0.727408	-0.371230
93	1	0	-1.157228	-2.789196	2.284808
94	1	0	-1.040363	-2.759352	0.518954
95	1	0	-3.137373	-1.637030	1.488005
96	1	0	-2.224172	-0.664116	0.365224
97	1	0	-2.357863	1.992881	2.667952
98	1	0	-3.183735	1.347672	1.241568
99	1	0	-1.108730	2.797452	0.750978
100	1	0	-1.140010	1.237989	-0.030736
101	1	0	1.748227	-1.427402	5.812371
102	1	0	1.654321	1.506788	5.508474
103	1	0	1.649145	0.334570	3.455274
104	1	0	-0.766464	0.000651	6.375642
105	1	0	-0.778421	-1.156353	4.319041
106	1	0	-0.490912	1.304077	4.265204
107	1	0	0.934502	-0.984588	4.298436
108	1	0	0.940449	0.100583	6.212982

7. Density Functional Theory (DFT) calculation for the structure of $[(Cn^*Ru)_2(\mu\text{-}H)_3]^{2+}$ (4^{2+}).

Density functional theory (DFT) calculations were carried out at the B3PW91 level[i] in conjunction with the Stuttgart/Dresden ECP[ii] and associated with triple-ζ SDD basis sets for Ru. For N and H, 6-311G(d,p) basis sets were employed, and for C, 6-31G(d) was done. All calculations were performed by utilizing the Gaussian03 program.[iii] The molecular structure was drawn by using the *GaussView version 4.1.2* program.[iv] Frequency calculations at the same level of theory as geometry optimizations were performed on optimized structure to ensure that minima exhibit only positive frequency. Two initial structures $[(Cn^*Ru)_2(\mu\text{-}H)_3]^{2+}$ (**4A**) and $[(Cn^*Ru)_2(\mu\text{-}H)_5]^{2+}$ (**4B**) (SFigure 9) were optimized and only **4A** reproduced the molecular structure of **4-BPh$_4$** as shown in Sfigure 10. Selected bond lengths (Å) and angles (°) are shown in STable 7.



SFigure 9. Initial structures of $\mathbf{4}^{2+}$; **4A** (left) and **4B** (right). Hydrogen atoms on Cn ligands are omitted for clarity. Calculations for **4A** afforded optimized structure shown in SFigure 5. Calculations for **4B** did not converge and optimized structure was not obtained.



SFigure 10. Optimized structure of $\mathbf{4}^{2+}$. Hydrogen atoms on carbons are omitted for clarity.

STable 7. Selected bond lengths (Å) and angles (°) of $\mathbf{4}^{2+}$

Ru(1)-Ru(2)	2.4001	Ru(1)-N(3)	2.1633	Ru(2)-N(5)	2.1633
Ru(1)-N(1)	2.1621	Ru(2)-N(4)	2.1659	Ru(2)-N(6)	2.1621
Ru(1)-N(2)	2.1659				
Ru(1)-H(1)	1.7965	Ru(1)-H(3)	1.7948	Ru(2)-H(2)	1.7948
Ru(1)-H(2)	1.7968	Ru(2)-H(1)	1.7965	Ru(2)-H(3)	1.7968
N(1)-Ru(1)-N(2)	81.26	N(2)-Ru(1)-N(3)	81.37	N(2)-Ru(1)-Ru(2)	131.27
N(1)-Ru(1)-N(3)	81.22	N(3)-Ru(1)-Ru(2)	131.24	N(1)-Ru(1)-Ru(2)	131.19
N(1)-Ru(1)-H(2)	178.94	N(3)-Ru(1)-H(1)	179.06	Ru(1)-H(2)-Ru(2)	83.86
N(2)-Ru(1)-H(3)	178.89	Ru(1)-H(1)-Ru(2)	83.83	Ru(1)-H(3)-Ru(2)	83.86

STable 8. Coordination of $\mathbf{4}^{2+}$

1	44	0	-0.010041	0.001460	4.999039
2	44	0	2.390042	-0.001460	4.999039
3	7	0	-1.435953	0.027943	3.372394
4	6	0	-0.778017	-0.178195	2.062850
5	6	0	-2.484468	-1.027997	3.579354
6	6	0	-2.024190	1.395820	3.418402
7	1	0	-0.361967	-1.185316	2.023388
8	1	0	0.028849	0.545174	1.949732
9	1	0	-1.499424	-0.053282	1.245782
10	1	0	-2.720192	-1.510854	2.626319
11	1	0	-3.408388	-0.550257	3.911046
12	1	0	-1.238757	2.084673	3.098409
13	1	0	-2.860100	1.487677	2.710982
14	7	0	-1.435592	-1.420677	5.786366
15	6	0	-0.774012	-2.443304	6.626565
16	6	0	-2.488491	-0.713494	6.591511
17	6	0	-2.021567	-2.070967	4.581367
18	1	0	-0.352030	-1.964534	7.510946
19	1	0	0.029937	-2.908198	6.056934
20	1	0	-1.493228	-3.210752	6.938491
21	1	0	-2.735406	-1.299706	7.481809
22	1	0	-3.406111	-0.657749	6.003031
23	1	0	-1.236646	-2.695081	4.147292
24	1	0	-2.857429	-2.728486	4.858243
25	7	0	-1.436909	1.396939	5.840438
26	6	0	-0.781667	2.635980	6.315041
27	6	0	-2.486647	1.740998	4.822541
28	6	0	-2.023369	0.671835	7.001820
29	1	0	-0.354621	3.166406	5.463413
30	1	0	0.016575	2.376889	7.010279
31	1	0	-1.507541	3.286226	6.819061
32	1	0	-2.725773	2.807234	4.879079
33	1	0	-3.408712	1.212837	5.072375
34	1	0	-1.237007	0.600626	7.757157
35	1	0	-2.857750	1.238805	7.437611
36	7	0	3.815954	-0.027943	3.372393
37	6	0	3.158016	0.178195	2.062850

38	6	0	4.864469	1.027998	3.579353
39	6	0	4.404190	-1.395820	3.418402
40	1	0	2.741966	1.185316	2.023389
41	1	0	2.351151	-0.545174	1.949733
42	1	0	3.879422	0.053282	1.245782
43	1	0	5.100192	1.510854	2.626318
44	1	0	5.788389	0.550258	3.911045
45	1	0	3.618757	-2.084672	3.098410
46	1	0	5.240100	-1.487678	2.710982
47	7	0	3.815593	1.420677	5.786366
48	6	0	3.154011	2.443304	6.626565
49	6	0	4.868491	0.713494	6.591511
50	6	0	4.401567	2.070968	4.581367
51	1	0	2.732030	1.964533	7.510946
52	1	0	2.350062	2.908197	6.056933
53	1	0	3.873227	3.210752	6.938491
54	1	0	5.115407	1.299706	7.481809
55	1	0	5.786111	0.657750	6.003032
56	1	0	3.616645	2.695080	4.147292
57	1	0	5.237428	2.728487	4.858242
58	7	0	3.816910	-1.396940	5.840438
59	6	0	3.161667	-2.635980	6.315040
60	6	0	4.866648	-1.740998	4.822541
61	6	0	4.403369	-0.671835	7.001820
62	1	0	2.734620	-3.166405	5.463412
63	1	0	2.363424	-2.376888	7.010278
64	1	0	3.887539	-3.286226	6.819061
65	1	0	5.105773	-2.807234	4.879078
66	1	0	5.788713	-1.212838	5.072375
67	1	0	3.617007	-0.600626	7.757156
68	1	0	5.237749	-1.238805	7.437612
69	1	0	1.190000	0.000000	6.335875
70	1	0	1.187133	-1.158103	4.333000
71	1	0	1.192867	1.158103	4.333000

8. X-ray diffraction studies.

Crystals suitable for X-ray analyses of **2a-BPh$_4$**, **3-BF$_4$** and **4-BPh$_4$** were obtained from the preparations described above and mounted on nylon Cryoloops with Paratone-N (Hampton Research Corp.). The X-ray diffraction experiments on **2a-BPh$_4$**, **3-BF$_4$** and **4-BPh$_4$** were carried out using a Rigaku R-AXIS RAPID imaging plate diffractometer with a graphite-monochromated Mo Kα radiation source (λ = 0.71069 Å). Cell refinement and data reduction were carried out using the PROCESS-AUTO program[vii]. The intensity data were corrected for Lorentz-polarization effects and empirical absorption. The structures of **2a-BPh$_4$**, **3-BF$_4$** and **4-BPh$_4$** were determined by direct methods using the SHELX-97 program[viii]. All non-hydrogen atoms were found by a difference Fourier synthesis. The refinement was carried out by the least-squares methods based on F^2 with all measured reflection data. Non-hydrogen atoms except one BF_4 anion and acetone included in **3-BF$_4$** were refined anisotropically. The hydrogen atoms except those bounded to metals were included in calculated positions and refined by using a riding model. The metal-bound hydrogen atoms of **3-BF$_4$** and **4-BPh$_4$** were located on difference Fourier maps and refined isotropically. Details of crystal data and results of analyses are listed in STable 9.

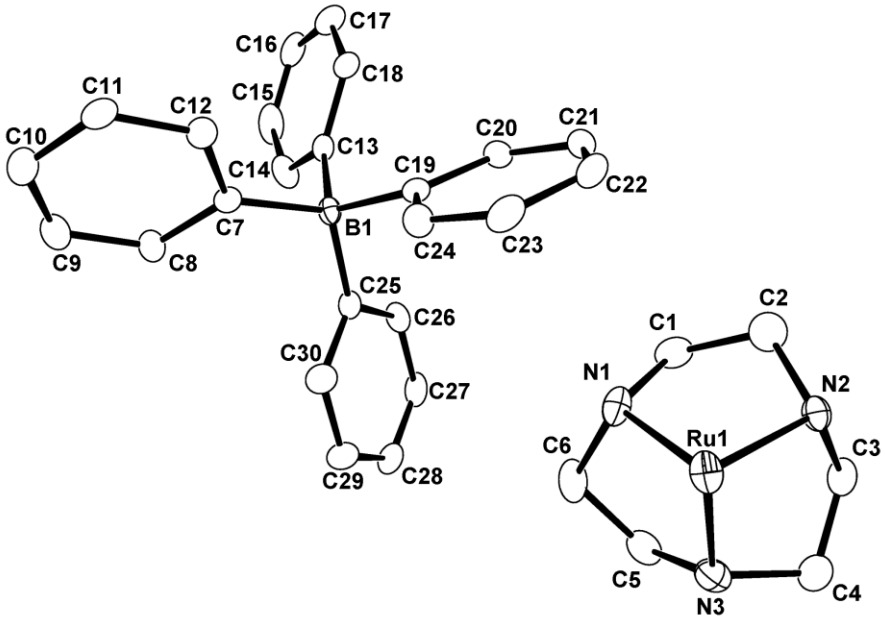
[vii] *PROCESS-AUTO*, Automatic Data Acquisition and Processing Package for Imaging Plate Diffractometer; Rigaku Corporation: TokyoJapan, 1998.

[viii] Sheldrick, G. M. *SHELX-97, Program for Crystal Structure Determination*; University of Göttingen: Göttingen, Germany, 1997.

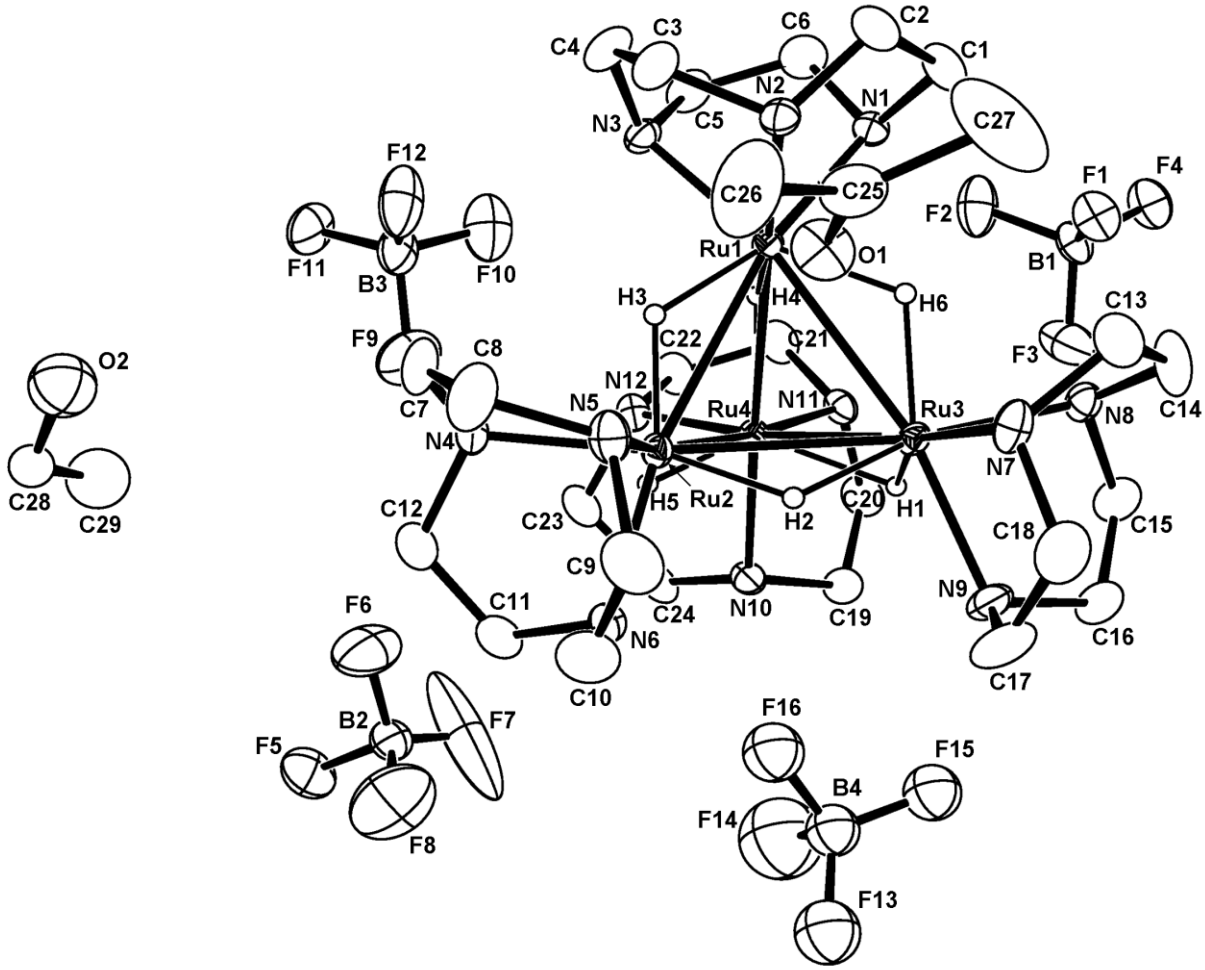
STable 9. Crystallographic Data of 2a-BPh_4, 3-BF_4 and 4-BPh_4

	2a-BPh_4	**3-BF_4**	**4-BPh_4**
empirical formula	$C_{30}H_{40}B_1N_3Ru_1$	$C_{24}H_{68}B_4F_{16}N_{12}Ru_4\cdot(C_3H_6O_1)_{1.5}$	$C_{66}H_{85}B_2N_6Ru_2$
fw	554.53	1363.54	1186.16
cryst description	needle	platelet	platelet
cryst color	colorless	red	purple
cryst size (mm)	0.71 × 0.09 × 0.07	0.46 × 0.30 × 0.06	0.41 × 0.13 × 0.03
crystallizing solution	acetonitrile (– 30 °C)	acetone (25 °C)	DMSO/Et_2O (25 °C)
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1$ (# 4)	$P2_1/n$ (# 14)	$P2_1/n$ (# 14)
a (Å)	9.7101(16)	11.9546(5)	12.6657(3)
b (Å)	10.2653(19)	21.0770(8)	35.4433(8)
c (Å)	13.582(2)	20.2021(8)	12.9853(3)
β (deg)	92.650(5)	93.9900(13)	90.1310(7)
volume (Å^3)	1352.3(4)	5077.9(4)	5829.3(2)
Z value	2	4	4
D_{calc} (g/cm^3)	1.362	1.784	1.352
measurement temp. (°C)	−120	−100	−100
μ (Mo Kα) (mm^{-1})	0.603	1.266	0.564
diffractometer	Rigaku R-AXIS RAPID	Rigaku R-AXIS RAPID	Rigaku R-AXIS RAPID
radiation	Mo Kα (λ = 0.71069 Å)	Mo Kα (λ = 0.71069 Å)	Mo Kα (λ = 0.71069 Å)
monochrometer	graphite	graphite	graphite
$2\theta_{max}$ (deg)	55	55	60
reflns collected	10212	38215	68655
indep reflns	3199 (R_{int} = 0.0478)	11701 (R_{int} = 0.0523)	17203 (R_{int} =0.0246)
reflns obsd (> 2σ)	5120	9638	14504
abs. correction type	empirical	empirical	empirical
abs. transmn	0.5334 (min.), 1.0000 (max.)	0.7250 (min.), 1.0000 (max.)	0.7164 (min.), 1.0000 (max.)
R_1 ($I > 2\sigma(I)$)	0.0467	0.0488	0.0343
wR_2 ($I > 2\sigma(I)$)	0.1157	0.1303	0.0871
R_1 (all data)	0.0566	0.0578	0.0422
wR_2 (all data)	0.1290	0.1376	0.0927
data / restraints / params	5808 / 1 / 316	11360 / 6 / 588	16866 / 0 / 699
goodness of fit on F^2	1.119	1.038	1.037
largest diff peak and hole (e Å^{-3})	1.396 and -1.049	1.591 and -1.463	3.102 and -0.768

SFigure 11. ORTEP drawing of **2a-BPh$_4$**



SFigure 12. ORTEP drawing of **3-BF$_4$**



SFigure 13. ORTEP drawing of **4-BPh$_4$**