Supplementary Material (ESI) for Journal of the Chemical Society, Dalton Transactions
The Royal Society of Chemistry 2017

Supporting Information

Stepwise synthesis of the heterotrimetallic chains $[MRu_2(dpa)_4X_2]^{0/1+}$ using group 7 to group 12 transition metal ions and $[Ru_2(dpa)_4Cl]$

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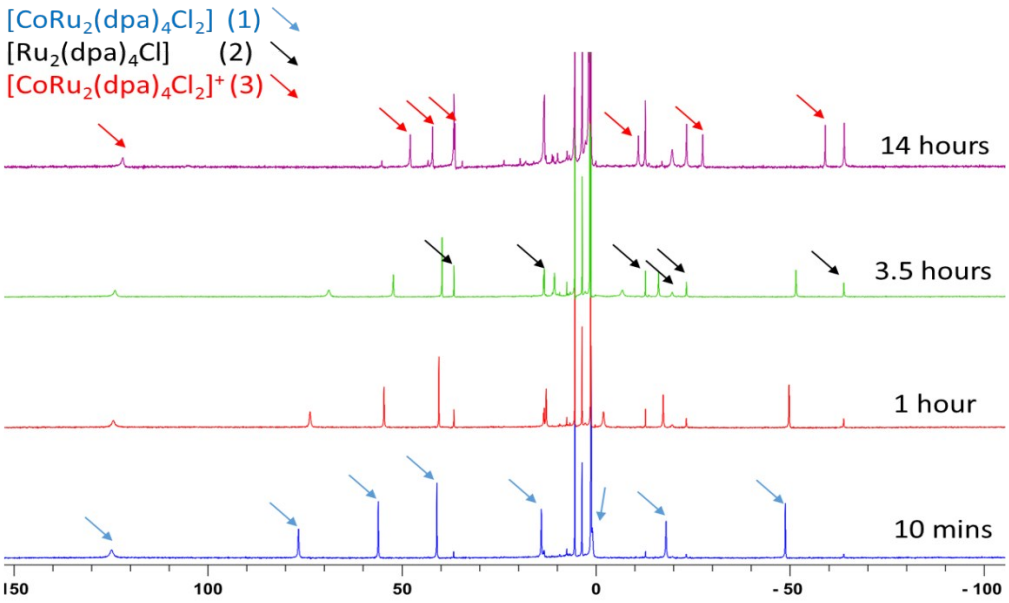


Figure S1. ^{1}H NMR spectrum of $[CoRu_2(dpa)_4Cl_2]$ (**1**) in CD_2Cl_2 under air.

Crystallographic Section:

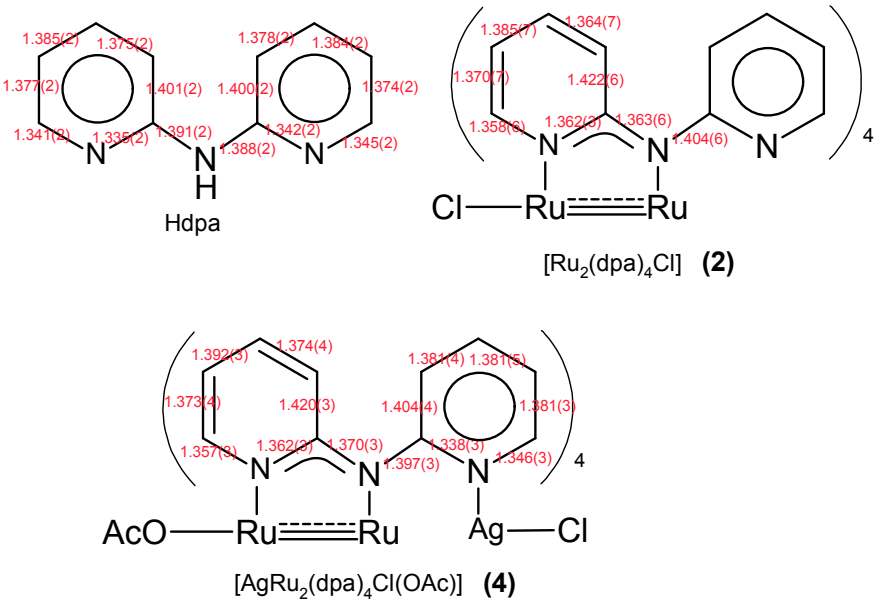


Figure S2. The bond lengths of Hdpa ligand[1] in comparison with its coordination counterparts in complexes **2** and **4**. The C and N atoms in three uncoordinated pyridyl groups in **2** are disordered, therefore, their distances are less accurate.

Table S1 : X-ray crystallographic data for compounds **1-11**.

Compound	**1**	**2**·CH_2Cl_2	**3**·CH_2Cl_2·$CHCl_3$	**4**·$2CH_2Cl_2$	**5**·$0.5CH_2Cl_2$·acetone	**6**·$1.5CH_2Cl_2$·$0.5Et_2O$
Formula	$C_{40}H_{32}ClN_{12}Ru_2$	$C_{41}H_{34}Cl_4CoN_{12}Ru_2$	$C_{42}H_{35}Cl_7CoF_6N_{12}PRu_2$	$C_{44}H_{39}AgCl_5N_{12}O_2Ru_2$	$C_{43.5}H_{39}Cl_4MnN_{12}O_5\ Ru_2$	$C_{43.5}H_{40}Cl_5F_6FeN_{12}OPRu_2$
Formula weight	918.36	1097.67	1362.01	1255.13	1208.74	1327.08
Temperature	150(2) K	150(2) K	150(2) K	150(2) K	150(2) K	150(2) K
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	Pnn2	$P2_1/n$	C2/c	$P2_1/n$	$P2_1/n$
a / Å	9.7288(4)	13.0347(3)	11.5837(8)	19.1716(7)	11.3404(3)	11.5723(4)
b / Å	18.8437(7)	14.1300(3)	21.4250(18)	16.5217(6)	21.4694(5)	21.3821(7)
c / Å	20.4662(8)	11.2290(3)	20.3563(17)	15.6164(5)	19.9024(4)	20.4312(7)
α/ º	90	90	90	90	90	90
β/ º	99.8469(12)	90	92.830(3)	108.8009(11)	93.7271(12)	92.9440(11)
γ/ º	90	90	90	90	90	90
V / $Å^3$	3696.7(3)	2068.16(9)	5045.9(7)	4682.5(3)	4835.4(2)	5048.8(3)
Z	4	2	4	4	4	4
Reflection collected	21765	11811	21845	19416	24577	32579
Independent reflections	8396	4298	8810	5381	11009	11585
R1, wR2 [I>2sigma(I)]	0.0481, 0.1130	0.0310, 0.0586	0.0728, 0.1489	0.0282, 0.0753	0.0535, 0.1157	0.0608, 0.1471
R1, wR2 (all data)	0.0901, 0.1294	0.0549, 0.0642	0.1891, 0.1909	0.0345, 0.0783	0.0904, 0.1265	0.0740, 0.1547
Goodness-of-fit on F^2	1.031	0.962	1.016	1.076	1.120	1.106

Compound	**7**·$2CH_2Cl_2$	**8**·$2CH_2Cl_2$·$0.398CH_3CN$	**9**·$3CH_2Cl_2$	**10**·$2.25CH_2Cl_2$	**11**·$2\ CH_2Cl_2$
Formula	$C_{42}H_{36}Cl_7N_{12}O_4Ru_2Zn$	$C_{42.79}H_{37.19}CdCl_7N_{12.4}O_4Ru_2$	$C_{43}H_{38}Cl_8PF_6N_{12}PdRu_2$	$C_{42.25}H_{36.5}Cl_{6.5}F_6N_{12}PRhRu_2$	$C_{42}H_{36}Cl_6F_6IrN_{12}PRu_2$
Formula weight	1288.49	1351.80	1459.96	1392.78	1460.84
Temperature	150(2) K	150(2) K	150(2) K	150(2) K	150(2) K
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	P2/n	$P2_1/n$	$P2_1/n$
a / Å	11.4703(3)	11.5728(1)	12.3353(5)	11.4470(4)	11.4236(3)
b / Å	21.0727(6)	21.0516(2)	10.3177(4)	21.2891(8)	21.3206(6)
c / Å	20.3128(7)	20.4882(2)	20.5839(8)	20.5063(8)	20.5318(6)
α/ º	90	90	90	90	90
β/ º	93.7692(12)	94.5106(7)	92.4271(10)	93.0985(12)	92.9580(9)
γ/ º	90	90	90	90	90
V / $Å^3$	4899.2(3)	4976.00(8)	2617.40(18)	4990.0(3)	4994.0(2)
Z	4	4	2	4	4
Reflection collected	28980	28617	20401	34072	37341
Independent reflections	11197	11314	6006	11437	11447
R1, wR2 [I>2sigma(I)]	0.0487, 0.1255	0.0705, 0.1478	0.0294, 0.0569	0.0429, 0.0971	0.0389, 0.0844
R1, wR2 (all data)	0.0824, 0.1401	0.0989, 0.1565	0.0351, 0.0592	0.0493, 0.1000	0.0459, 0.0871
Goodness-of-fit on F^2	1.031	1.031	1.137	1.113	1.116

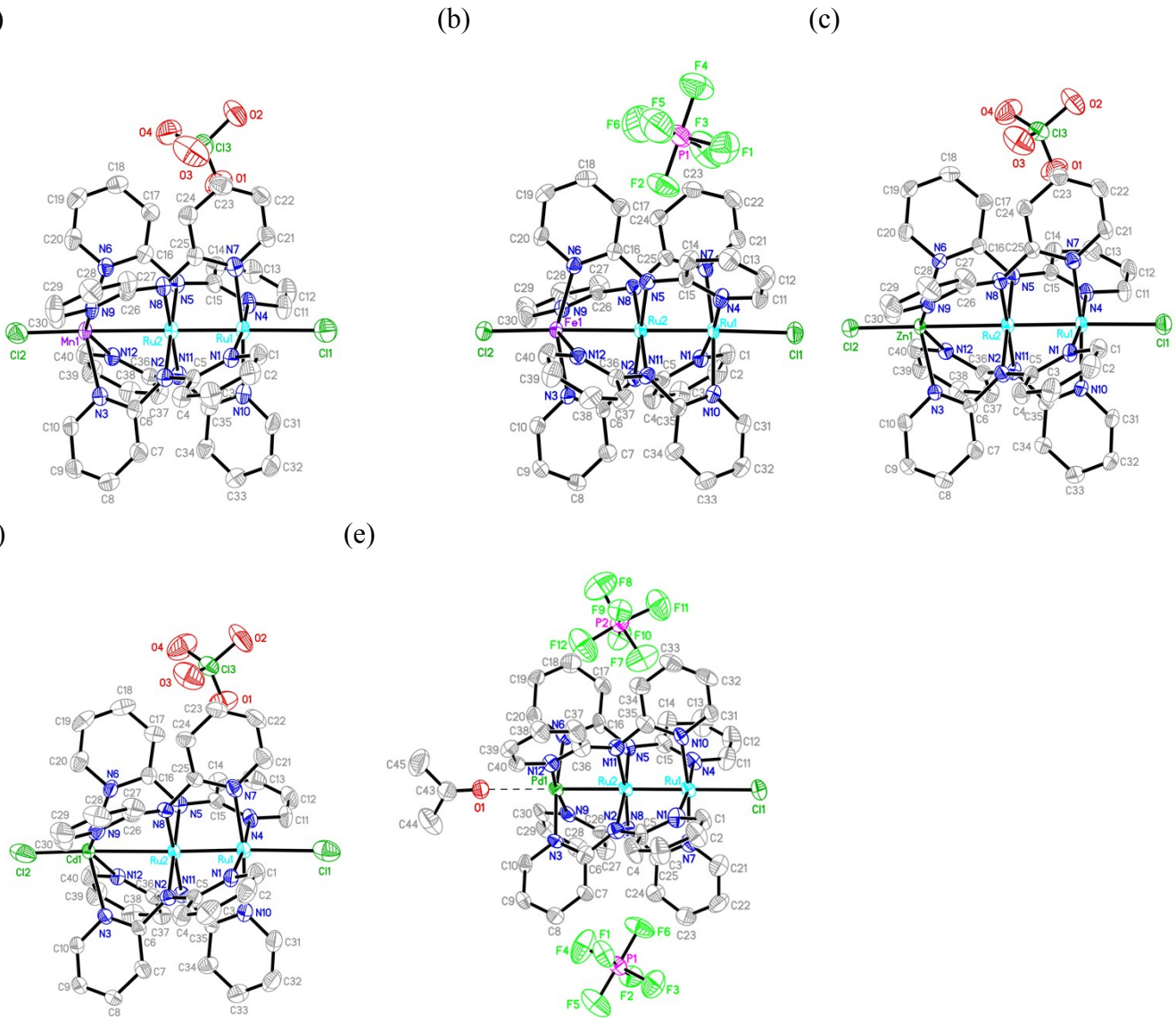


Figure S3. ORTEP view of the molecular structures of **5** (a), **6** (b), **7** (c), **8** (d) and **[**$PdRu_2(dpa)_4Cl(OC(CH_3)_2)](PF_6)_2$ (e). All atoms are drawn at the 50% probability level and hydrogen atoms are omitted for clarity. Crystal data for $[PdRu_2(dpa)_4Cl(OC(CH_3)_2)](PF_6)_2$: $C_{45}H_{45}ClF_{12}N_{12}O_{3.5}P_2PdRu_2$, *M*w = 1443.86, Triclinic, space group Pī., *a* = 9.8959(3) Å, *b* = 17.3019(5) Å, *c* = 17.8514(5) Å, α= 98.5142(14)°, β = 100.5271(15)°, γ = 98.7123(14)°, *V* = 2921.39(15) $Å^3$, *Z* = 2, T = 150(2) K, 34873 reflection collected, 16339 independent, R1 = 0.0984, wR2 = 0.2661[I>2sigma(I)], R1 = 0.1420, wR2 = 0.3137 for all data, crystal size 0.300 x 0.160 x 0.030 mm^3. This structural refinement was not satisfactory due to the thin-plate shape crystal. Hence, it is less accurate in C−C bond distances. However, the distances of heavy atoms (Ru and Pd) are still reliable. (Ru1−Ru2 = 2.2584(13); Ru2···Pd1 = 2.4910(13)).

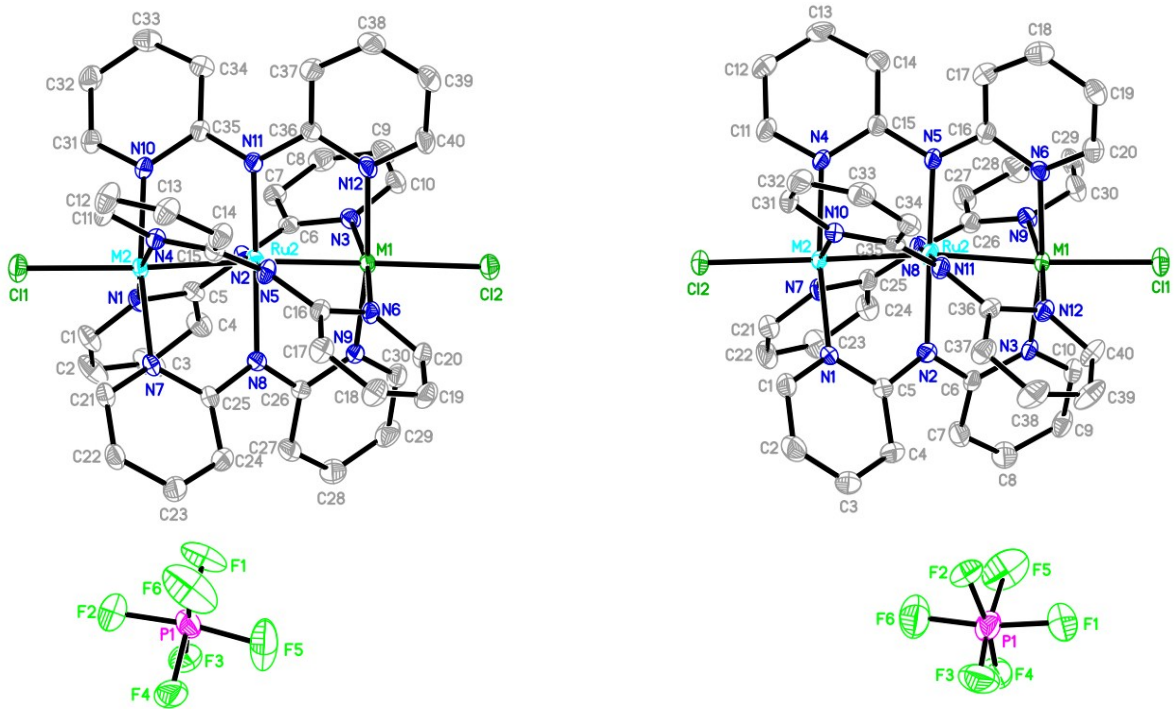


Figure S4. The crystal structures of $[RhRu_2(dpa)_4Cl_2](PF_6)$ (**10**) (left) and $[IrRu_2(dpa)_4Cl_2](PF_6)$ (**11**)(right). The solvent molecules and hydrogen atoms are omitted for clarity. Occupancy contributions: M1 = 0.53 Rh / 0.47 Ru and M2 = 0.47 Rh / 0.53 Ru for $[RhRu_2(dpa)_4Cl_2]^+$; M1 = 0.523 Ir / 0.477 Ru and M2 = 0.477 Ir / 0.523 Ru for $[IrRu_2(dpa)_4Cl_2]^+$

Spectroscopic Characterization:

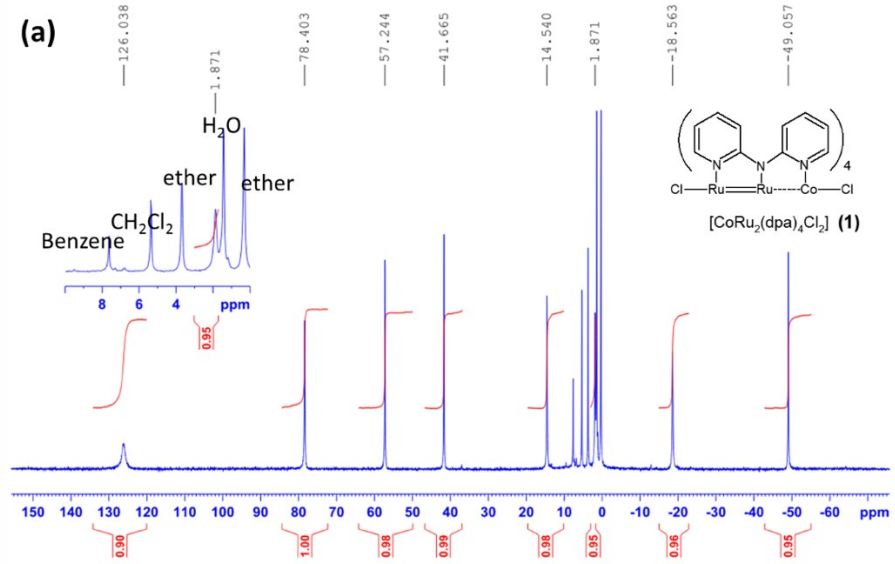


Figure S5. (a) ^{1}H NMR spectrum of **(1)** in CD_2Cl_2

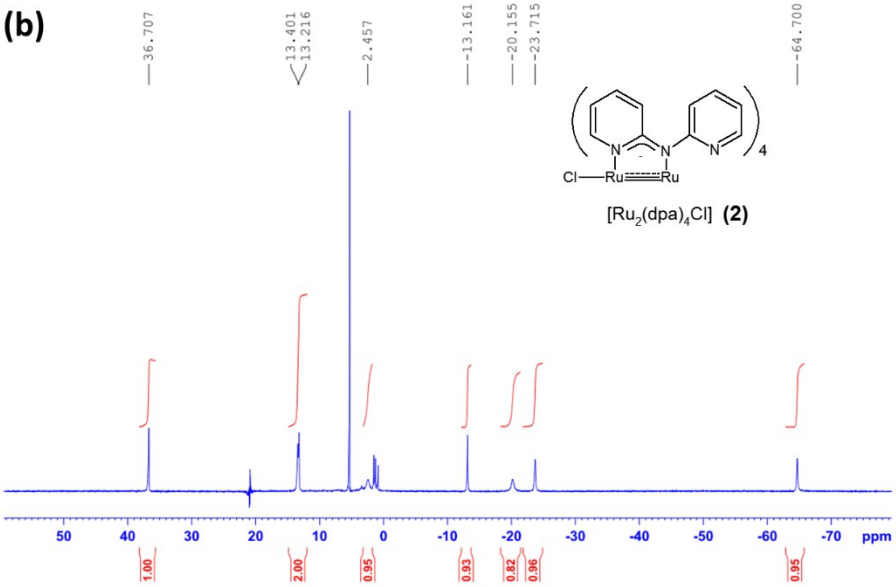


Figure S5. (b) ^{1}H NMR spectrum of **(2)** in CD_2Cl_2

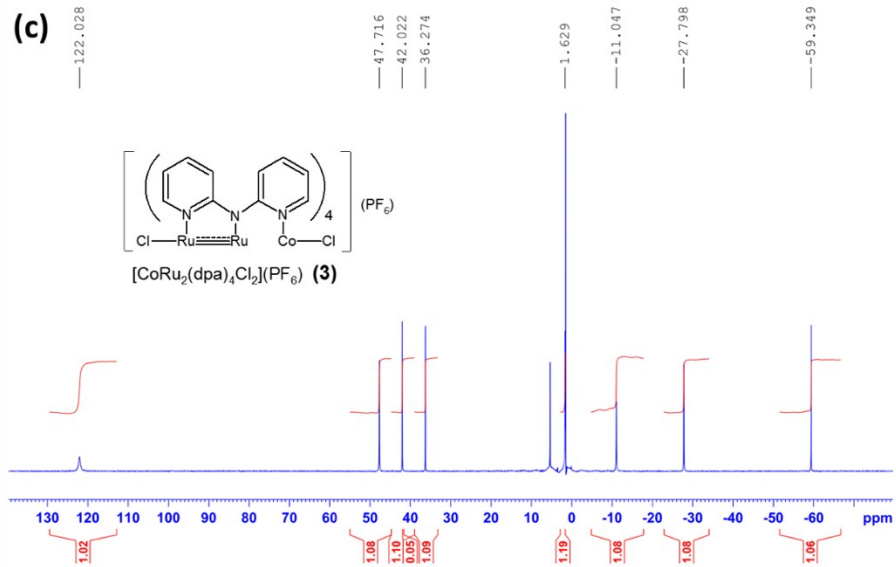


Figure S5. (c) ^{1}H NMR spectrum of **(3)** in CD_2Cl_2

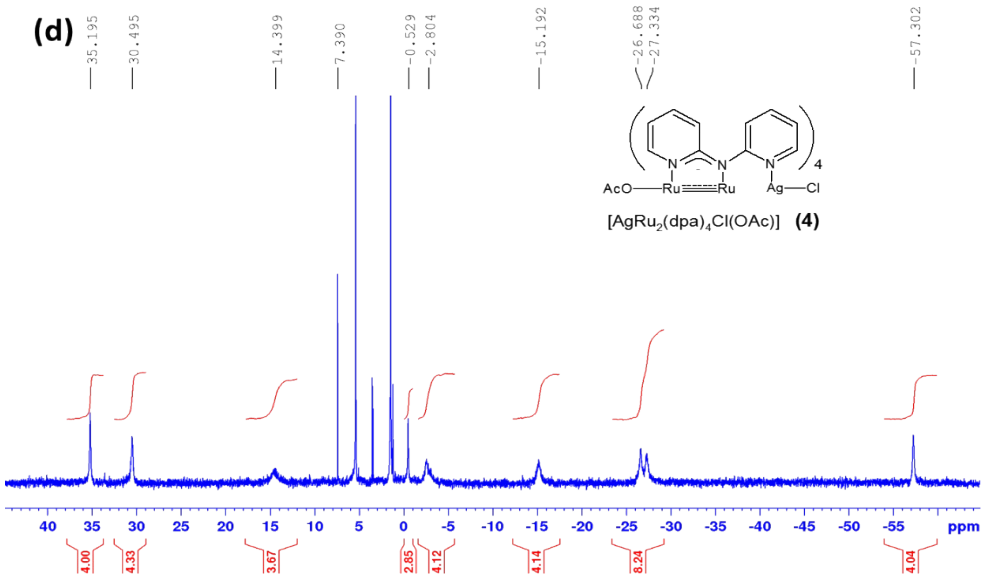


Figure S5. (d) ^{1}H NMR spectrum of **(4)** in CD_2Cl_2

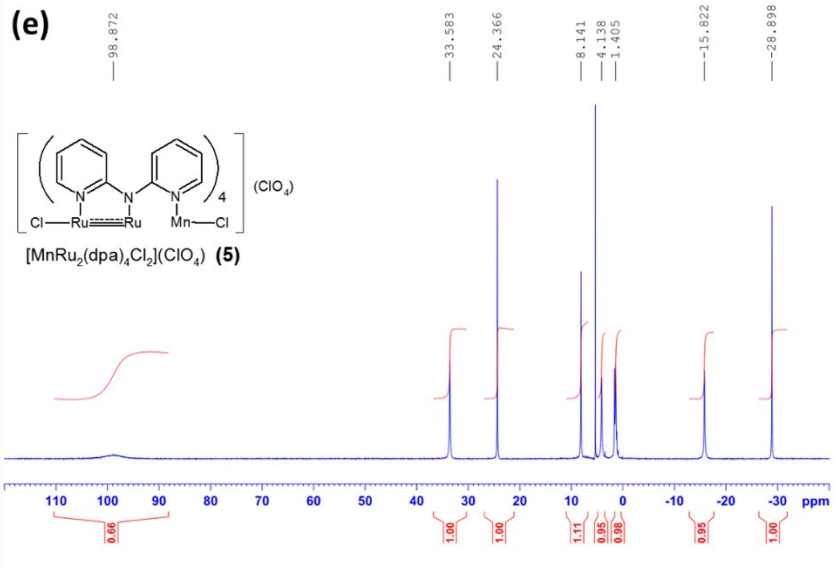


Figure S5. (e) ^{1}H NMR spectrum of **(5)** in CD_2Cl_2

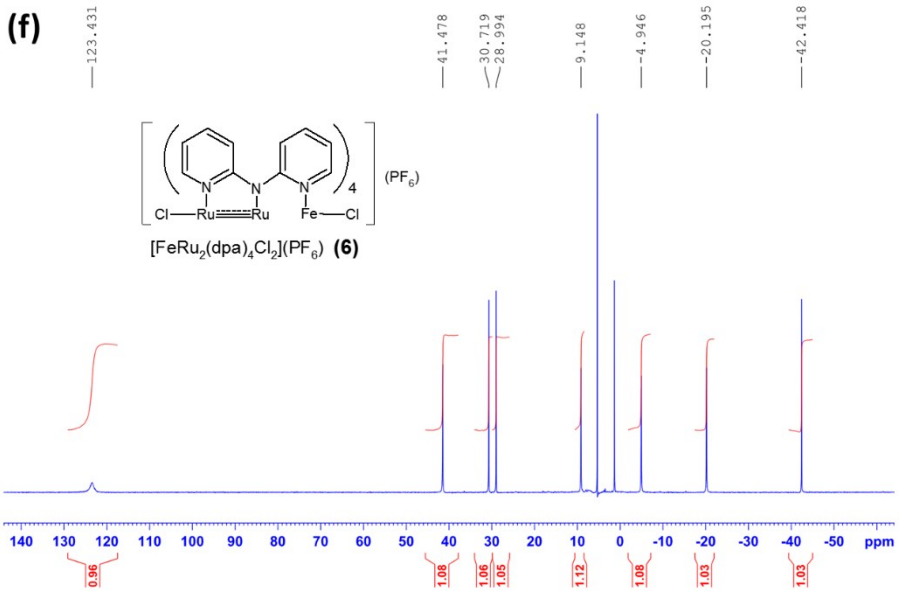


Figure S5. (f) ^{1}H NMR spectrum of **(6)** in CD_2Cl_2

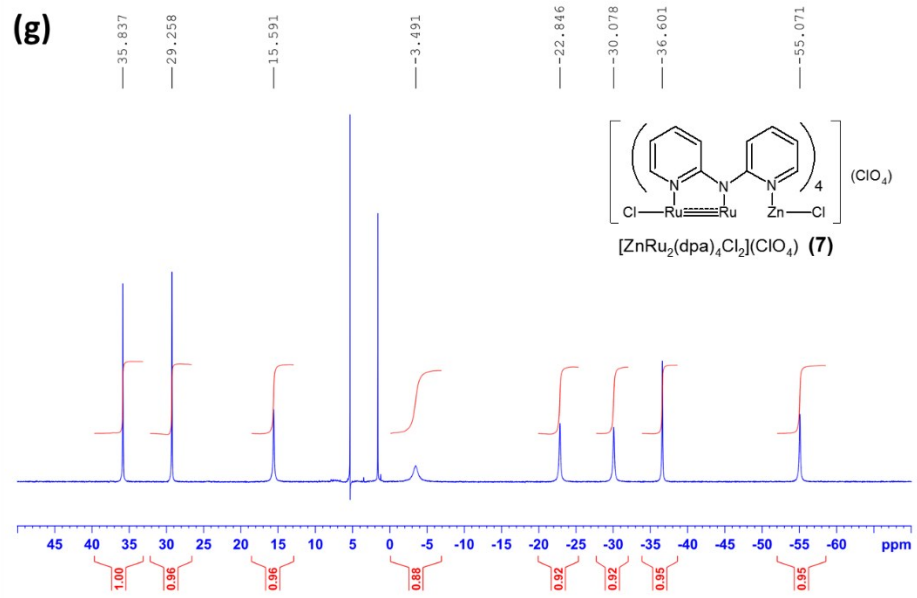


Figure S5. (g) ^{1}H NMR spectrum of **(7)** in CD_2Cl_2

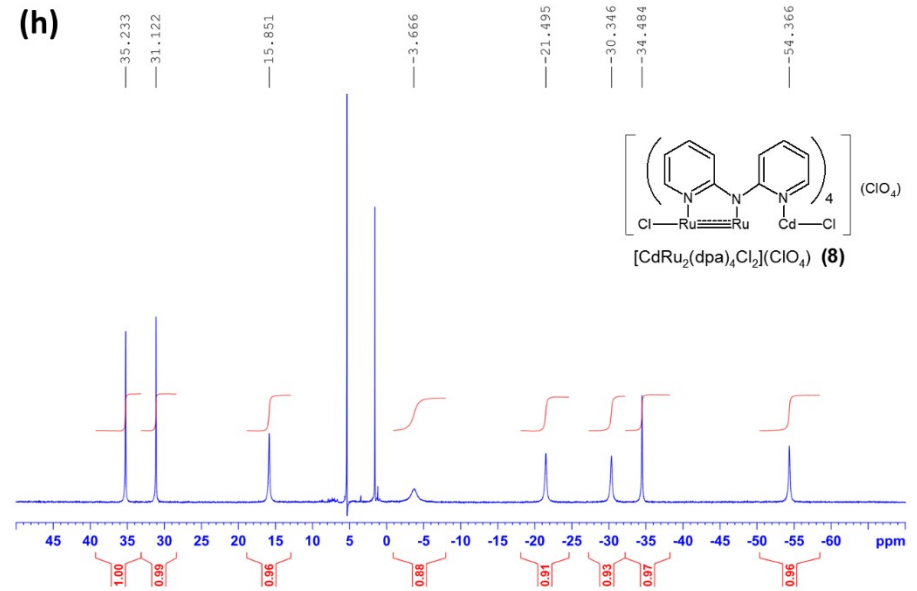


Figure S5. (h) ^{1}H NMR spectrum of **(8)** in CD_2Cl_2

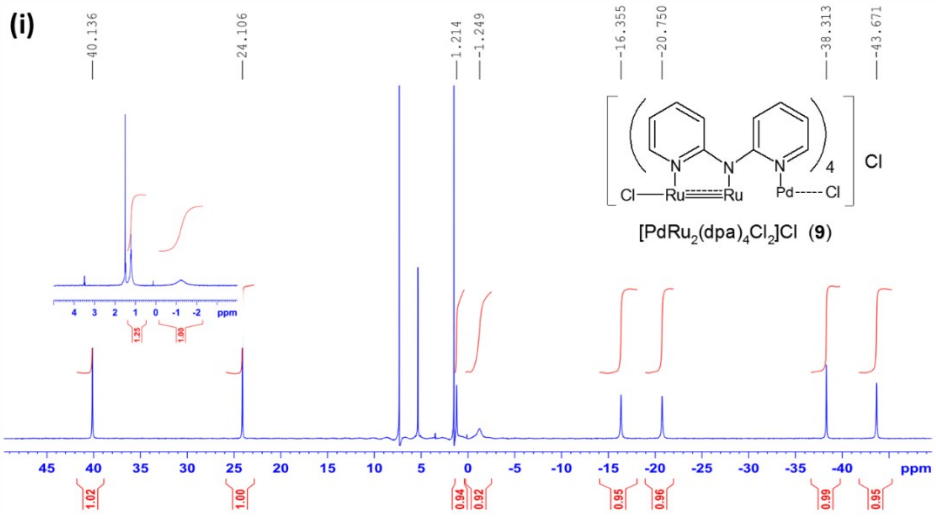


Figure S5. (i) ^{1}H NMR spectrum of **(9)** in CD_2Cl_2

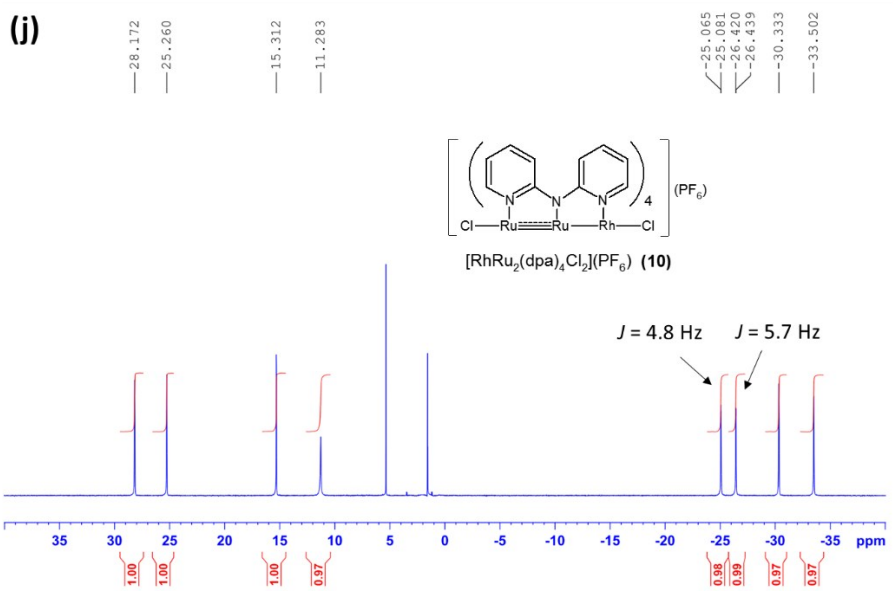


Figure S5. (j) ^{1}H NMR spectrum of **(10)** in CD_2Cl_2

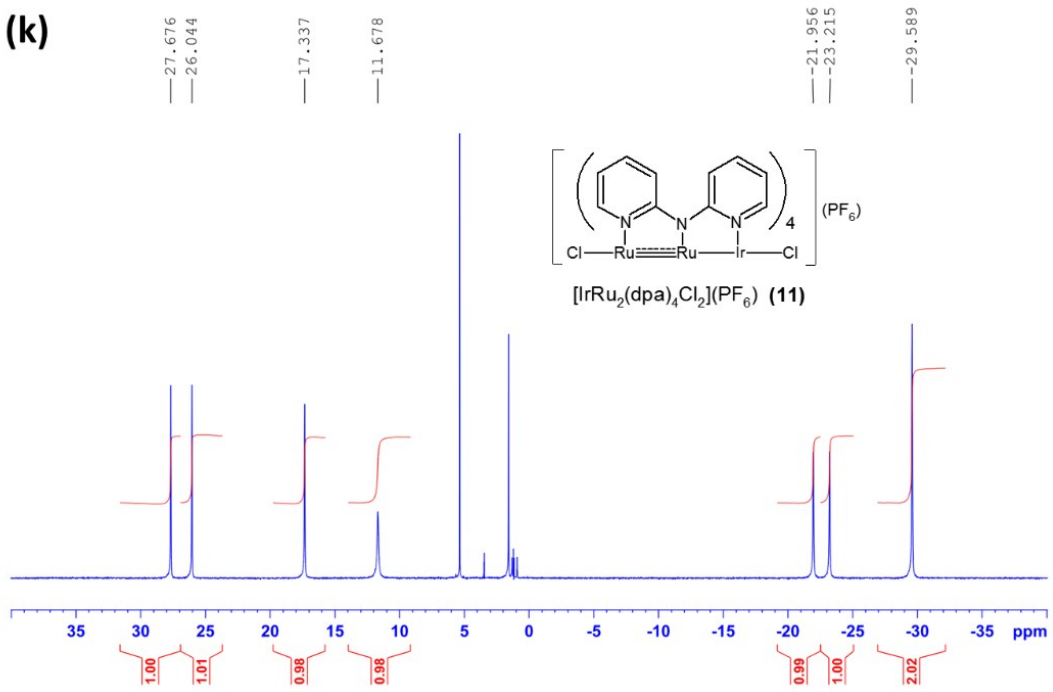


Figure S5. (k) ^{1}H NMR spectrum of **(11)** in CD_2Cl_2

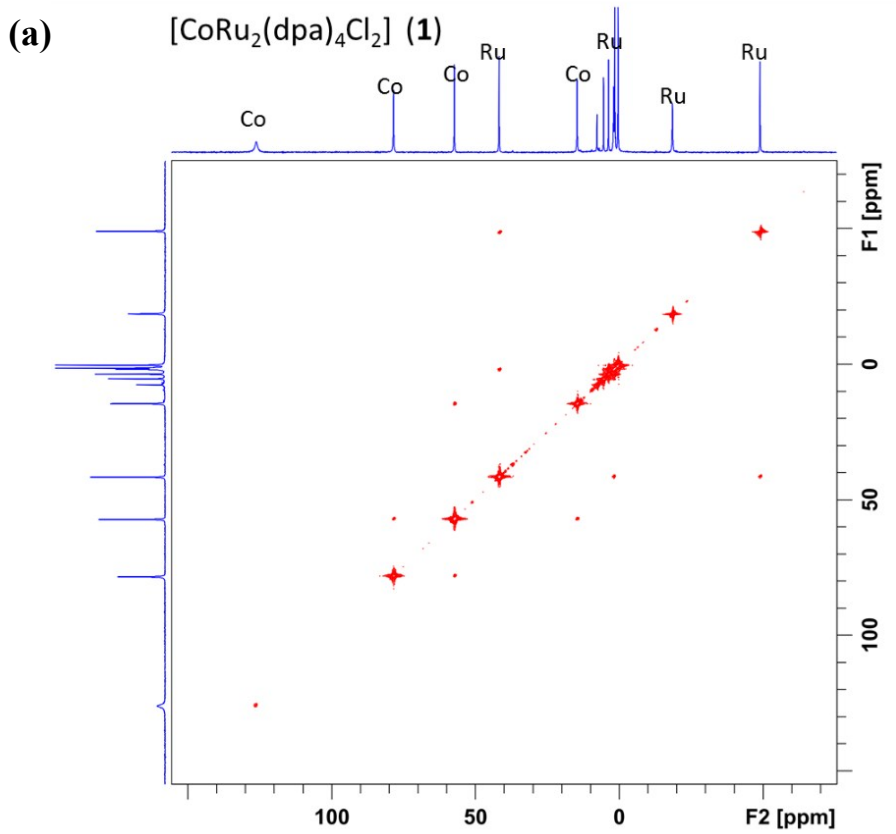


Figure S6. (a) 2D COSY NMR spectrum of (**1**) in CD_2Cl_2.

The "Ru" and "Co" marks represent the protons of pyridine coordinated to the correlated metal. All below figures use the same assignment. The peaks assignment of "Co" and "Fe" refers to the known dpa^- complexes. [2,3]

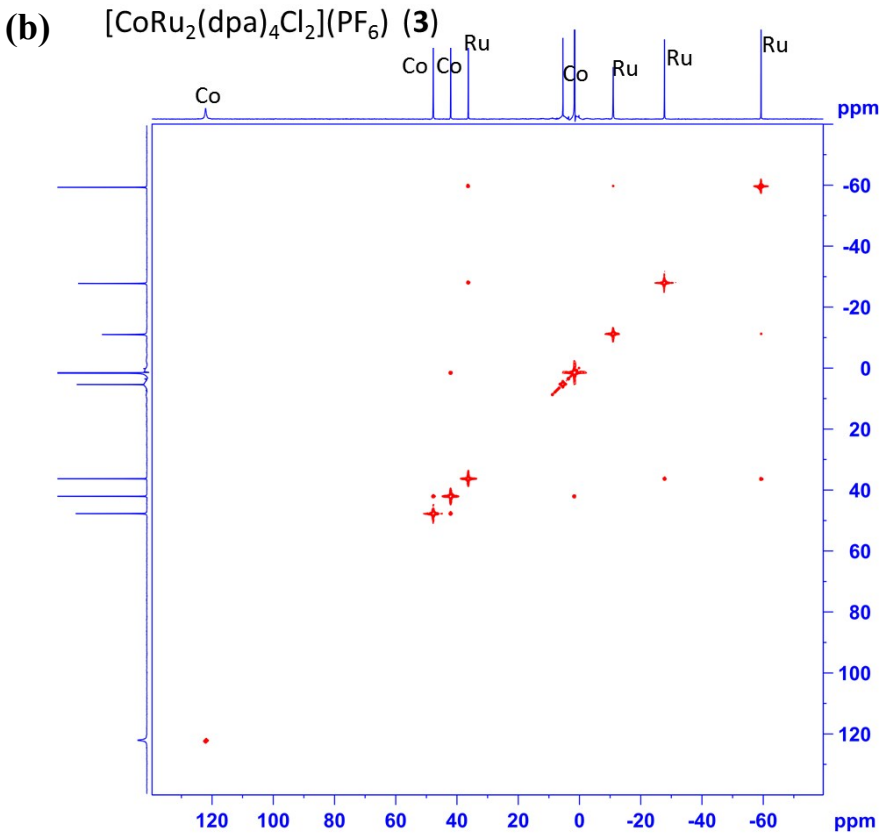


Figure S6. (b) 2D COSY NMR spectrum of (**3**) in CD_2Cl_2.

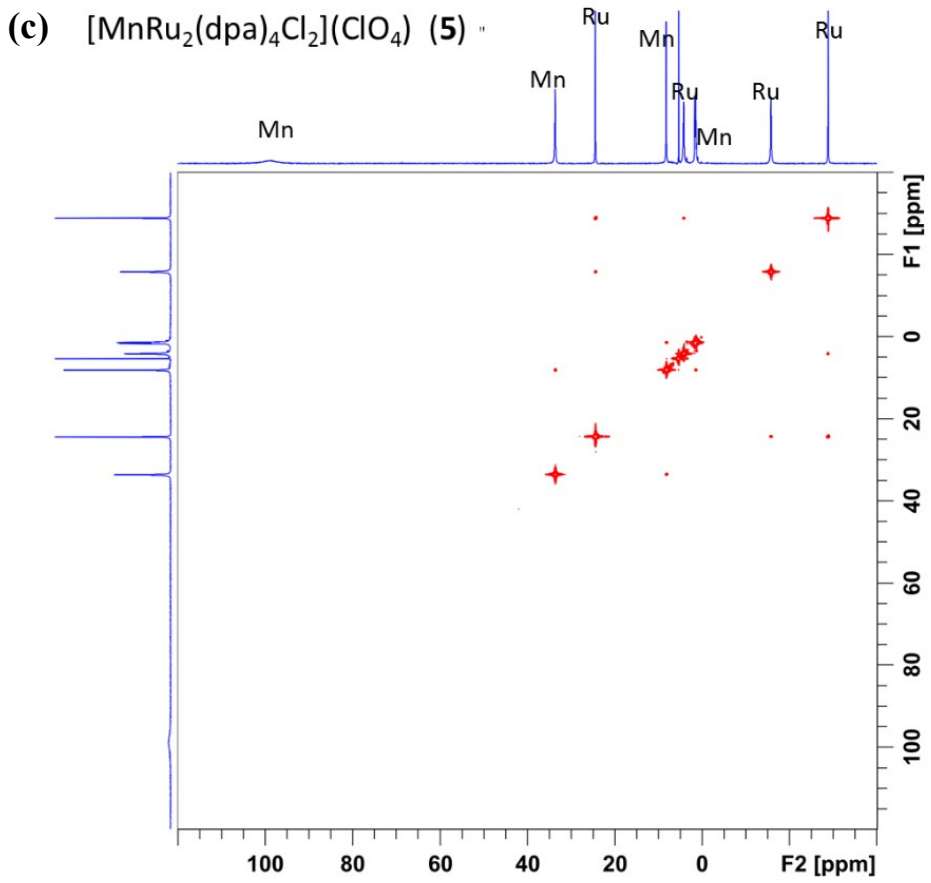


Figure S6. (c) 2D COSY NMR spectrum of (**5**) in CD_2Cl_2.

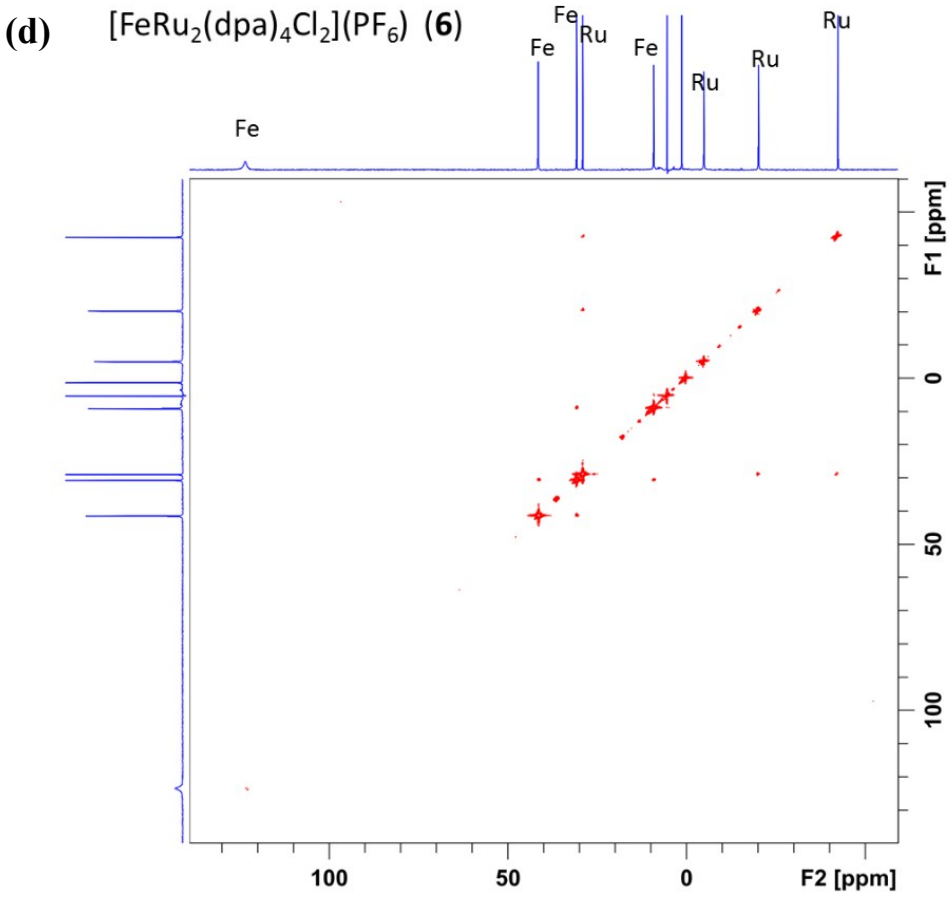


Figure S6. (d) 2D COSY NMR spectrum of (**6**) in CD_2Cl_2.

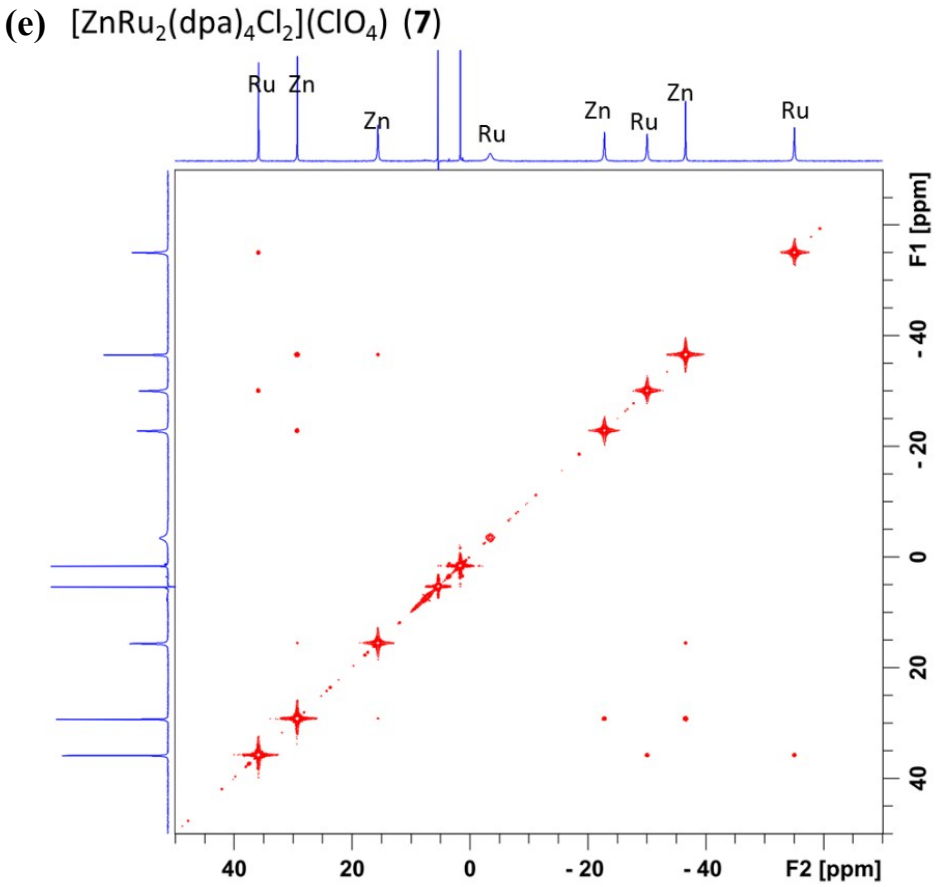


Figure S6. (e) 2D COSY NMR spectrum of (**7**) in CD_2Cl_2.

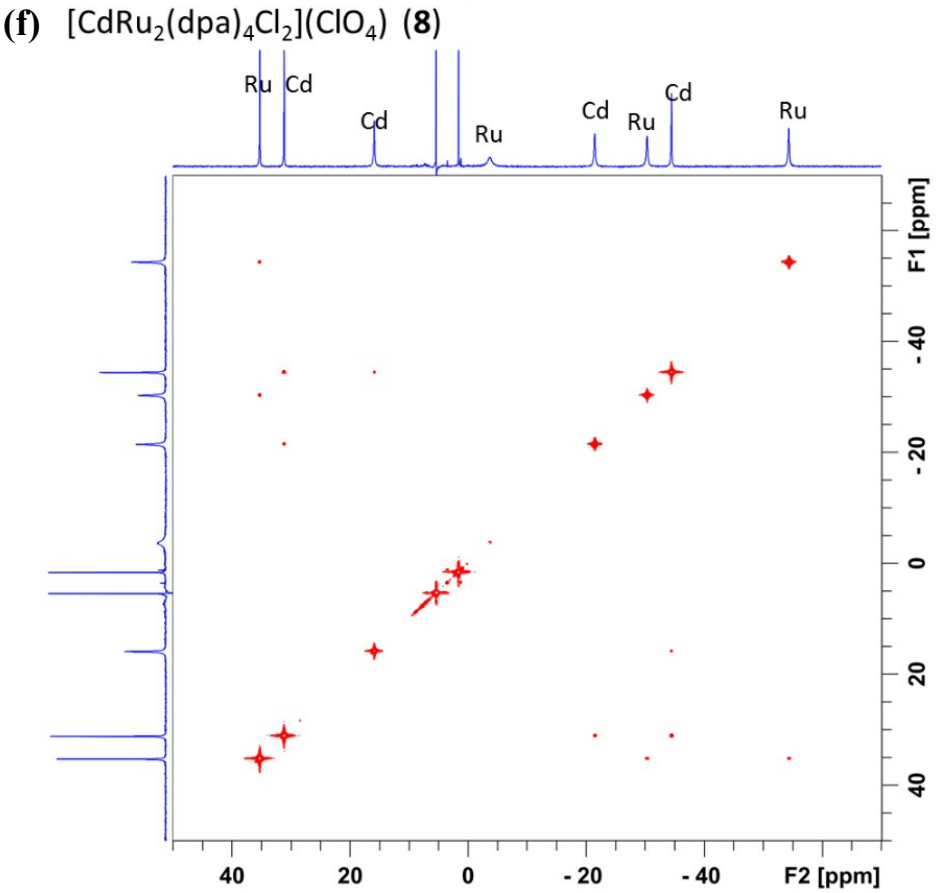


Figure S6. (f) 2D COSY NMR spectrum of (**8**) in CD_2Cl_2.

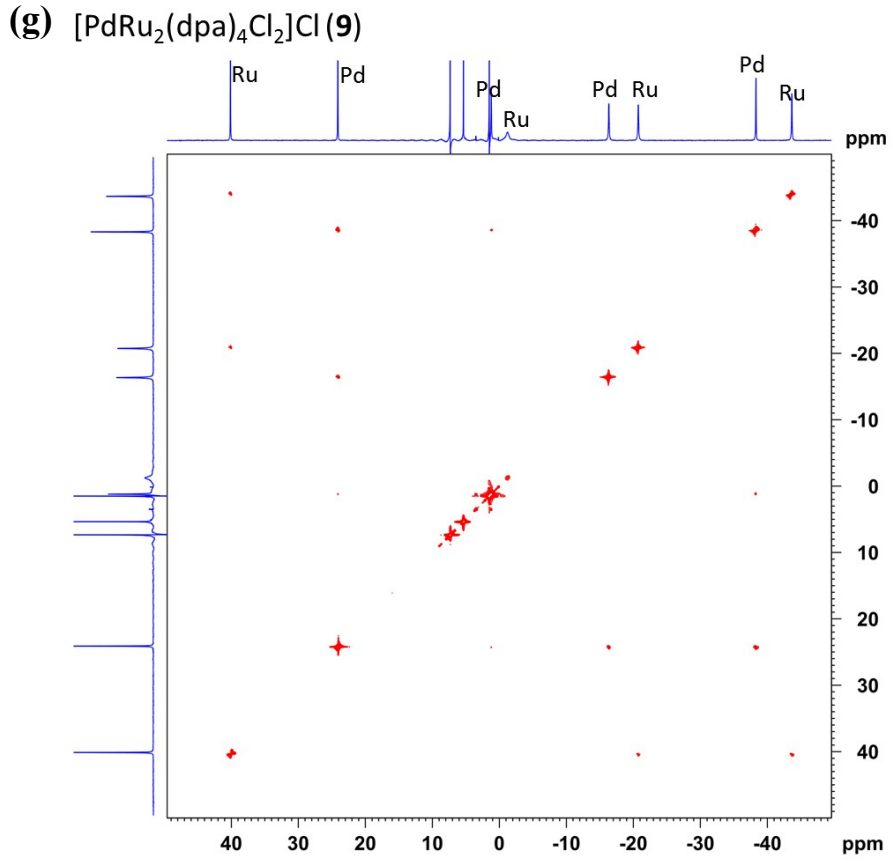


Figure S6. (g) 2D COSY NMR spectrum of (**9**) in CD_2Cl_2.

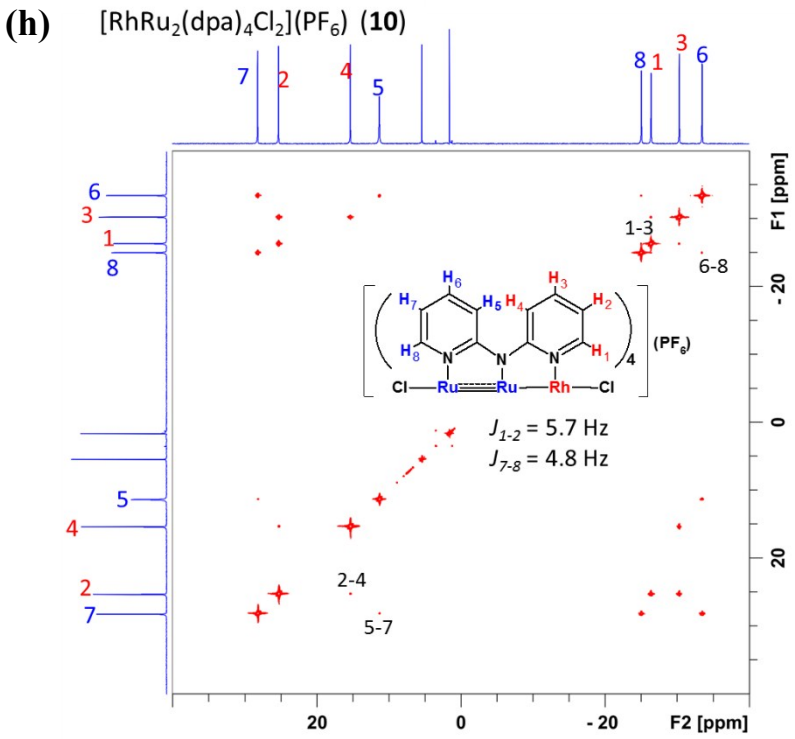


Figure S6. (h) 2D COSY NMR spectrum of (**10**) in CD_2Cl_2. The assignment of protons is according to previous study on $[NiCoRh(dpa)_4Cl](PF_6)$.[3] Typically, the coupling constant of proton in *meta* position of pyridyl ring is higher than that in *ortho* position (in $[NiCoRh(dpa)_4Cl](PF_6)$, coupling constants are 5.7 and ~8 Hz for the protons on the *ortho* and *meta* positions, respectively). The doublet peaks of H_1 in **10** (J = 5.7

Hz) could be therefore, assigned to an *ortho* position, as shown in the figure S6 (h). All protons can be then assigned according to their correlated peaks. The small red dots (lower intensity) are from long range coupling.

(i)

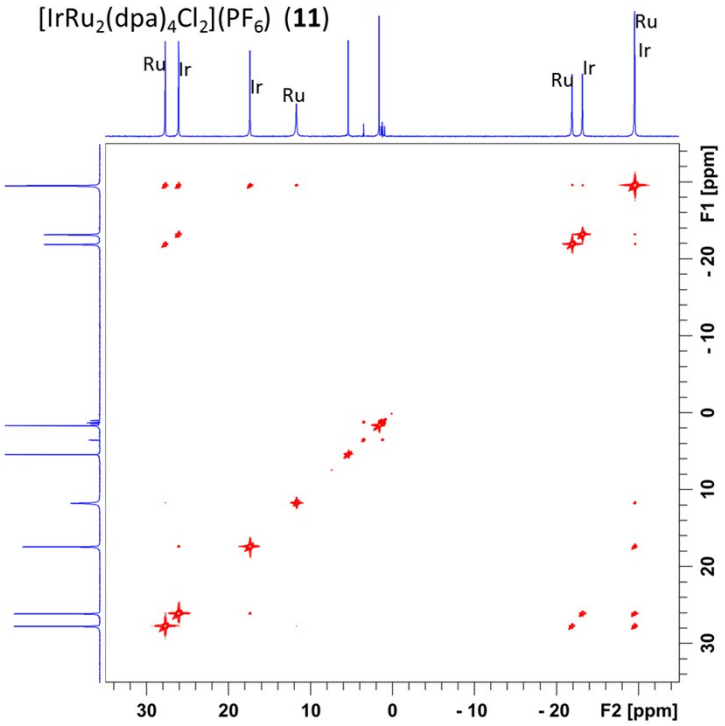
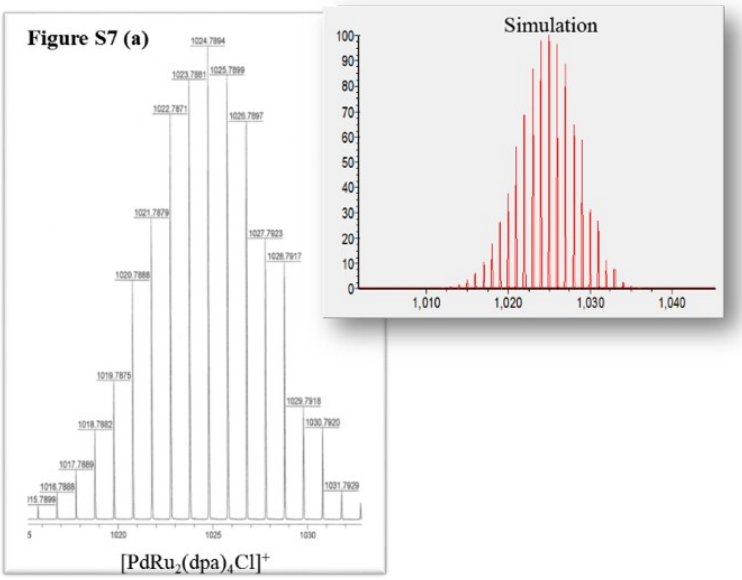
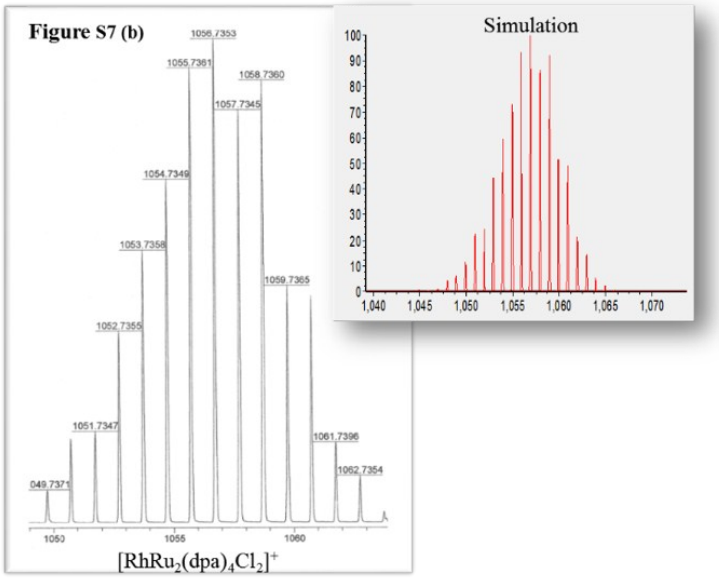


Figure S6. (i) 2D COSY NMR spectrum of (**11**) in CD_2Cl_2.

Table S2. Summary of ^1H NMR chemical shifts. (δ :ppm)

Compounds	H_{py} coordinated to 'M'	H_{py} coordinated to Ru_{outer}
$[CoRu_2(dpa)_4Cl_2]$ (1)	126.04 (broad), 78.40, 57.24, 14.54	41.67, 1.87, -18.56, -49.06.
$[CoRu_2(dpa)_4Cl_2](PF_6)$ (3)	122.01 (broad), 47.72, 42.02, 1.63	36.27, -11.05, -27.80, -59.35
$[MnRu_2(dpa)_4Cl_2](ClO_4)$ (5)	98.87 (broad), 33.58, 8.14, 1.41	24.37, 4.14,-15.82, -28.9
$[FeRu_2(dpa)_4Cl_2](PF_6)$ (6)	123.43 (broad), 41.48, 30.72, 9.15	29.00, -4.95, -20.2, -42.42
$[ZnRu_2(dpa)_4Cl_2](ClO_4)$ (7)	29.26, 15.59, -22.85, -36.6	35.84, -3.49, -30.08, -55.07
$[CdRu_2(dpa)_4Cl_2](ClO_4)$ (8)	31.12, 15.85, -21.5, -34.48	35.23, -3.67, -30.35, -54.37
$[PdRu_2(dpa)_4Cl_2](PF_6)$ (9)	24.11, 1.21, -16.36, , -38.31	40.14, -1.25, -20.75, -43.67
$[RhRu_2(dpa)_4Cl_2](PF_6)$ (10)	25.26, 15.31, -26.43(d), -30.33	28.17, 11.28, -26.07(d), -33.5
$[IrRu_2(dpa)_4Cl](PF_6)$ (11)	26.04, 17.34, -23.22, -29.59	27.68, 11.68, -21.96, -29.59





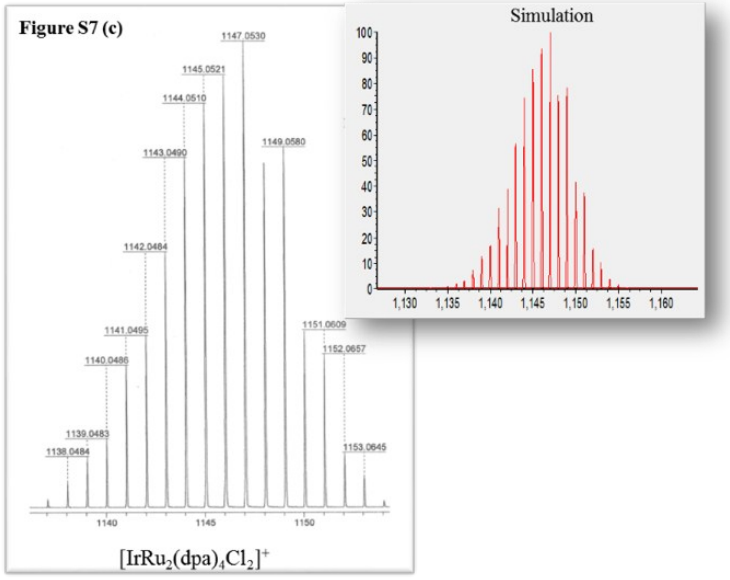


Figure S7. The high-resolution mass spectra (MALDI-TOF) of complexes **9**(a), **10**(b) and **11**(c). The red peaks are simulated results.

DFT Calculation:

Table S3. Experimental and calculated bond distances (Å) and angles (°) for **10** (Rh) and **11** (Ir)

	10[a]	**10** (DFT)	**11**[a]	**11** (DFT)
Ru-Ru	2.3254(4)	2.297	2.3312(4)	2.304
Ru-M	2.3352(4)	2.401	2.3472(4)	2.408
M-Cl	2.4869(10)	2.508	2.4782(11)	2.429
Ru-Cl	2.4888(10)	2.423	2.4746(11)	2.512
$M-N_{outer}$	2.046−2.175	2.030−2.146	2.053−2.141	2.034−2.139
$Ru-N_{outer}$	2.044−2.151	2.026−2.233	2.057−2.163	2.022−2.242
$Ru-N_{inner}$	1.965−2.096	1.961−2.126	1.967−2.101	1.960−2.134
∠ M−Ru−Ru	167.48(2)	166.2	167.61(2)	165.9

[a] The data set is from higher occupancy of two disordered molecular.

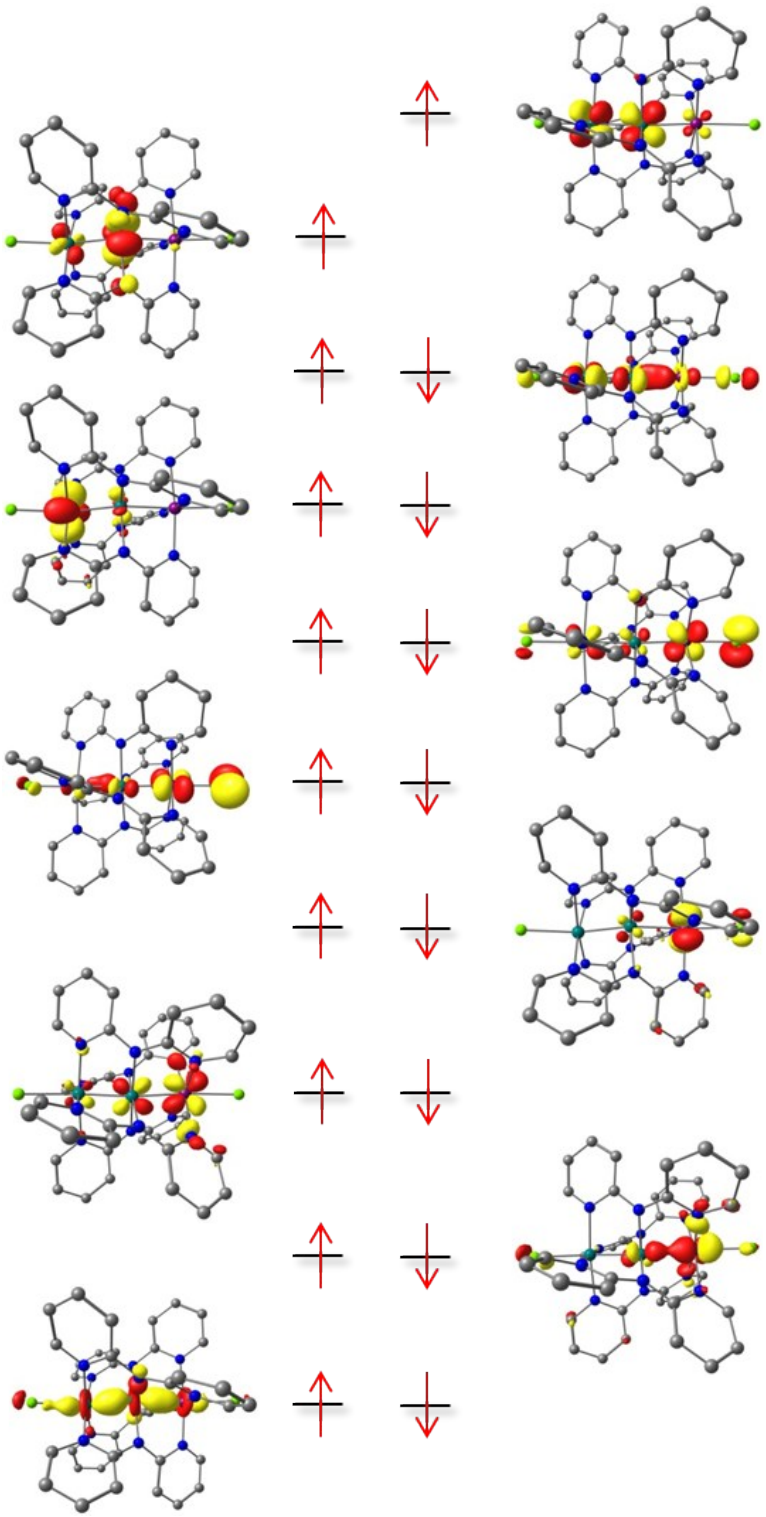


Figure S8. Orbital scheme from localized quasi-restricted orbitals (doubly occupied) and quasi-restricted orbitals (singly occupied) for S = 1 configuration of $[RhRu_2(dpa)_4Cl_2](PF_6)$ **10**. Hydrogen atoms are omitted for clarity.

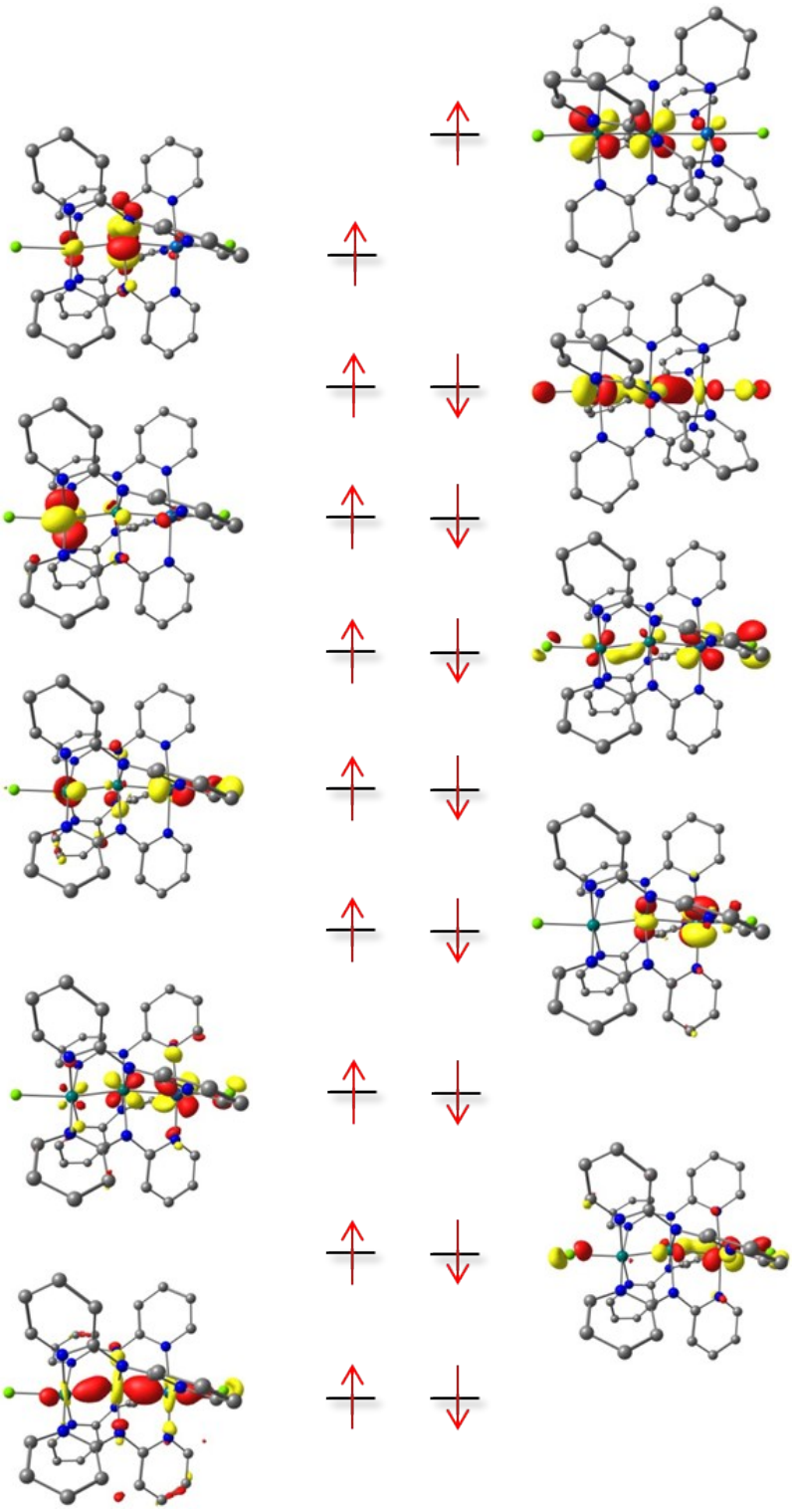


Figure S9. Orbital scheme from localized quasi-restricted orbitals (doubly occupied) and quasi-restricted orbitals (singly occupied) for S = 1 configuration of $[IrRu_2(dpa)_4Cl_2]^+$ (**11**). Hydrogen atoms are omitted for clarity.

Table S4. XYZ Coordinates for $[RhRu_2(dpa)_4Cl_2]^+$

Rh	0.282386	−0.420638	−2.288418
Ru	0.071078	−0.001768	2.351399
Ru	0.115581	0.068292	0.056222
Cl	−0.156930	0.381042	4.733040
Cl	0.435423	−0.618803	−4.783466
N	0.884875	−1.852871	2.481624
N	0.234706	−2.045263	0.249009
N	−0.390719	−2.313257	−1.993169
N	−0.764277	2.033912	1.972295
N	0.047469	2.009918	−0.210365
N	0.938916	1.621596	−2.330736
N	2.019057	0.826047	2.295262
N	2.158439	0.068469	0.092646
N	2.208575	−1.041284	−1.965654
N	−1.847543	−0.818097	2.178198
N	−1.885219	−0.133815	−0.050937
N	−1.715700	0.245090	−2.352218
C	1.559142	−2.297489	3.570987
H	1.514789	−1.638524	4.437449
C	2.236107	−3.502578	3.582904
H	2.750824	−3.822778	4.486558
C	2.255428	−4.272397	2.409301
H	2.813593	−5.207942	2.369190
C	1.580829	−3.822378	1.288348
H	1.614849	−4.376242	0.351968
C	0.867832	−2.604021	1.329780
C	−0.318974	−2.835197	−0.727535
C	−0.905532	−4.093698	−0.468242
H	−0.895407	−4.472541	0.551881
C	−1.518018	−4.800870	−1.486733
H	−1.977496	−5.767007	−1.277507
C	−1.564364	−4.252645	−2.776293
H	−2.034848	−4.775665	−3.606327
C	−1.005431	−3.004601	−2.982353
H	−1.003667	−2.508996	−3.953201
C	−1.505568	2.621982	2.939269
H	−1.593839	2.050347	3.861149
C	−2.104547	3.865013	2.797979
H	−2.685511	4.276160	3.621529
C	−1.958719	4.546628	1.586891
H	−2.437142	5.512769	1.426287
C	−1.218158	3.960538	0.572659
H	−1.134556	4.434131	−0.403235
C	−0.618128	2.705050	0.778692
C	0.707869	2.513953	−1.308923
C	1.227697	3.821159	−1.373177
H	1.083239	4.488255	−0.526344
C	1.962896	4.219769	−2.478475
H	2.376774	5.227466	−2.522174
C	2.185397	3.308092	−3.514970
H	2.758269	3.574432	−4.401157
C	1.668352	2.026982	−3.394870
H	1.803031	1.273167	−4.170794
C	2.531624	1.523256	3.338547
H	1.888127	1.575785	4.215812
C	3.778226	2.125597	3.304368

H	4.133712	2.670430	4.176973
C	4.537653	2.036605	2.131433
H	5.507587	2.528217	2.055425
C	4.025629	1.336649	1.051575
H	4.562531	1.283389	0.106294
C	2.764264	0.717302	1.147529
C	2.847767	-0.721033	-0.792903
C	4.107901	-1.295864	-0.515892
H	4.577140	-1.095339	0.444886
C	4.707756	-2.139531	-1.433737
H	5.675173	-2.587570	-1.206669
C	4.051272	-2.427736	-2.637154
H	4.488334	-3.081131	-3.389642
C	2.802834	-1.872309	-2.853544
H	2.227072	-2.053887	-3.760856
C	-2.395896	-1.490408	3.219587
H	-1.809219	-1.471423	4.136841
C	-3.611351	-2.146967	3.138404
H	-4.001640	-2.665775	4.011715
C	-4.293107	-2.143731	1.914438
H	-5.233357	-2.682955	1.799156
C	-3.747728	-1.466294	0.838273
H	-4.229691	-1.485941	-0.136673
C	-2.524245	-0.777758	0.980091
C	-2.495677	0.262974	-1.222850
C	-3.805671	0.777107	-1.273799
H	-4.382725	0.833184	-0.352792
C	-4.318532	1.250889	-2.470544
H	-5.327317	1.662570	-2.506744
C	-3.516181	1.218231	-3.615997
H	-3.873223	1.582705	-4.577254
C	-2.226489	0.722000	-3.510918
H	-1.549347	0.668883	-4.363863

Table S5. XYZ Coordinates for $[IrRu_2(dpa)_4Cl_2]^+$

Ir	−0.276046	−0.409568	−2.299620
Ru	−0.043156	−0.017617	2.354794
Ru	−0.194750	0.076449	0.057768
Cl	−0.368894	−0.608774	−4.802304
Cl	−0.042366	0.383207	4.750542
N	−1.977359	−0.799061	2.352092
N	−2.205228	−0.101259	0.136427
N	−2.260013	0.265920	−2.180131
N	1.912131	0.769270	2.114857
N	1.838554	0.042030	−0.104346
N	1.675794	−1.048072	−2.174808
N	−0.870925	2.041934	2.041185
N	−0.259644	2.017007	−0.207507
N	0.383820	1.620829	−2.423165
N	0.732956	−1.884274	2.411577
N	−0.098795	−2.047685	0.235190
N	−0.935414	−2.301153	−1.944235
C	−2.436488	−1.474885	3.434103
H	−1.776041	−1.453247	4.299918
C	−3.651087	−2.137655	3.451005
H	−3.966398	−2.659846	4.352088
C	−4.429742	−2.136254	2.286133
H	−5.372286	−2.682223	2.244679
C	−3.978885	−1.450364	1.171777
H	−4.541185	−1.467940	0.240744
C	−2.752228	−0.754103	1.215215
C	−2.921851	0.292397	−0.972229
C	−4.228639	0.812007	−0.894209
H	−4.704707	0.873412	0.082351
C	−4.862746	1.281774	−2.031627
H	−5.868303	1.696761	−1.965008
C	−4.182123	1.241577	−3.254047
H	−4.634686	1.603114	−4.175235
C	−2.891621	0.743013	−3.282058
H	−2.308940	0.687132	−4.201010
C	2.531584	1.442245	3.115334
H	1.969035	1.493432	4.046697
C	3.781034	2.022831	2.976575
H	4.224070	2.548006	3.820625
C	4.428893	1.937399	1.738939
H	5.397278	2.411900	1.580913
C	3.807486	1.262153	0.701630
H	4.258240	1.214081	−0.288042
C	2.549562	0.663136	0.903392
C	2.427280	−0.746492	−1.058365
C	3.698914	−1.341903	−0.903763
H	4.251429	−1.160664	0.015313
C	4.205550	−2.180354	−1.879526
H	5.182730	−2.643668	−1.743692
C	3.441115	−2.444844	−3.023948
H	3.801129	−3.093502	−3.819999
C	2.185641	−1.875768	−3.122372
H	1.530453	−2.044290	−3.976351
C	−1.519291	2.634842	3.069937
H	−1.534778	2.059682	3.993866
C	−2.113213	3.885593	2.985405

H	−2.615617	4.299645	3.857624
C	−2.064108	4.571696	1.768948
H	−2.542204	5.544373	1.653632
C	−1.421036	3.981096	0.692671
H	−1.415224	4.456822	−0.285563
C	−0.821842	2.717104	0.842222
C	0.280391	2.511569	−1.371218
C	0.810077	3.811256	−1.486999
H	0.774823	4.469975	−0.622155
C	1.419302	4.214272	−2.663609
H	1.841212	5.216228	−2.743464
C	1.508204	3.310454	−3.727082
H	1.980593	3.577092	−4.670353
C	0.994052	2.035567	−3.560562
H	1.033759	1.289128	−4.352962
C	1.477974	−2.354409	3.443189
H	1.517377	−1.700036	4.313456
C	2.121366	−3.576776	3.395915
H	2.694569	−3.917527	4.255899
C	2.029830	−4.338289	2.220287
H	2.557277	−5.288124	2.132679
C	1.282650	−3.862067	1.157434
H	1.227630	−4.409471	0.218561
C	0.606147	−2.626576	1.261518
C	−0.756676	−2.824153	−0.684109
C	−1.345427	−4.069458	−0.369952
H	−1.250657	−4.444145	0.647118
C	−2.061192	−4.768898	−1.323327
H	−2.519689	−5.723842	−1.066824
C	−2.211604	−4.224862	−2.607498
H	−2.764062	−4.741566	−3.389567
C	−1.651732	−2.990196	−2.869948
H	−1.730696	−2.497634	−3.838497

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