Electronic Supporting Information (ESI)

New series of heteronuclear metal strings, $MRhRh(dpa)_4Cl_2$ and $MRhRhM(dpa)_4X_2$, from reactions of $Rh_2(dpa)_4$ with metal ions of group 7 to group 12

Ming-Chuan Cheng, Gene-Hsiang Lee, Tien-Sung Lin, Yu-Chiao Liu, Ming-Hsi Chiang and Shie-Ming Peng*

Table of Contents

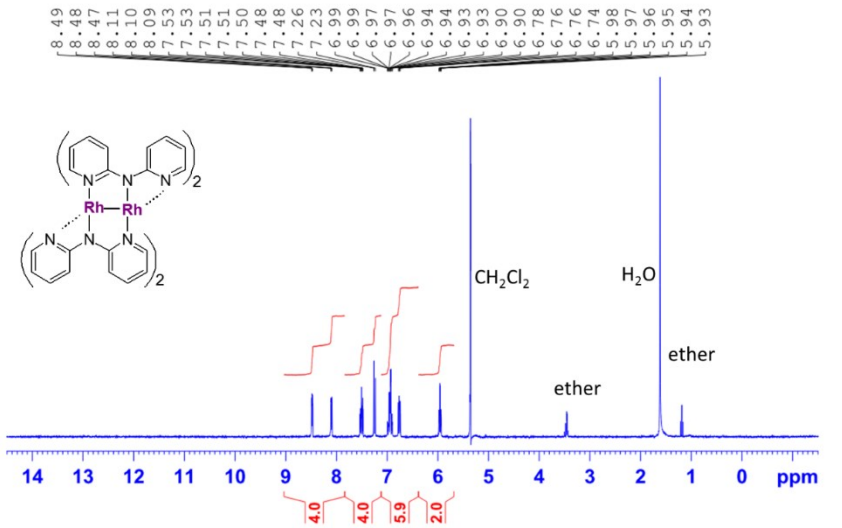

Figure S1. ^{1}H NMR spectrum of **(1)** in CD_2Cl_2

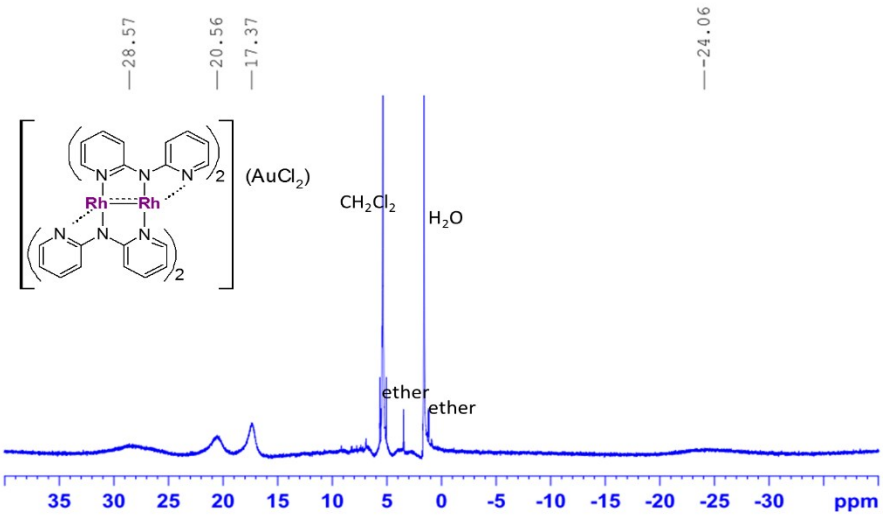

Figure S2. ^{1}H NMR spectrum of **(1^{+})** in CD_2Cl_2

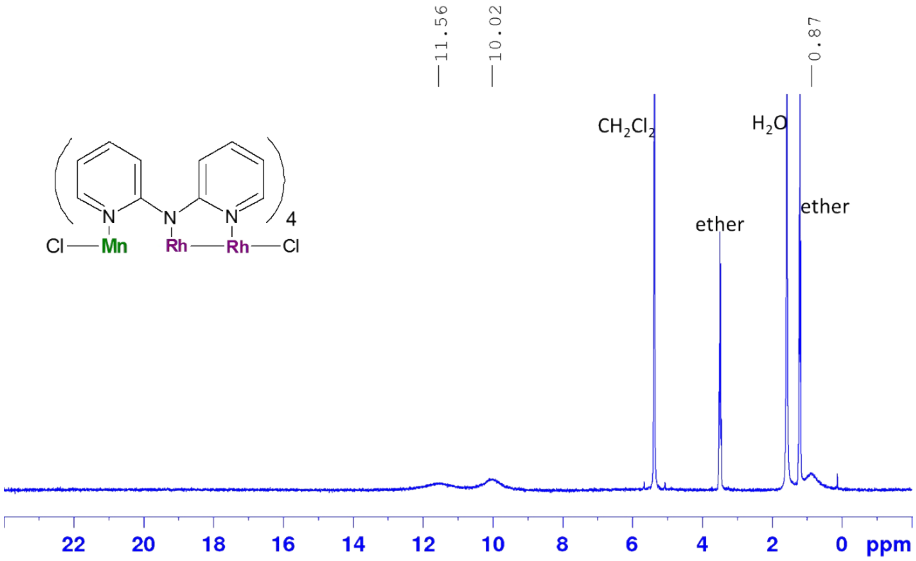

Figure S3. ^{1}H NMR spectrum of **(2)** in CD_2Cl_2

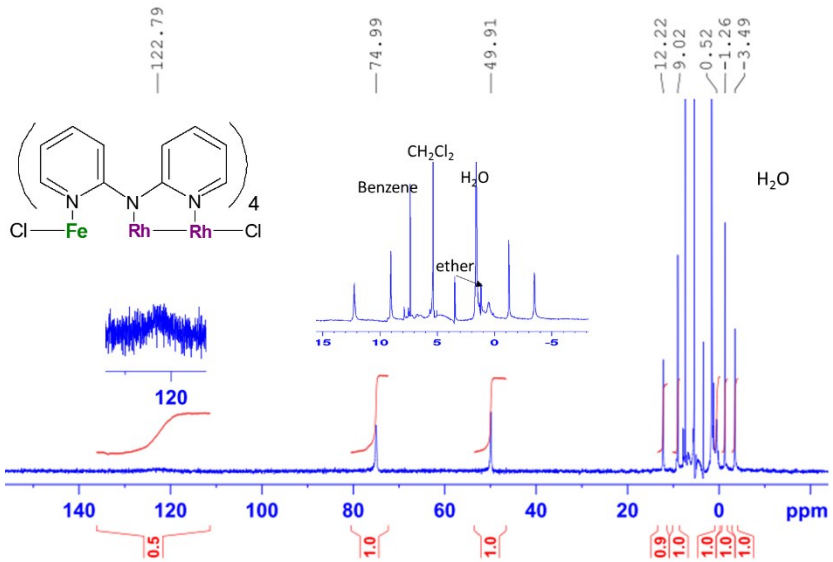

Figure S4. ^{1}H NMR spectrum of **(3)** in CD_2Cl_2

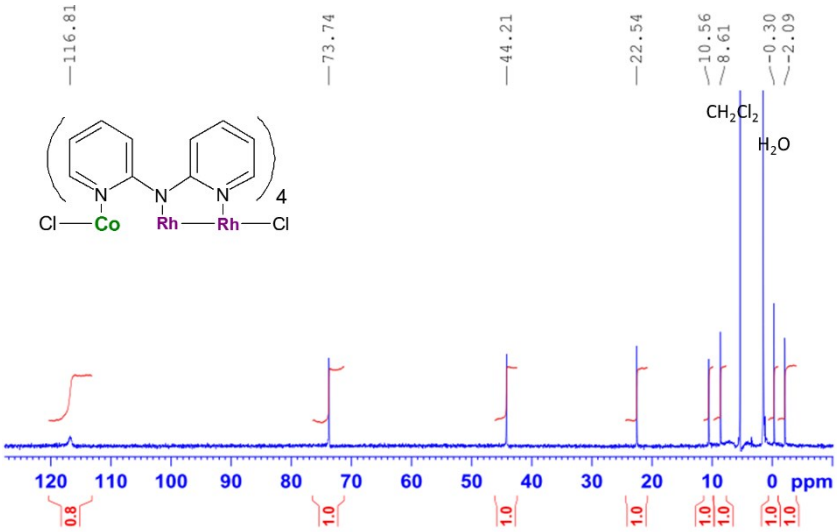

Figure S5. ^{1}H NMR spectrum of **(4)** in CD_2Cl_2

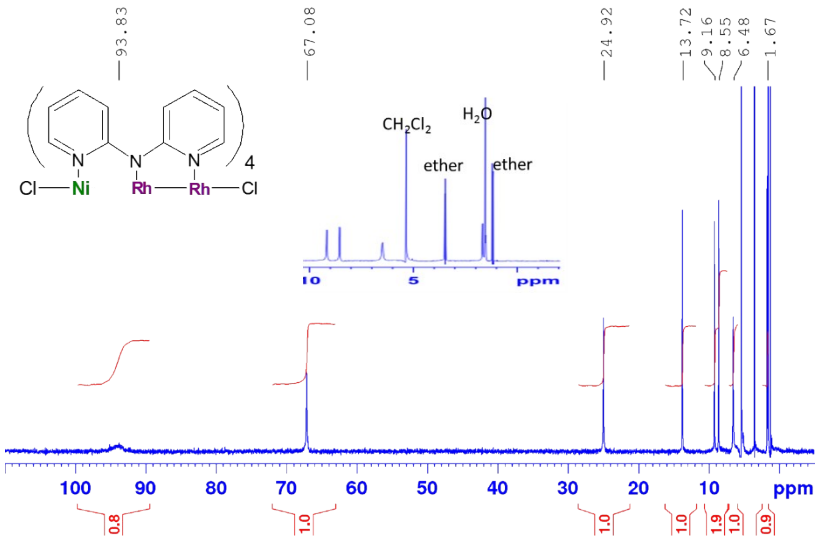

Figure S6. ^{1}H NMR spectrum of **(5)** in CD_2Cl_2

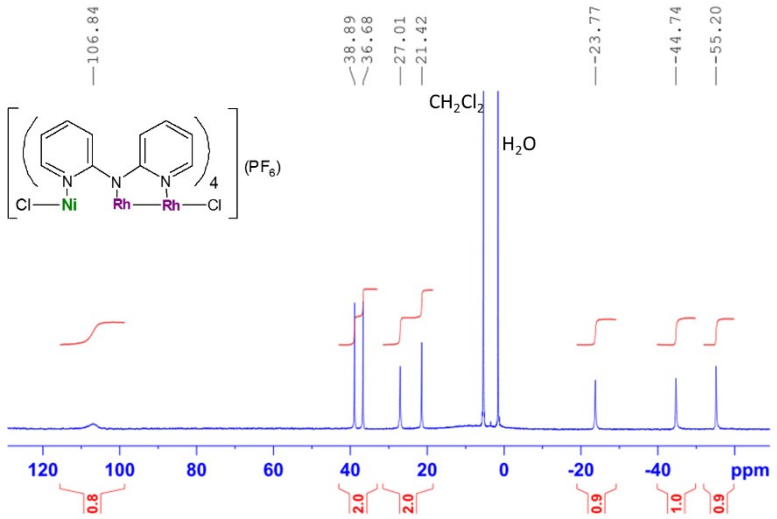

Figure S7. ^{1}H NMR spectrum of **(5^{+})** in CD_2Cl_2

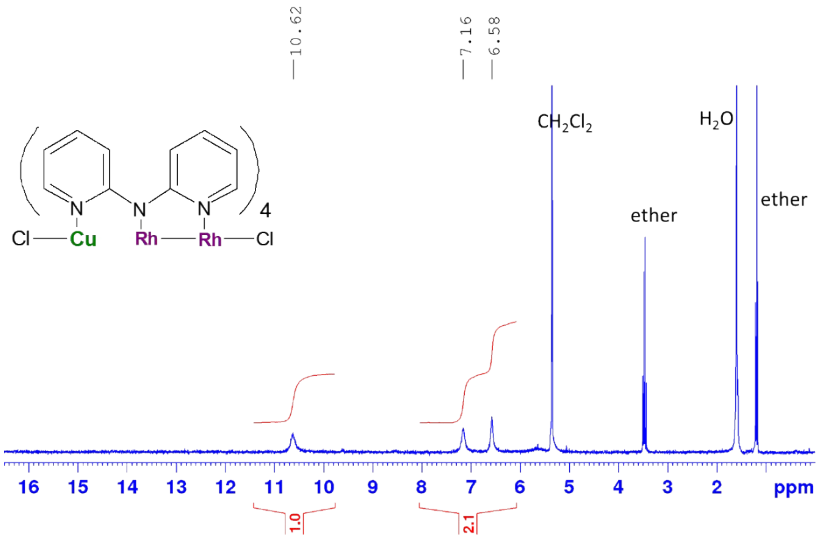

Figure S8. ^{1}H NMR spectrum of **(6)** in CD_2Cl_2

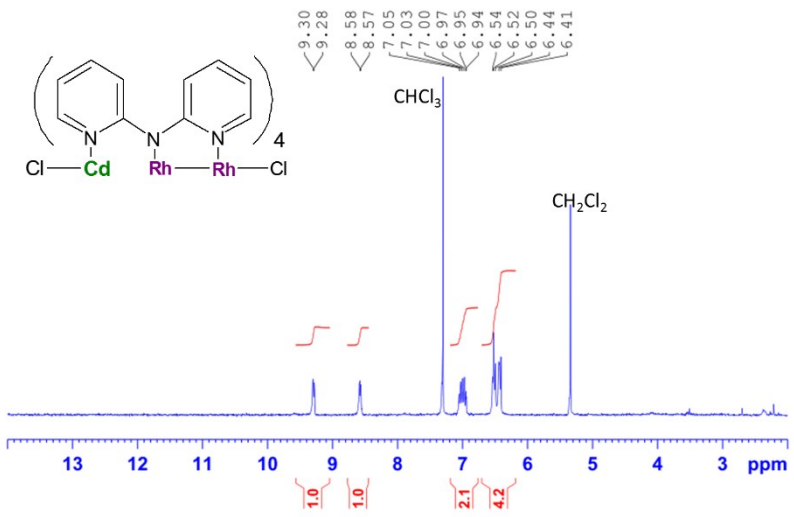

Figure S9. ^{1}H NMR spectrum of **(7)** in CD_2Cl_2

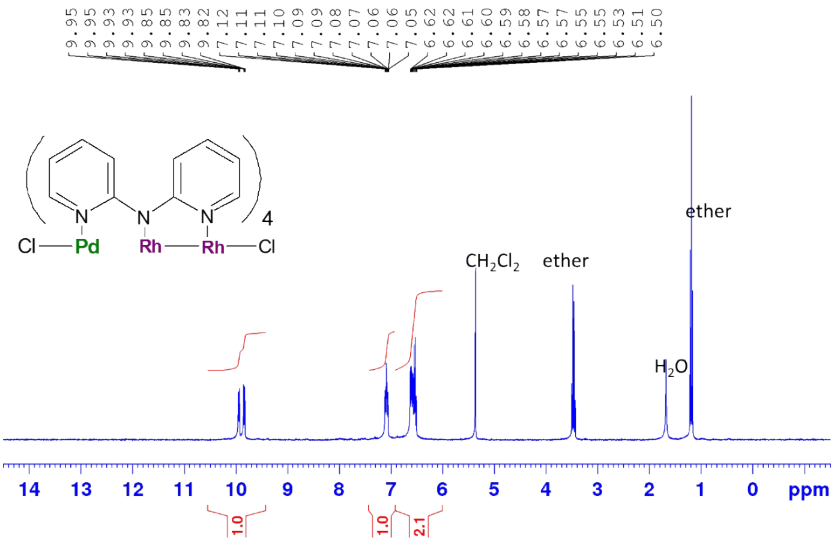

Figure S10. ^{1}H NMR spectrum of **(8)** in CD_2Cl_2

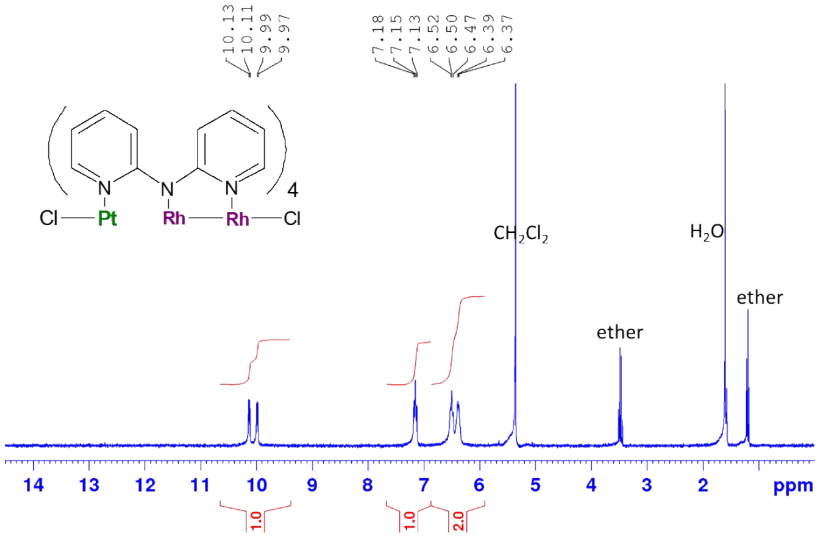

Figure S11. ^{1}H NMR spectrum of **(9)** in CD_2Cl_2

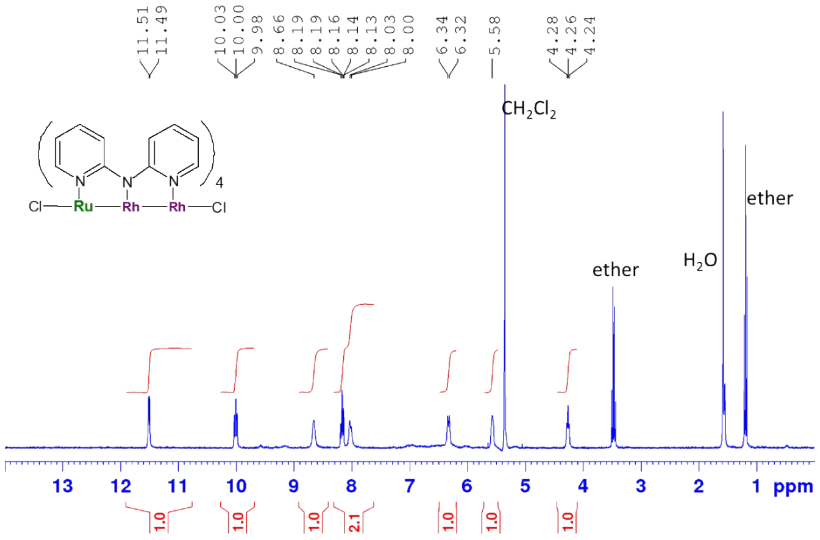

Figure S12. ^{1}H NMR spectrum of **(10)** in CD_2Cl_2

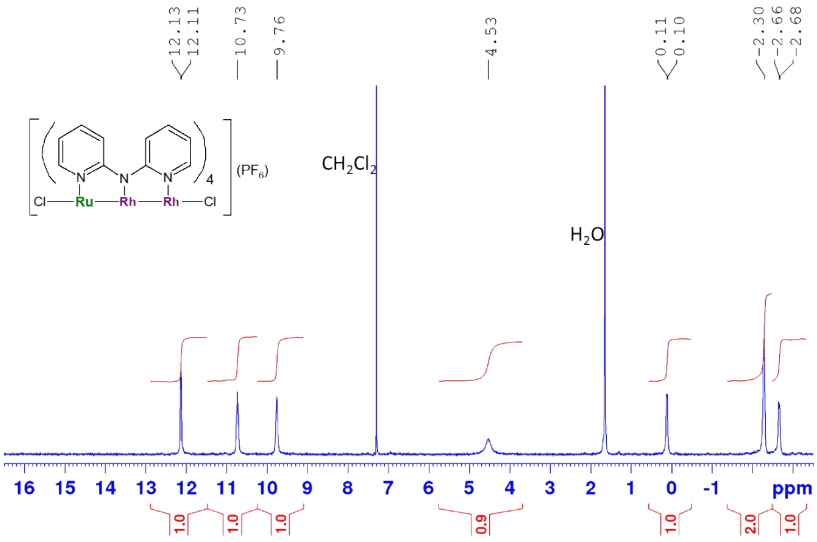

Figure S13. ^{1}H NMR spectrum of **(10^{+})** in CD_2Cl_2

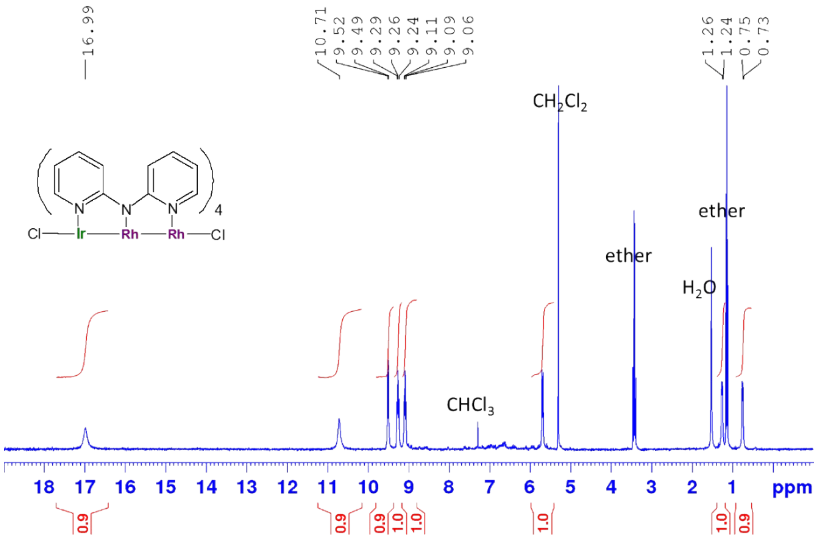

Figure S14. ^{1}H NMR spectrum of **(11)** in CD_2Cl_2

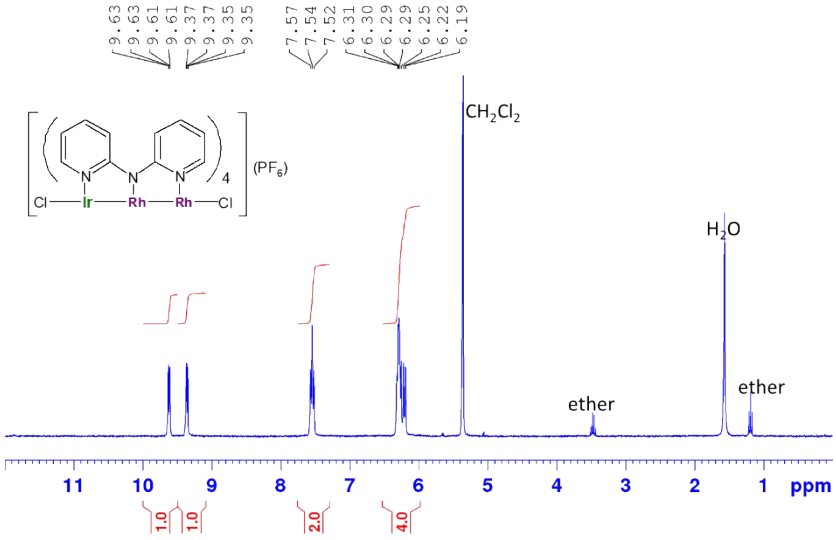

Figure S15. ^{1}H NMR spectrum of **(11^{+})** in CD_2Cl_2

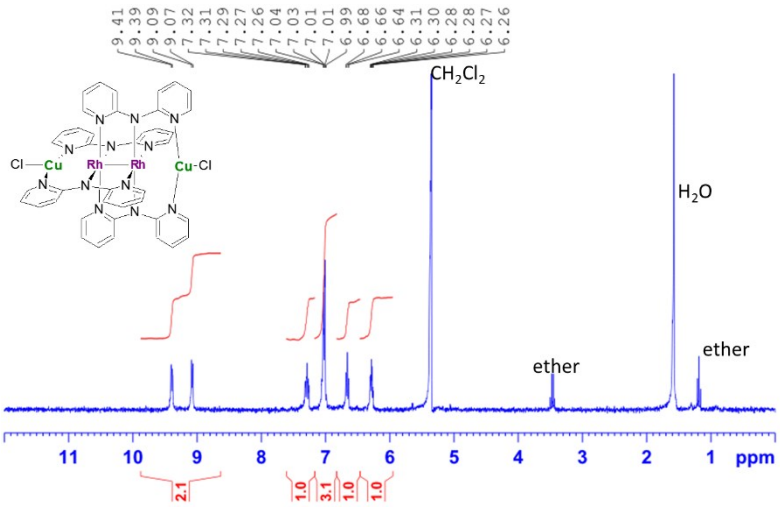

Figure S16. ^{1}H NMR spectrum of **(13)** in CD_2Cl_2

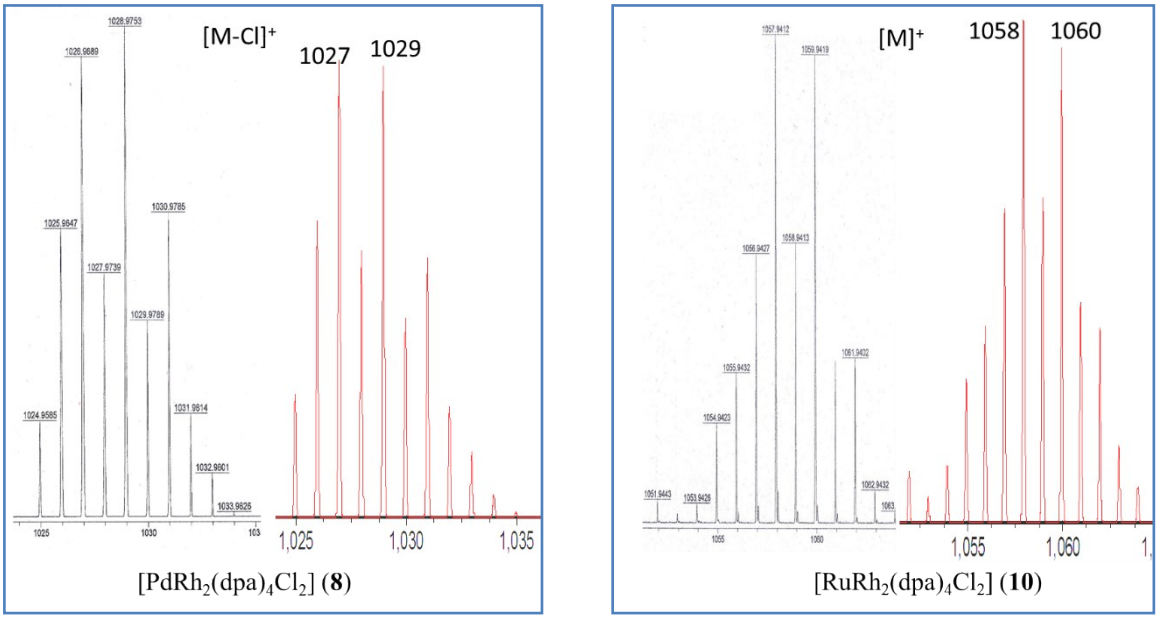

Figure S17: High resolution MALDI spectra (black) of $[PdRh_2(dpa)_4Cl_2]$ **(8)** (left) and $[RuRh_2(dpa)_4Cl_2]$ **(10)** (right) and their simulation (red).

Table S1 : X-ray crystallographic data for all compounds.

Compound	**1**	**1**·2CH_2Cl_2	**1**$^+$·1.5$CHCl_3$	**2**·Et_2O	**3**·Et_2O
Formula	$C_{40}H_{32}N_{12}Rh_2$	$C_{42}H_{36}Cl_4N_{12}Rh_2$	$C_{41.5}H_{33.5}AuCl_{6.5}N_{12}Rh_2$	$C_{44}H_{42}Cl_2MnN_{12}ORh_2$	$C_{44}H_{42}Cl_2FeN_{12}ORh_2$
Formula weight	886.59	1056.45	1333.51	1086.55	1087.46
Temperature	200(2) K	150(2) K	150(2) K	150(2) K	150(2) K
Crystal system	Tetragonal	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
Space group	$I4_1/a$	Pbcn	$P2_1/c$	$P2_1/c$	$P2_1/c$
a / Å	34.3409(4)	22.5312(13)	8.9453(2)	16.0445(8)	16.0644(7)
b / Å	34.3409(4)	9.2175(5)	34.2269(9)	15.7818(8)	15.7547(7)
c / Å	11.70360(10)	19.9260(12)	15.0001(4)	17.0632(9)	16.9905(7)
α/ º	90	90	90	90	90
β/ º	90	90	95.1383(9)	98.5713(12)	98.7876(10)
γ/ º	90	90	90	90	90
V / Å^3	13802.0(3)	4138.3(4)	4574.1(2)	4272.3(4)	4249.6(3)
Z	16	4	4	4	4
Reflection collected	38863	22488	26318	32563	32377
Independent reflections	7907	4733	10427	9815	9768
R1, wR2 [I>2sigma(I)]	0.0348, 0.0749	0.0298, 0.0638	0.0427, 0.0856	0.0551, 0.1119	0.0343, 0.0717
R1, wR2 (all data)	0.0666, 0.0846	0.0395, 0.0673	0.0771, 0.0985	0.0619, 0.1146	0.0448, 0.0755
Goodness-of-fit on F^2	0.968	1.030	1.019	1.220	1.057
Disorder occupancy	N/A	N/A	N/A	60/40	52/48
Compound	**4**·Et_2O	**5**·Et_2O	**5**$^+$·CH_2Cl_2·$CHCl_3$	**6**·Et_2O	**7**·Et_2O
Formula	$C_{44}H_{42}Cl_2CoN_{12}ORh_2$	$C_{44}H_{42}Cl_2NiN_{12}ORh_2$	$C_{42}H_{35}Cl_7NiN_{12}Rh_2PF_6$	$C_{44}H_{42}Cl_2CuN_{12}ORh_2$	$C_{44}H_{42}Cl_2CdN_{12}ORh_2$
Formula weight	1208.74	1090.32	1365.47	1095.15	1144.01
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	$P2_1/c$	$P2_1/c$	$P2_1/n$	$P2_1/c$	$P2_1/c$
a / Å	16.0245(2)	15.9696(7)	11.5346(8)	16.0407(8)	16.1176(7)
b / Å	15.7742(2)	15.7425(8)	21.3695(13)	15.7566(7)	15.8659(6)
c / Å	17.0123(3)	16.9763(8)	20.2834(13)	16.9543(8)	17.1805(7)
α/ º	90	90	90	90	90
β/ º	98.6876(9)	98.6045(12)	92.693(2)	99.4159(12)	98.6243(9)
γ/ º	90	90	90	90	90
V / Å^3	4250.92(11)	4219.8(3)	4994.1(6)	4227.4(3)	4343.7(3)
Z	4	4	4	4	4
Reflection collected	27811	32210	38132	32248	33084
Independent reflections	9733	9688	11460	9704	9963
R1, wR2 [I>2sigma(I)]	0.0475, 0.1179	0.0369, 0.0735	0.0534, 0.1282	0.0355, 0.0766	0.0590, 0.1078
R1, wR2 (all data)	0.0926, 0.1368	0.0491, 0.0783	0.0851, 0.1432	0.0497, 0.0825	0.0653, 0.1101
Goodness-of-fit on F^2	1.030	1.052	1.024	1.015	1.315
Disorder occupancy	50/50	50/50	51/49	50/50	67/33

Table S1 : X-ray crystallographic data for all compounds. (Continued.)

Compound	**8**·Et_2O	**9**·Et_2O	**10**·Et_2O	**10**$^{+}$·$2CH_2Cl_2$	**11**·Et_2O
Formula	$C_{44}H_{42}Cl_2PdN_{12}ORh_2$	$C_{44}H_{42}Cl_2PtN_{12}ORh_2$	$C_{44}H_{42}Cl_2RuN_{12}ORh_2$	$C_{42}H_{36}Cl_6F_6N_{12}PRh_2Ru$	$C_{44}H_{42}Cl_2IrN_{12}ORh_2$
Formula weight	1138.01	1226.70	1132.68	1373.39	1223.81
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	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/n$	$P2_1/c$
a / Å	16.1881(8)	16.2210(10)	16.0136(8)	11.4541(4)	16.0711(8)
b / Å	15.7720(8)	15.8110(10)	15.7306(7)	21.2908(6)	15.7264(8)
c / Å	16.9596(9)	16.9816(10)	16.9756(8)	20.3660(6)	16.9371(8)
α/ º	90	90	90	90	90
β/ º	100.6022(11)°	100.7660(10)	98.7610(11)	93.0367(9)	99.5862(11)
γ/ º	90	90	90	90	90
V / Å^3	4256.2(4)	4278.6(5)	4226.3(3)	4959.6(3)	4220.9(4)
Z	4	4	4	4	4
Reflection collected	27372	27376	32228	40306	29670
Independent reflections	9771	9826	9680	14416	9683
R1, wR2 [I>2sigma(I)]	0.0317, 0.0694	0.0544, 0.0931	0.0466, 0.0912	0.0467, 0.1051	0.0341, 0.0739
R1, wR2 (all data)	0.0428, 0.0736	0.0726, 0.0982	0.0626, 0.0968	0.0651, 0.1185	0.0439, 0.0783
Goodness-of-fit on F^2	1.027	1.163	1.106	1.057	1.038
Disorder occupancy	64/36	54/46	71/29	59/41	54/46

Compound	**11**$^{+}$·1.5acetone·Et_2O	**13**	**14**	$ZnRh_2Zn(dpa)_4Cl_4·CH_2Cl_2·Et_2O$
Formula	$C_{48.5}H_{51}Cl_2F_6IrN_{12}O_{2.5}P\ Rh_2$	$C_{40}H_{32}Cl_2Cu_2N_{12}Rh_2$	$C_{40}H_{32}Cl_2Ag_2N_{14}O_6Rh_2$	$C_{45}H_{44}Cl_6N_{12}ORh_2Zn_2$
Formula weight	1455.90	1084.57	1226.35	1318.18
Temperature	150(2) K	150(2) K	150(2) K	150(2) K
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	C2/c	$P2_1/c$	$P2_1/c$	C2/c
a / Å	51.972(2)	14.4313(2)	14.8400(3)	22.3384(15)
b / Å	11.8446(5)	16.7886(2)	16.9282(4)	11.8646(8)
c / Å	18.1292(8)	16.4651(2)	16.3244(3)	20.0326(14)
α/ º	90	90	90	90
β/ º	108.4130(10)	96.6949(6)	96.1754(12)	113.0623(14)
γ/ º	90	90	90	90
V / Å^3	10588.7(8)	3961.98(9)	4077.13(15)	4885.0(6)
Z	8	4	4	4
Reflection collected	36617	23932	21338	18565
Independent reflections	12175	9048	9304	5626
R1, wR2 [I>2sigma(I)]	0.0437, 0.0997	0.0320, 0.0619	0.0355, 0.0687	0.0412, 0.0981
R1, wR2 (all data)	0.0588, 0.1062	0.0634, 0.0727	0.0643, 0.0768	0.0491, 0.1023
Goodness-of-fit on F^2	1.039	1.031	1.022	1.046
Disorder occupancy	50/50	55/45 (Cu1,Cu1')	N/A	N/A

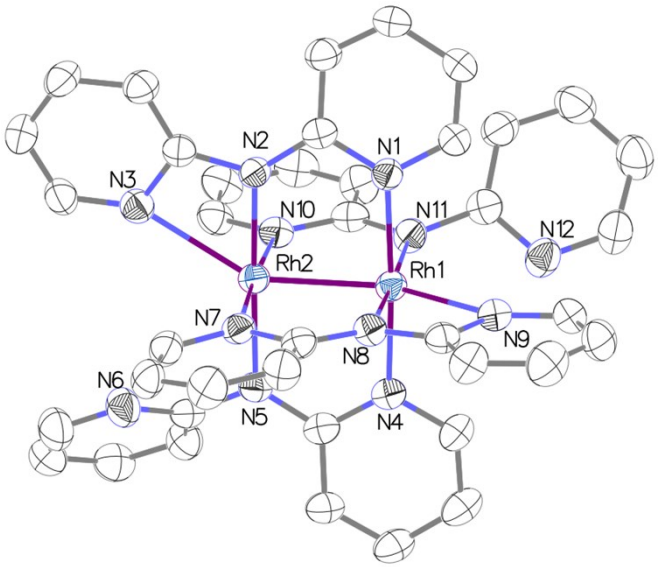

Figure S18. ORTEP structure of **1**. All atoms are drawn at the 50% probability level. Solvents and hydrogen atoms are omitted for clarity.

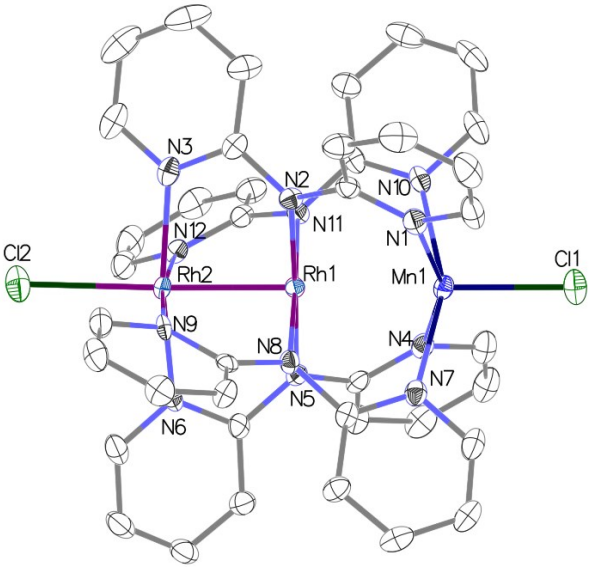

Figure S19. ORTEP structure of **2**(Mn). All atoms are drawn at the 50% probability level. Solvents and hydrogen atoms are omitted for clarity.

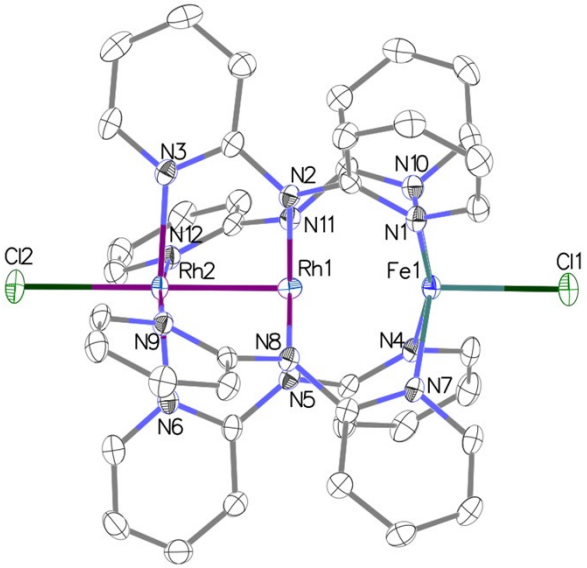

Figure S20. ORTEP structure of **3**(Fe). All atoms are drawn at the 50% probability level. Solvents and hydrogen atoms are omitted for clarity.

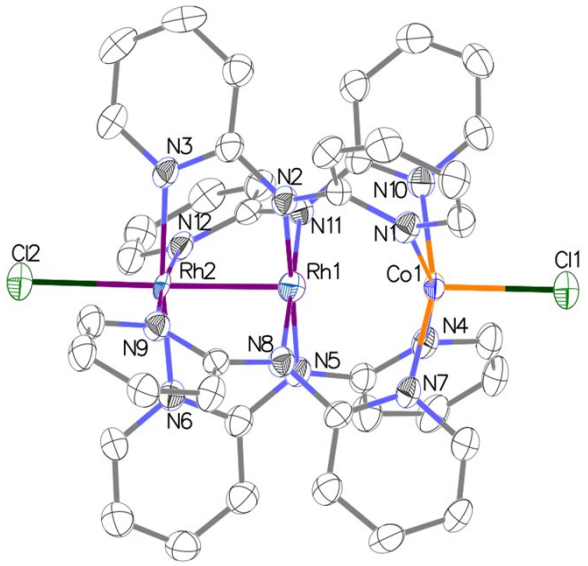

Figure S21. ORTEP structure of **4**(Co). All atoms are drawn at the 50% probability level. Solvents and hydrogen atoms are omitted for clarity.

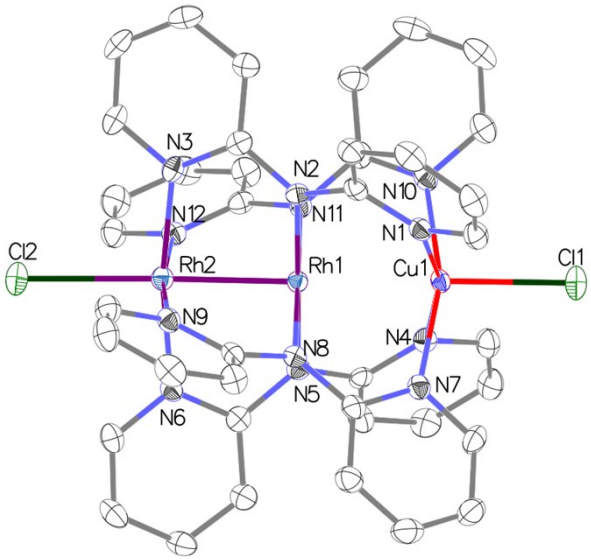

Figure S22. ORTEP structure of **6**(Cu). All atoms are drawn at the 50% probability level. Solvents and hydrogen atoms are omitted for clarity.

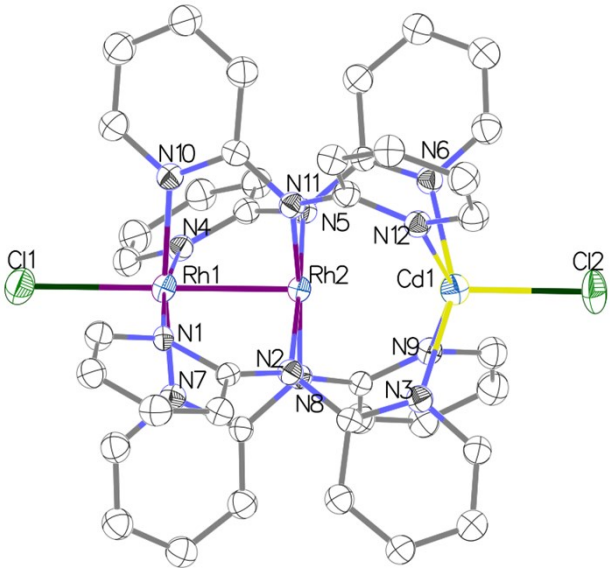

Figure S23. ORTEP structure of **7**(Cd). All atoms are drawn at the 50% probability level. Solvents and hydrogen atoms are omitted for clarity.

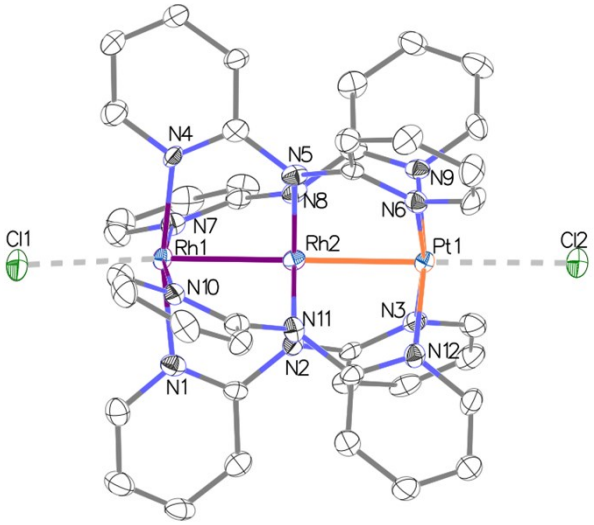

Figure S24. ORTEP structure of **9**(Pt). All atoms are drawn at the 50% probability level. Solvents and hydrogen atoms are omitted for clarity.

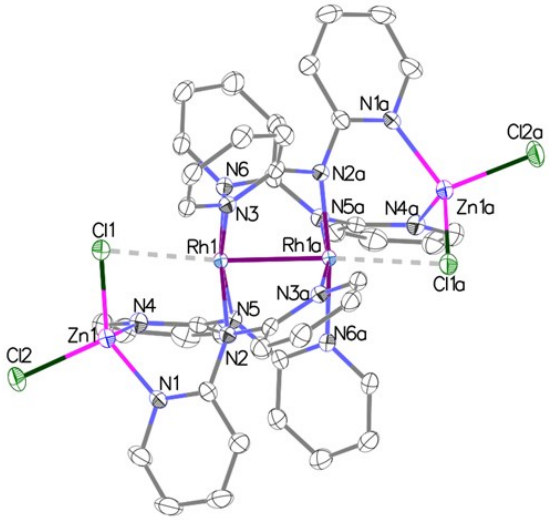

Figure S25. ORTEP structure of *cis*-(2,2)-$ZnRh_2Zn(dpa)_4Cl_4$. All atoms are drawn at the 50% probability level. Solvents and hydrogen atoms are omitted for clarity. The molecules crystalize in space group C2/c and locate at special position with Z' = 0.5 (number of molecules in the asymmetric unit). Rh1-Rh1a: 2.4221(5) Å, Zn1···Rh1: 3.1621(5) Å, Rh1-N_{av}: 2.070(3) Å, Rh1···Cl1: 2.7020(9), Zn1-Cl1: 2.193(3) Å, Zn1-Cl2: 2.2419(11) Å, ∠Zn1Rh1Rh1a: 145°.

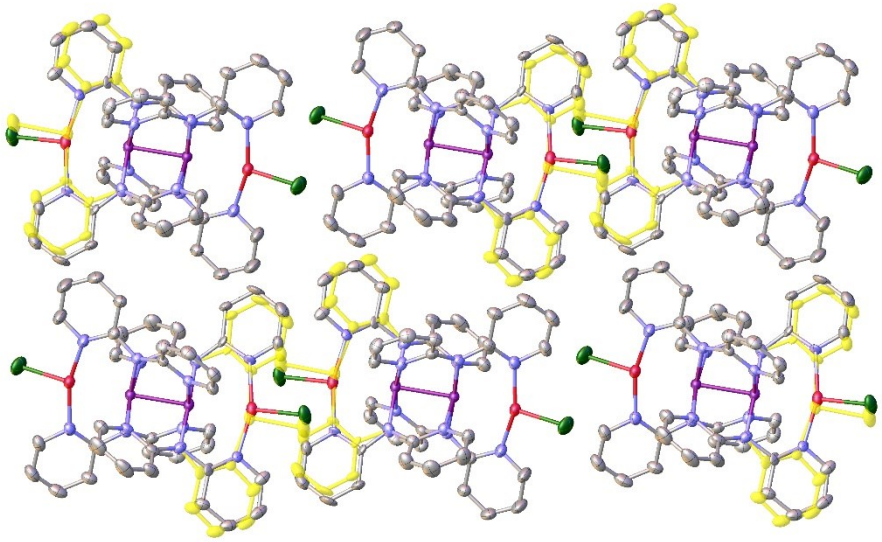

Figure S26. The molecular packing of $[CuRh_2Cu(dpa)_4Cl_2]$ (**13**) in head-to-head packing mode. The bonds and atoms in yellow color are the disordered part of molecules.

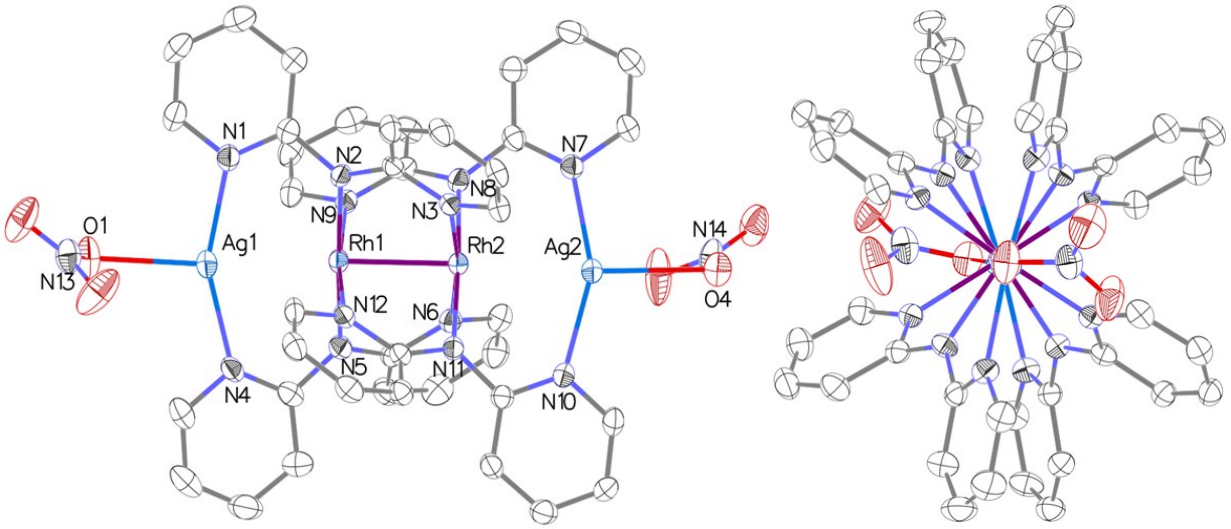

Figure S27. ORTEP structure of [$AgRh_2Ag(dpa)_4Cl_2$] **14**.(Left), top view along the metal cores.(Right) All atoms are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.