Electronic Supplementary Information

Comparison of ancillary ligand effects between 2,2'-bipyridine and 2-(2'-pyridyl)phenyl in the linkage and bridging isomerism of 5-methyltetrazolato iridium(III) and/or rhodium(III) complexes

Asuka Takayama, Takayoshi Suzuki,* Miyu Ikeda, Yukinari Sunatsuki and Masaaki Kojima

Department of Chemistry, Faculty of Science, Okayama University, Tsushima-naka 3-1-1, Okayama 700-8530, Japan

Contents:

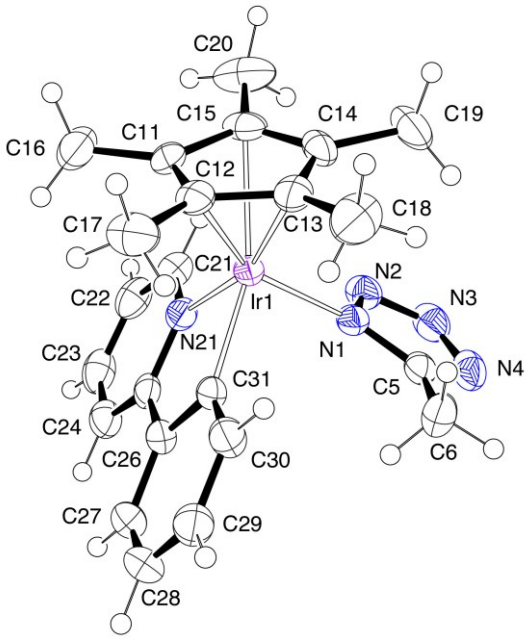


Fig. S1 An ORTEP (50% probability level, H-atoms are omitted for clarity) of [Cp*Ir(ppy)(MeCN$_4$-κN^1)] (**3**).

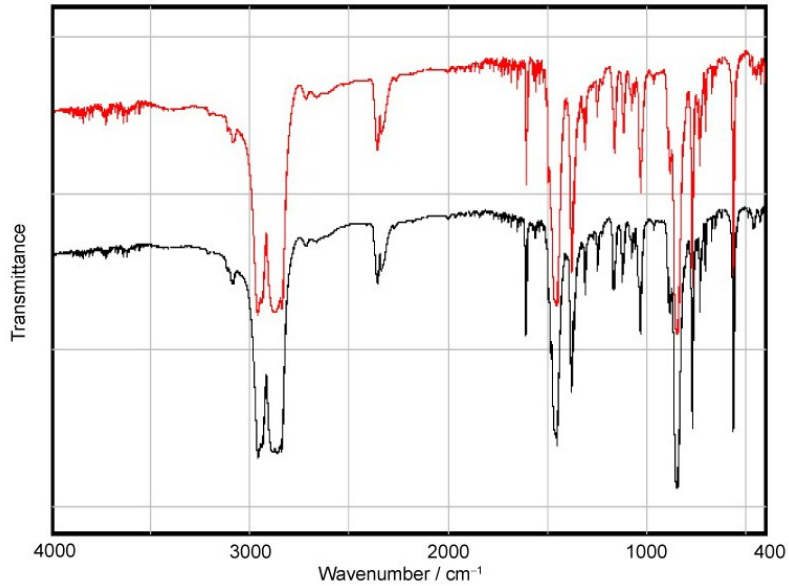


Fig. S2 Infrared spectra (Nujol mull) of bulk samples of [Cp*Ir(bpy)(MeCN$_4$)]PF$_6$ (**1**: black, lower) and [Cp*Rh(bpy)(MeCN$_4$)]PF$_6$ (**2**: red, upper).

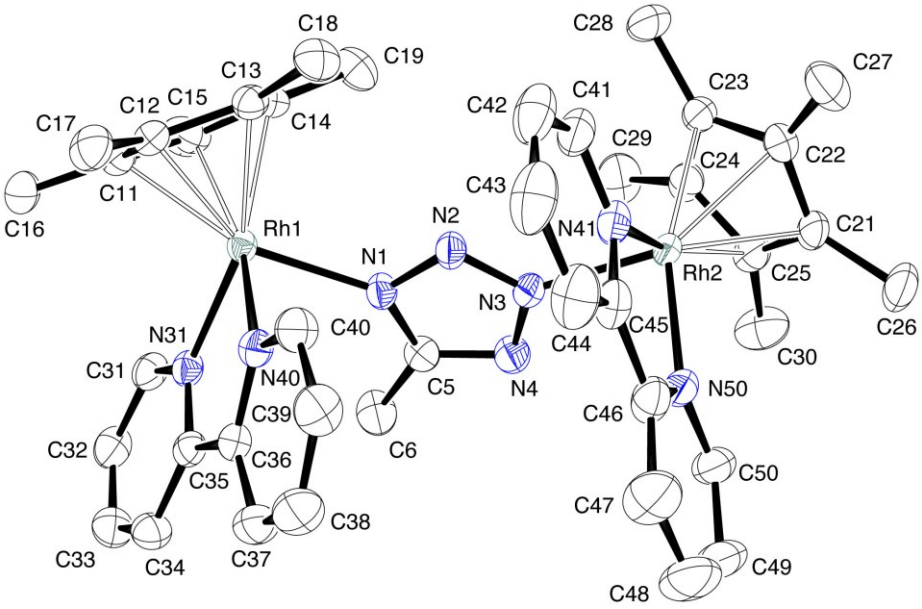


Fig. S3 An ORTEP (50% probability level, H-atoms are omitted for clarity) of the cationic part in [{Cp*Rh(bpy)}$_2$(μ-MeCN$_4$)](PF$_6$)$_3$•CH$_3$CN (**6**•CH$_3$CN).

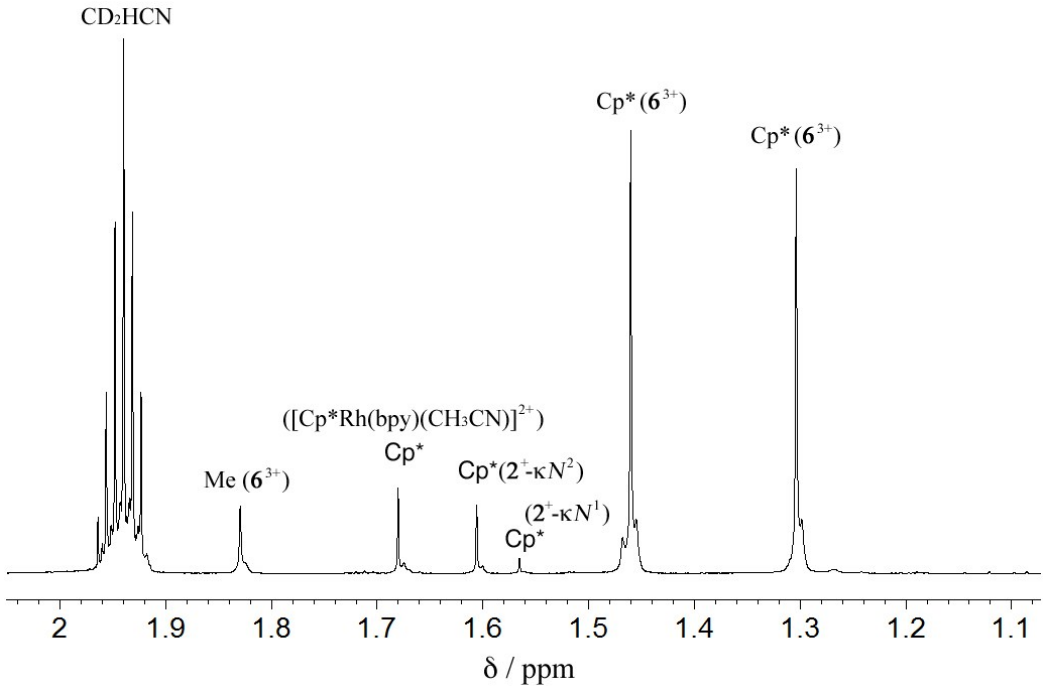


Fig. S4 ^{1}H NMR (CDCl$_3$, 300 MHz, 22 °C) spectrum of [{Cp*Rh(bpy)}$_2$(μ-MeCN$_4$)](PF$_6$)$_3$ (**6**).

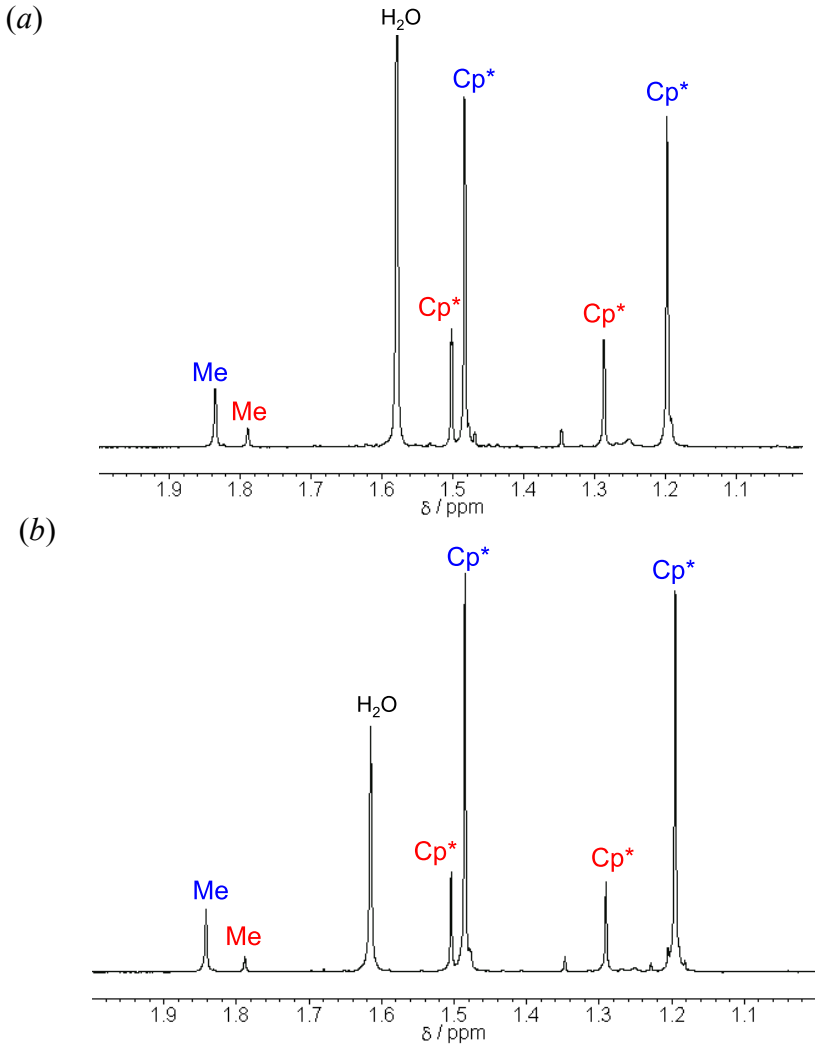


Fig. S5 ^{1}H NMR ($CDCl_3$, 300 MHz, 22 °C) spectra of (*a*) [{Cp*Ir(ppy)}$_2$(μ-MeCN$_4$)]PF_6 (**7**) and (*b*) [{Cp*Ir(ppy)}$_2$(μ-MeCN$_4$)]BF_4 (**7B**).

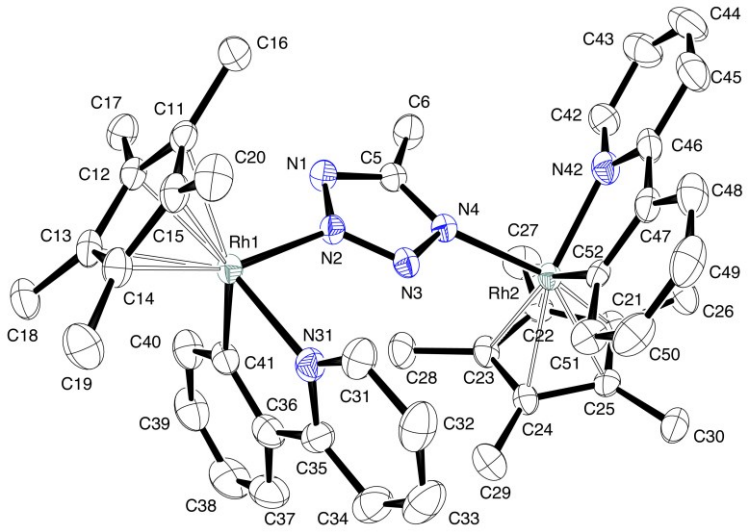


Fig. S6 An ORTEP (50% probability level, H-atoms are omitted for clarity) of the cationic part in [{Cp*Rh(ppy)}$_2$(μ-MeCN$_4$-κN^1:κN^3)]PF_6•CH_2Cl_2•Et_2O (**8**•CH_2Cl_2•Et_2O).

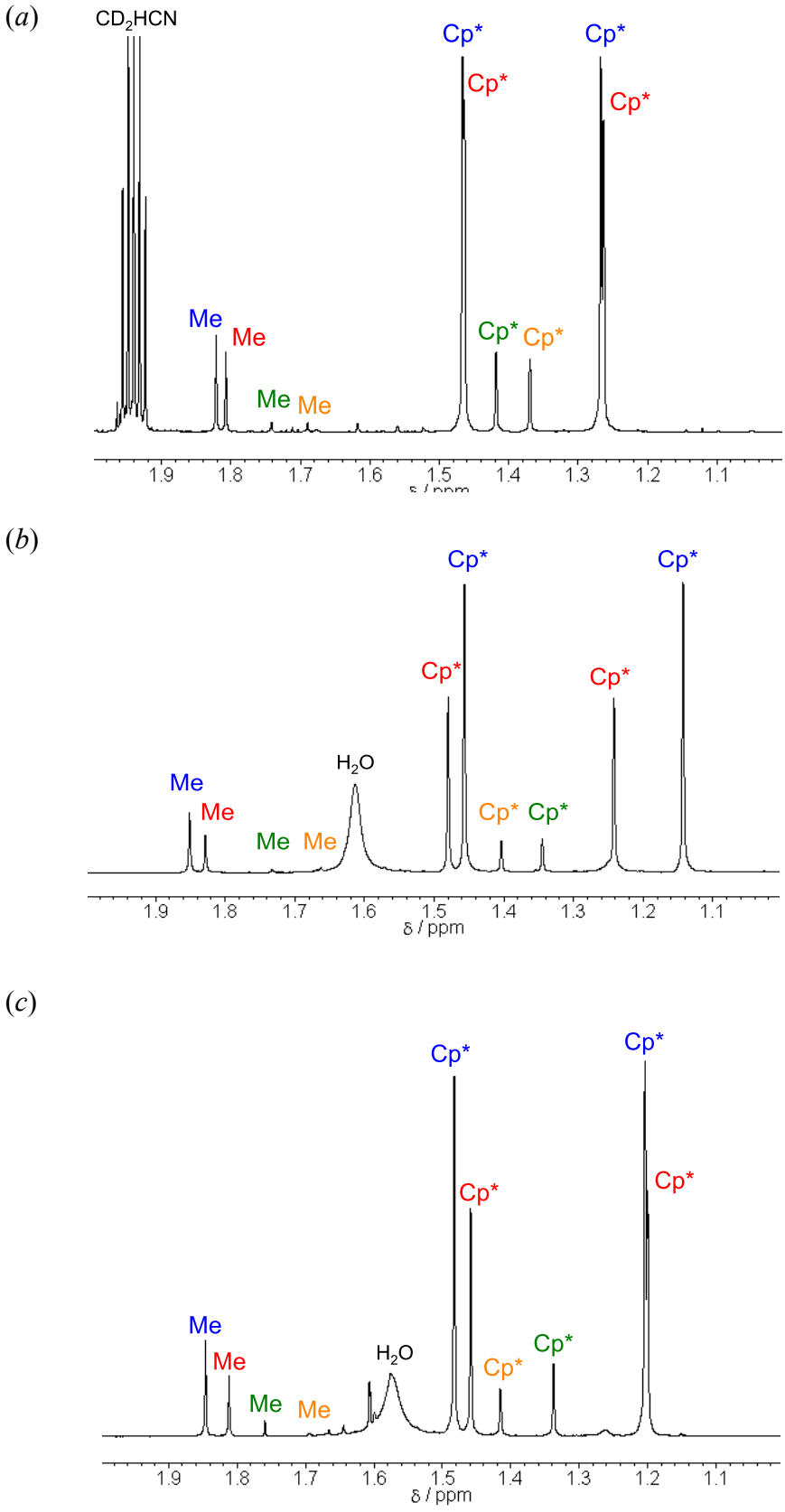


Fig. S7 ^{1}H NMR (300 MHz, 22 °C) spectra of [{Cp*Rh(ppy)}$_2$(μ-MeCN$_4$)]PF$_6$ (**8**) in (*a*) CD_3CN, (*b*) CD_2Cl_2, and (*c*) $CDCl_3$.

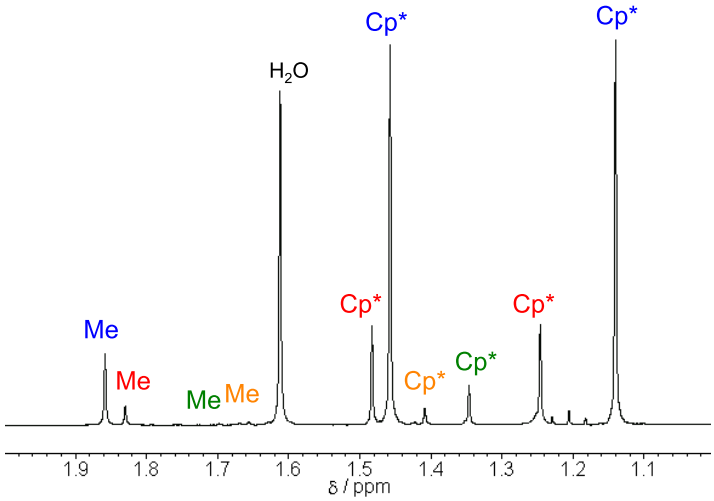


Fig. S8 ^{1}H NMR ($CDCl_3$, 300 MHz, 22 °C) spectrum of [{Cp*Rh(ppy)}$_2$(μ-MeCN$_4$)]BF_4 (**8B**).

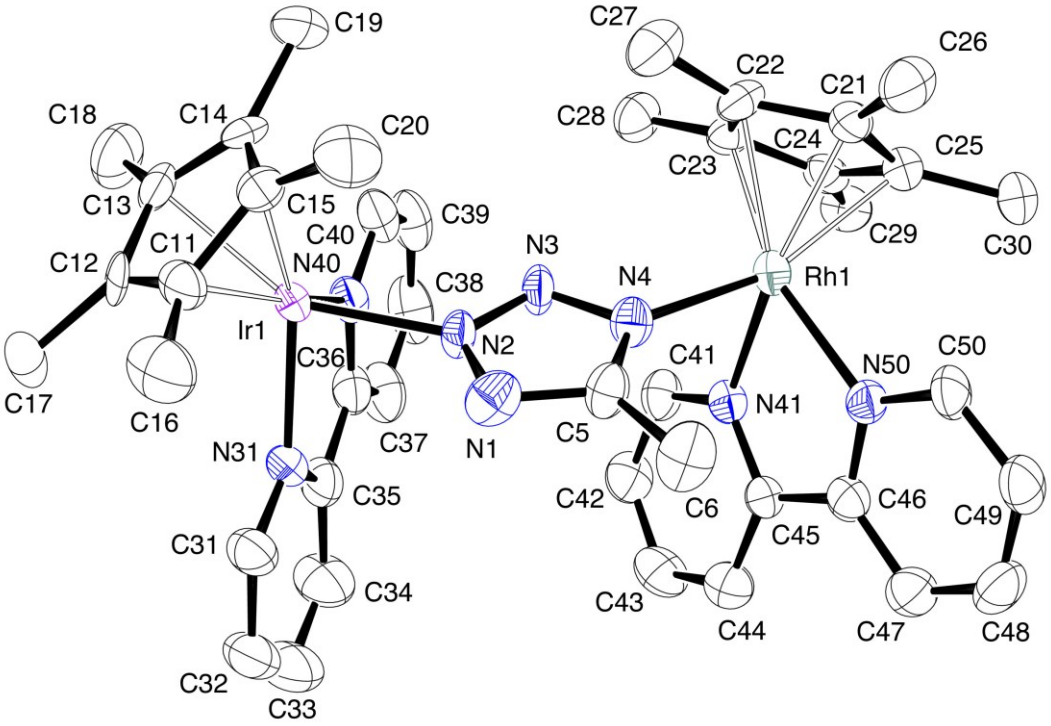


Fig. S9 ORTEP (50% probability level, H atoms omitted for clarity) of the cation in [Cp*Ir(bpy)(μ-MeCN$_4$)Rh(bpy)Cp*](PF_6)$_3$•CH_3CN (**9**•CH_3CN: one of the possible orientations for the disordered Ir/Rh atoms).

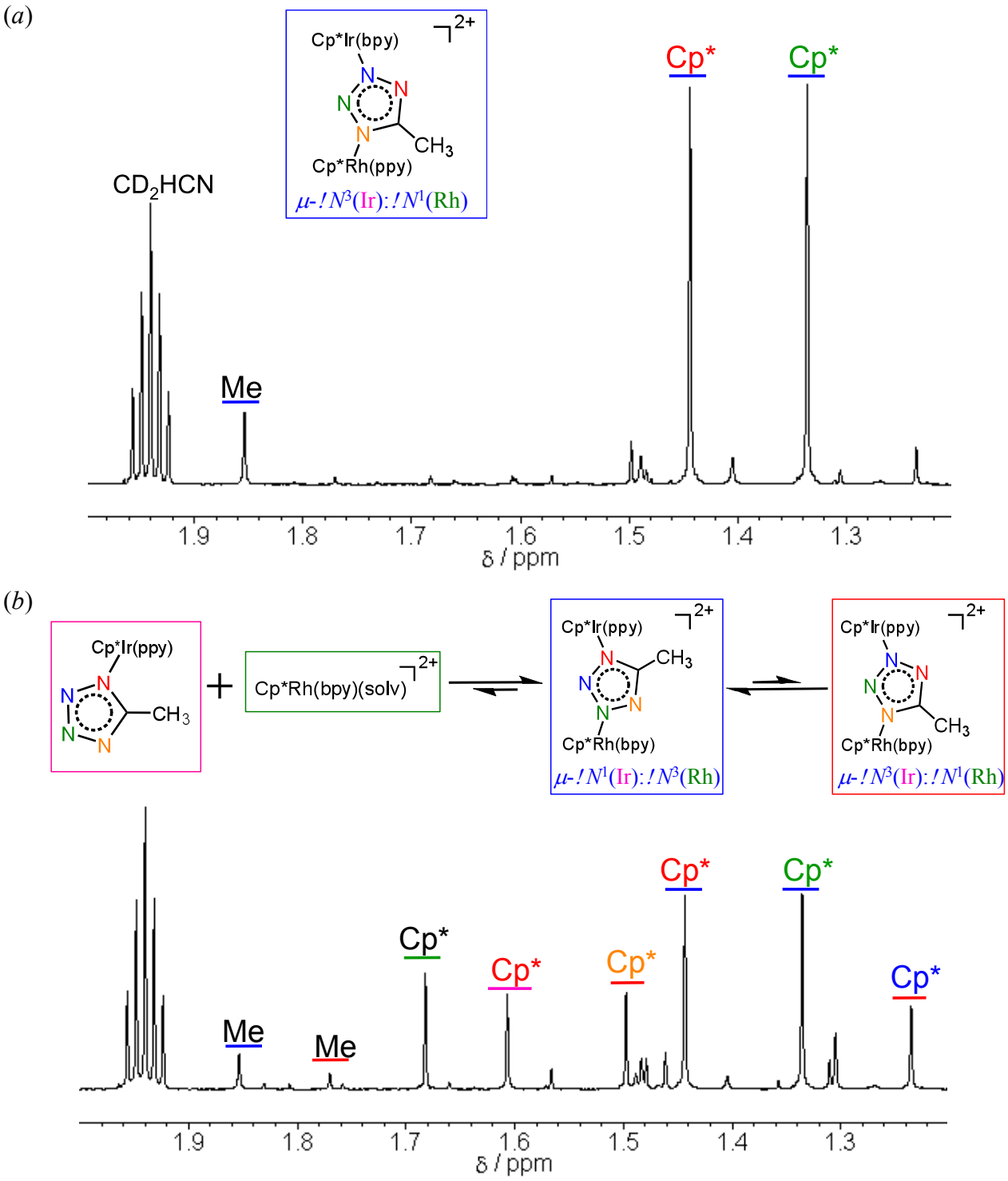
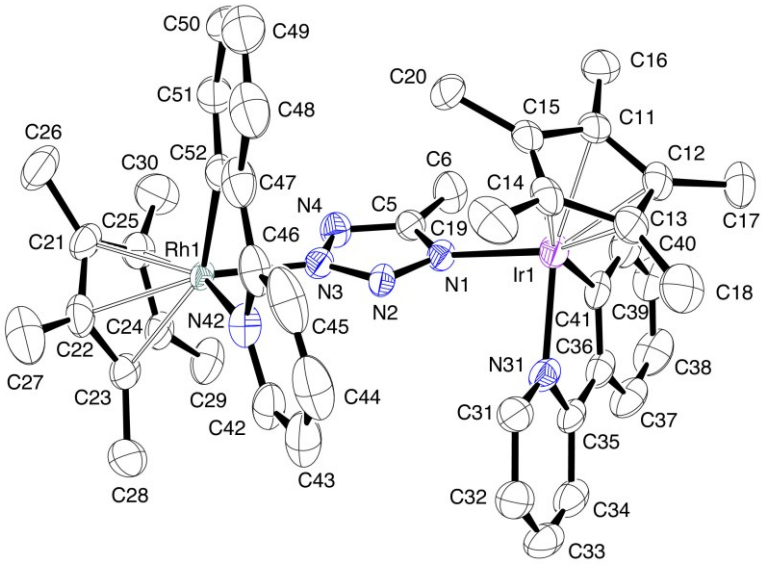


Fig. S10 ^{1}H NMR spectra (at 22 °C, 300 MHz) of a CD_3CN solution of **11** (the isolated crystals): (*a*) immediately after dissolving and (*b*) after standing at room temperature for 24 h.

(*a*)



(*b*)

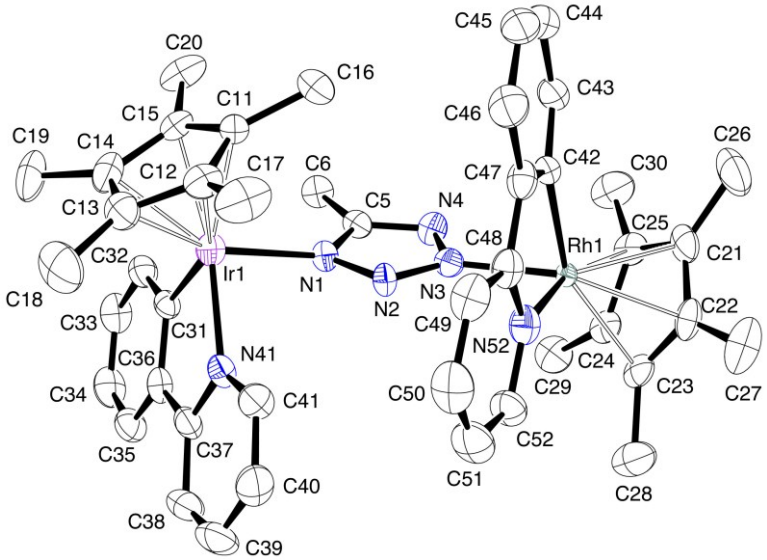


Fig. S11 ORTEPs (50% probability level, H atoms omitted for clarity) of the cationic parts in (*a*) [Cp*Ir(ppy){μ-MeCN$_4$-κN^1(Ir):κN^3(Rh)}Rh(ppy)Cp*]BF_4•$^1/_2$$CH_3CN$•$^1/_4$$H_2O$ (**12B**•$^1/_2$$CH_3CN$ •$^1/_4$$H_2O$) and (*b*) [Cp*Ir(ppy){$\mu$-MeCN$_4$-$\kappa N^1$(Ir):$\kappa N^3$(Rh)}Rh(ppy)Cp*]$BPh_4$•$CH_2Cl_2$•2$Et_2O$ (**12BP**•CH_2Cl_2•2Et_2O).

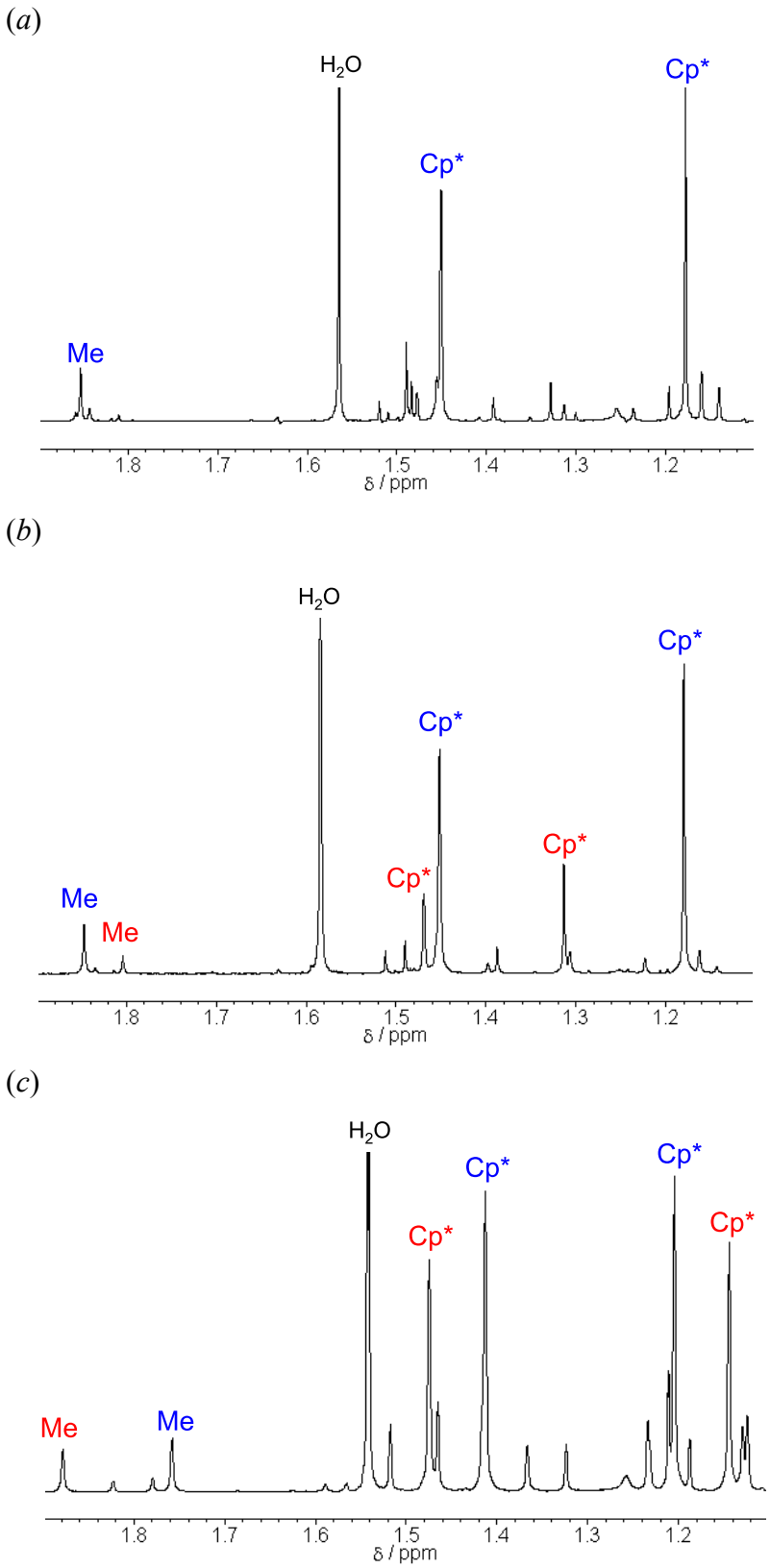


Fig. S12 ^{1}H NMR spectra (at 22 °C, 300 MHz) of $CDCl_3$ solutions of (*a*) the recrystallised sample of [Cp*Ir(ppy)(μ-MeCN$_4$)Rh(ppy)Cp*]BF_4 (**12B**), (*b*) the crude reaction products of [Cp*Ir(ppy)(μ-MeCN$_4$)Rh(ppy)Cp*]PF_6 (**12**) resulting from the addition of NH_4PF_6, and (*c*) the recrystallised sample of [Cp*Ir(ppy)(μ-MeCN$_4$)Rh(ppy)Cp*]BPh_4•CH_2Cl_2•$2Et_2O$ (**12BP**•CH_2Cl_2•$2Et_2O$).

Table S1 Crystallographic data for complexes.

	2	**3**	**4**•CH_2Cl_2	**6**•CH_3CN	**8**	**8**•CH_2Cl_2•Et_2O
Chemical formula	$C_{22}H_{26}F_6N_6PRh$	$C_{23}H_{26}IrN_5$	$C_{24}H_{28}Cl_2N_5Rh$	$C_{44}H_{52}F_{18}N_9P_3Rh_2$	$C_{44}H_{49}F_6N_6PRh_2$	$C_{49}H_{61}Cl_2F_6N_6OPRh_2$
Formula weight	622.37	564.69	560.32	1347.68	1012.68	1171.73
T / K	193(2)	192(2)	191(2)	193(2)	193(2)	193(2)
Crystal color and shape	yellow, block	yellow, columnar	orange, block	yellow, plate	yellow, plate	yellow, block
Size of specimen / mm	0.15 × 0.15 × 0.12	0.25 × 0.06 × 0.06	0.4 × 0.4 × 0.2	0.5 × 0.3 × 0.1	0.2 × 0.1 × 0.1	0.3 × 0.2 × 0.2
Crystal system	monoclinic	orthorhombic	monoclinic	monoclinic	triclinic	triclinic
Space group, Z	$P2_1/n$, 4	$Pbca$, 8	$C2/c$, 8	$P2_1/c$, 4	$P\bar{1}$, 2	$P\bar{1}$, 2
a / Å	8.8647(6)	8.7519(5)	34.5018(19)	12.9484(6)	13.0022(7)	13.8507(12)
b / Å	28.4028(15)	14.9783(7)	7.6323(5)	21.5240(9)	13.3883(8)	14.1135(12)
c / Å	9.9019(6)	31.9899(14)	22.3074(15)	20.3894(9)	14.0886(8)	14.1254(12)
α / °	90	90	90	90	71.928(3)	114.573(2)
β / °	93.770(4)	90	125.421(2)	108.669(1)	80.972(2)	96.515(3)
γ / °	90	90	90	90	63.631(2)	95.075(3)
U / Å^3	2487.7(3)	4193.5(3)	4787.0(5)	5383.6(4)	2088.4(2)	2466.7(4)
D_{calc} / Mg m^{-3}	1.662	1.789	1.555	1.663	1.610	1.578
μ(Mo Kα) / mm^{-1}	0.819	6.387	0.959	0.806	0.896	0.876
R_{int}	0.0436	0.0455	0.0222	0.0309	0.0653	0.0256
No. reflns / params.	5662/328	4801/268	5456/296	12324/682	9454/522	11230/579
$R1$ (F^2: $F_o^2 > 2\sigma(F_o^2)$)	0.0497	0.0208	0.0246	0.0319	0.0613	0.0454
$wR2$ (F^2: all data)	0.1219	0.0500	0.0666	0.0883	0.1833	0.1291
S	1.058	1.023	1.064	1.085	1.147	1.074

Table S1 (Continued)

	8B•$^1/_2$$CH_3CN$•$^1/_4$$H_2O$	**9**•CH_3CN	**10**•H_2O	**11**	**12B**•$^1/_2$$CH_3CN$•$^1/_4$$H_2O$	**12BP**•CH_2Cl_2•$2Et_2O$
Chemical formula	$C_{45}H_{51}BF_4N_{6.5}O_{0.25}Rh_2$	$C_{44}H_{52}F_{18}IrN_9P_3Rh$	$C_{43}H_{51}F_{12}IrN_7OP_2Rh$	$C_{43}H_{49}F_{12}IrN_7P_2Rh$	$C_{45}H_{51}BF_4IrN_{6.5}O_{0.25}Rh$	$C_{77}H_{91}BCl_2IrN_6O_2Rh$
Formula weight	979.55	1436.97	1266.96	1248.94	1068.84	1509.38
T / K	185(2)	183(2)	193(2)	191(2)	192(2)	192(2)
Crystal color and shape	orange, block	yellow, needle	yellow, needle	yellow, needle	yellow, plate	orange, plate
Size of specimen / mm	0.4 × 0.4 × 0.2	0.2 × 0.1 × 0.1	0.3 × 0.15 × 0.15	0.35 × 0.15 × 0.1	0.4 × 0.2 × 0.1	0.35 × 0.3 × 0.05
Crystal system	triclinic	monoclinic	tetragonal	tetragonal	triclinic	triclinic
Space group, Z	$P\bar{1}$, 2	$P2_1/c$, 4	$P\bar{4}2_1c$, 8	$P\bar{4}2_1c$, 8	$P\bar{1}$, 2	$P\bar{1}$, 2
a / Å	11.6756(8)	12.9890(4)	26.125(1)	26.0416(5)	11.6443(9)	13.7305(4)
b / Å	14.2627(9)	21.3738(5)	—	—	14.1518(8)	15.6553(9)
c / Å	14.4068(8)	20.4689(4)	14.4637(5)	14.3561(3)	14.4628(8)	18.2761(8)
α / °	99.704(2)	90	90	90	99.082(2)	67.466(3)
β / °	111.325(2)	109.311(1)	90	90	111.484(3)	76.436(2)
γ / °	96.083(2)	90	90	90	96.501(4)	82.757(2)
U / Å^3	2166.0(2)	5363.0(2)	9871.8(6)	9735.8(3)	2151.6(2)	3524.5(3)
D_{calc} / Mg m^{-3}	1.502	1.780	1.705	1.704	1.650	1.422
μ(Mo Kα) / mm^{-1}	0.820	2.981	3.179	3.220	3.531	2.246
R_{int}	0.0217	0.0842	0.0737	0.0405	0.0349	0.0383
No. reflns / params.	9821/515	12261/670	11301/576	11104/567	9779/515	16053/811
$R1$ (F^2: $F_o^2 > 2\sigma(F_o^2)$)	0.0404	0.0477	0.0508	0.0494	0.0463	0.0560
$wR2$ (F^2: all data)	0.1079	0.1354	0.1389	0.1507	0.1241	0.1664
S	1.055	1.126	1.141	1.038	1.123	1.077

Table S2 Selected bond lengths (l/Å) and angles (ϕ/°) of complexes **1**–**4**.

M = Ir or Rh	**1**[a]	**2**	**3**	**4**•CH_2Cl_2
M1–N1 ($MeCN_4$)	—	—	2.091(2)	2.0840(17)
M1–N2 ($MeCN_4$)	2.075(4)	2.079(3)	—	—
M1–N31 (bpy)	2.096(4)	2.106(3)	—	—
M1–N40 (bpy)	2.086(4)	2.094(3)	—	—
M1–N21 (ppy)	—	—	2.093(2)	2.0932(16)
M1–C31 (ppy)	—	—	2.053(3)	2.0442(19)
M1–C11 (Cp*)	2.184(5)	2.183(4)	2.176(3)	2.1883(19)
M1–C12 (Cp*)	2.156(5)	2.148(4)	2.170(3)	2.2464(19)
M1–C13 (Cp*)	2.184(5)	2.177(4)	2.180(3)	2.2335(19)
M1–C14 (Cp*)	2.176(5)	2.173(4)	2.233(3)	2.1744(19)
M1–C15 (Cp*)	2.166(5)	2.158(4)	2.252(3)	2.1722(19)
N31–M1–N40	76.57(15)	77.06(12)	—	—
N21–M1–C31	—	—	77.97(11)	78.69(7)
N31–M1–N2	86.57(14)	87.82(12)	—	—
N40–M1–N2	85.27(15)	86.63(12)	—	—
N21–M1–N1	—	—	84.29(10)	86.40(6)
C31–M1–N1	—	—	91.42(10)	91.04(7)
M1–N2–N1	125.3(3)	125.4(2)	—	—
M1–N2–N3	123.0(3)	123.3(3)	—	—
M1–N1–N2	—	—	117.94(18)	116.62(12)
M1–N1–C5	—	—	135.4(2)	134.28(13)
N1–N2–N3	111.5(4)	111.1(3)	107.8(3)	108.06(16)
C5–N1–N2	103.1(4)	103.3(3)	106.2(2)	105.92(16)

[a] M. Kotera, Y. Sekioka and T. Suzuki, *Inorg. Chem.*, 2008, **47**, 3498–3508.

Table S3 Selected bond lengths (l/Å) and angles (ϕ/°) of complexes **5**•2H_2O, **6**•CH_3CN, and **9**•CH_3CN.

M = Ir or Rh	**5**•2H_2O[a]	**6**•CH_3CN	M1 = Ir1 / Rh2 M2 = Rh1 / Ir2	**9**•CH_3CN
M1–N1 ($MeCN_4$)	2.108(4)	2.138(2)	M2–N4 ($MeCN_4$)	2.133(4)
M1–N31 (bpy)	2.093(4)	2.104(2)	M2–N41 (bpy)	2.092(4)
M1–N40 (bpy)	2.094(4)	2.110(2)	M2–N50 (bpy)	2.108(4)
M2–N3 ($MeCN_4$)	2.092(3)	2.092(2)	M1–N2 ($MeCN_4$)	2.094(4)
M2–N41 (bpy)	2.093(4)	2.096(2)	M1–N31 (bpy)	2.099(4)
M2–N50 (bpy)	2.094(4)	2.104(2)	M1–N40 (bpy)	2.113(5)
M1–C11 (Cp*)	2.164(4)	2.160(2)	M1–C11 (Cp*)	2.151(6)
M1–C12 (Cp*)	2.161(5)	2.165(2)	M1–C12 (Cp*)	2.166(5)
M1–C13 (Cp*)	2.171(5)	2.159(2)	M1–C13 (Cp*)	2.172(5)
M1–C14 (Cp*)	2.181(4)	2.184(2)	M1–C14 (Cp*)	2.160(5)
M1–C15 (Cp*)	2.169(4)	2.171(2)	M1–C15 (Cp*)	2.168(5)
M2–C21 (Cp*)	2.165(4)	2.162(2)	M2–C21 (Cp*)	2.162(5)
M2–C22 (Cp*)	2.161(4)	2.166(3)	M2–C22 (Cp*)	2.171(5)
M2–C23 (Cp*)	2.169(4)	2.161(3)	M2–C23 (Cp*)	2.163(5)
M2–C24 (Cp*)	2.168(4)	2.174(3)	M2–C24 (Cp*)	2.175(5)
M2–C25 (Cp*)	2.195(5)	2.152(3)	M2–C25 (Cp*)	2.152(5)
N31–M1–N40	76.77(14)	76.89(8)	N50–M2–N41	77.06(17)
N31–M1–N1	89.68(14)	91.33(8)	N50–M2–N4	81.91(17)
N40–M1–N1	80.83(14)	81.90(8)	N41–M2–N4	90.36(17)
N41–M2–N50	76.62(15)	76.95(9)	N31–M1–N40	77.12(18)
N41–M2–N3	85.85(14)	86.28(8)	N31–M1–N2	85.62(17)
N50–M2–N3	85.24(14)	85.98(8)	N40–M1–N2	85.56(17)
M1–N1–N2	115.3(3)	114.30(15)	M2–N4–N3	114.2(3)
M1–N1–C5	135.9(3)	138.69(17)	M2–N4–C5	136.8(4)
C5–N1–N2	108.7(4)	106.7(2)	C5–N4–N3	108.7(4)
M2–N3–N2	123.1(3)	124.52(16)	M1–N2–N1	123.2(3)
M2–N3–N4	123.0(3)	123.34(16)	M1–N2–N3	123.3(3)
N2–N3–N4	111.8(4)	112.0(2)	N1–N2–N3	113.2(4)

[a] M. Kotera, Y. Sekioka and T. Suzuki, *Inorg. Chem.*, 2008, **47**, 3498–3508.

Table S4 Selected bond lengths (*l*/Å) and angles (*ϕ*/°) of complexes **8**, **8**•CH_2Cl_2•Et_2O and **8B**•$^1/_2CH_3CN$•$^1/_4H_2O$.

	8	**8**•CH_2Cl_2•Et_2O	**12B**•$^1/_2CH_3CN$•$^1/_4H_2O$
Rh1–N1	2.110(5)	—	—
Rh1–N2	—	2.090(3)	2.092(3)
Rh1–N31	2.071(6)	2.086(3)	2.077(3)
Rh1–C41	2.061(7)	2.035(4)	2.042(3)
Rh2–N4	2.101(6)	2.092(3)	2.098(2)
Rh2–N42	2.092(5)	2.079(3)	2.093(3)
Rh2–C52	2.064(7)	2.055(3)	2.054(3)
Rh1–C11	2.210(7)	2.249(4)	2.245(3)
Rh1–C12	2.165(7)	2.160(4)	2.167(3)
Rh1–C13	2.204(7)	2.189(4)	2.186(3)
Rh1–C14	2.213(8)	2.166(4)	2.158(3)
Rh1–C15	2.190(7)	2.270(4)	2.253(3)
Rh2–C21	2.183(6)	2.173(4)	2.179(3)
Rh2–C22	2.207(7)	2.227(4)	2.249(3)
Rh2–C23	2.235(7)	2.221(4)	2.230(3)
Rh2–C24	2.187(6)	2.204(4)	2.188(3)
Rh2–C25	2.141(7)	2.180(4)	2.174(3)
N31–Rh1–C41	79.2(3)	78.99(15)	78.83(15)
N31–Rh1–N1	85.3(2)	—	—
N31–Rh1–N2	—	88.25(12)	87.92(11)
C41–Rh1–N1	91.8(2)	—	—
C41–Rh1–N2	—	83.29(14)	86.23(12)
N42–Rh2–C52	78.4(3)	78.77(14)	78.73(14)
N42–Rh2–N4	86.4(2)	92.12(12)	87.95(10)
C52–Rh2–N4	94.4(3)	88.13(12)	92.32(11)
Rh1–N1–N2	118.4(4)	—	—
Rh1–N1–C5	135.4(5)	—	—
C5–N1–N2	106.2(5)	103.7(3)	103.9(3)
Rh1–N2–N3	—	125.1(2)	125.5(2)
Rh1–N2–N1	—	122.2(2)	122.58(19)
N1–N2–N3	108.9(5)	112.2(3)	111.7(3)
Rh2–N4–N3	119.2(4)	118.7(2)	116.17(19)
Rh2–N4–C5	133.5(5)	133.7(3)	135.3(2)
N3–N4–C5	106.9(6)	106.4(3)	106.9(2)

Table S5 Selected bond lengths (l/Å) and angles (ϕ/°) of complexes **10**•H_2O and **11**.

10•H_2O		**11**	
Ir1–N2	2.078(7)	Rh1–N3	2.104(6)
Ir1–N31	2.082(8)	Rh1–N42	2.098(7)
Ir1–N40	2.108(8)	Rh1–N51	2.082(8)
Rh1–N4	2.122(7)	Ir1–N1	2.094(7)
Rh1–N41	2.102(7)	Ir1–N31	2.074(6)
Rh1–C51	2.054(8)	Ir1–C41	2.054(7)
Ir1–C11	2.197(8)	Ir1–C11	2.146(9)
Ir1–C12	2.191(9)	Ir1–C12	2.230(9)
Ir1–C13	2.183(9)	Ir1–C13	2.237(9)
Ir1–C14	2.185(9)	Ir1–C14	2.162(8)
Ir1–C15	2.158(9)	Ir1–C15	2.174(8)
Rh1–C21	2.176(9)	Rh1–C21	2.176(8)
Rh1–C22	2.170(9)	Rh1–C22	2.159(8)
Rh1–C23	2.230(8)	Rh1–C23	2.149(8)
Rh1–C24	2.227(8)	Rh1–C24	2.165(8)
Rh1–C25	2.156(9)	Rh1–C25	2.205(8)
N31–Ir1–N40	76.8(3)	N42–Rh1–N51	77.9(3)
N31–Ir1–N2	82.8(3)	N42–Rh1–N3	87.3(3)
N40–Ir1–N2	86.7(3)	N51–Rh1–N3	83.5(3)
N41–Rh1–C51	77.9(3)	N31–Ir1–C41	78.4(3)
N41–Rh1–N4	87.9(3)	N31–Ir1–N1	87.3(2)
C51–Rh1–N4	92.9(3)	C41–Ir1–N1	93.4(3)
Ir1–N2–N1	120.3(5)	Rh1–N3–N4	122.0(5)
Ir1–N2–N3	126.9(5)	Rh1–N3–N2	125.7(5)
N1–N2–N3	111.9(6)	N4–N3–N2	111.3(6)
Rh1–N4–N3	116.8(5)	Ir1–N1–N2	118.5(5)
Rh1–N4–C5	134.2(5)	Ir1–N1–C5	133.1(5)
C5–N4–N3	108.0(7)	C5–N1–N2	107.5(7)

Table S6 Selected bond lengths (l/Å) and angles (ϕ/°) of complexes **12B**•$^1/_2CH_3CN$•$^1/_4H_2O$ and **12BP**•CH_2Cl_2•$2Et_2O$.

12B•$^1/_2CH_3CN$•$^1/_4H_2O$		**12BP**•CH_2Cl_2•$2Et_2O$	
Ir1–N1	2.086(4)	Ir1–N1	2.099(5)
Ir1–N31	2.094(5)	Ir1–N41	2.090(5)
Ir1–C41	2.061(6)	Ir1–C31	2.043(6)
Rh1–N3	2.098(5)	Rh1–N3	2.082(5)
Rh1–N42	2.082(6)	Rh1–N52	2.093(5)
Rh1–C52	2.046(6)	Rh1–C42	2.055(6)
Ir1–C11	2.183(6)	Ir1–C11	2.233(6)
Ir1–C12	2.157(6)	Ir1–C12	2.251(6)
Ir1–C13	2.184(6)	Ir1–C13	2.164(7)
Ir1–C14	2.245(6)	Ir1–C14	2.148(7)
Ir1–C15	2.220(6)	Ir1–C15	2.161(6)
Rh1–C21	2.176(6)	Rh1–C21	2.195(6)
Rh1–C22	2.152(6)	Rh1–C22	2.168(6)
Rh1–C23	2.254(6)	Rh1–C23	2.228(6)
Rh1–C24	2.243(6)	Rh1–C24	2.222(6)
Rh1–C25	2.166(6)	Rh1–C25	2.200(6)
N31–Ir1–C41	77.8(2)	N41–Ir1–C31	78.6(2)
N31–Ir1–N1	86.28(19)	N41–Ir1–N1	88.15(19)
C41–Ir1–N1	91.4(2)	C31–Ir1–N1	92.3(2)
N42–Rh1–C52	78.5(3)	N52–Rh1–C42	78.5(2)
N42–Rh1–N3	87.7(2)	N52–Rh1–N3	87.4(2)
C52–Rh1–N3	86.4(2)	C42–Rh1–N3	84.9(2)
Ir1–N1–N2	117.3(4)	Ir1–N1–N2	117.4(4)
Ir1–N1–C5	133.8(4)	Ir1–N1–C5	133.5(4)
C5–N1–N2	107.3(5)	C5–N1–N2	106.7(5)
Rh1–N3–N4	122.4(4)	Rh1–N3–N4	121.1(4)
Rh1–N3–N2	124.9(4)	Rh1–N3–N2	126.5(4)
N4–N3–N2	112.3(5)	N4–N3–N2	112.1(5)