Electronic Supplementary Information.

Table 1. Crystal data and structure refinement of the complexes *cis*-[RuCl$_2$(dppe)(bipy)], *cis*-[RuCl$_2$(dppp)(bipy)] and *cis*-[RuCl(CH$_3$OH)(dppb)(bipy)](PF$_6$).

	cis-[RuCl$_2$(dppe)(bipy)]	*cis*-[RuCl$_2$(dppp)(bipy)]	*cis*[RuCl(CH$_3$OH)(dppb)(bipy)](PF$_6$)
Empirical formula	C$_{36}$H$_{32}$Cl$_2$N$_2$P$_2$Ru	C$_{74}$H$_{68}$Cl$_4$N$_4$P$_4$Ru$_2$	[RuC$_{39}$H$_{40}$ON$_2$ClP$_2$]PF$_6$.CH$_3$OH
Formula weight	726.55	1481.14	928.20
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	P2$_1$/c	P2$_1$/c	Pbca
Unit cell dimensions			
a(Å)	10.1088(3)	10.8260(1)	18.8352(11)
b(Å)	28.6127(9)	30.221(2)	19.9178(7)
c(Å)	11.8642(2)	21.141(2)	21.3951(6)
α(°)			90
β(°)	110.620(2)°	94.401(4)°	103.876(5)
γ (°)			90
V(Å^3)	3211.76(15)	6896.4(10)	4307(3)
Z	4	4	4
Density (calculated) (Mg/m^3)	1.503	1.427	1.396
Absorption coefficient (mm^{-1})	0.783	0.731	0.594
F(000)	1480	3024	1840
Crystal size (mm^3)	0.47 x 0.31 x 0.05	0.27 x 0.11 x 0.2	0.23 x 0.14 x 0.05
Theta range for data collection	3.13 to 26.03°	2.98 to 25.35°	2.92 to 26.39
Index ranges	-12 ≤ h ≤ 12	-13 ≤ h ≤ 13	-13 ≤ h ≤ 13
	-35 ≤ k ≤ 35	-34 ≤ k ≤ 36	-28 ≤ k ≤ 28
	-14 ≤ l ≤ 14	-25 ≤ l ≤ 25	-22 ≤ l ≤ 22
Reflections collected	29448	19731	31481
Independent reflections	6307 [R(int) = 0.0675]	11986 [R(int) = 0.1309]	8787 [R(int) = 0.0639]
Completeness to theta maximum (%)	99.3	94.8	99.5
Max. and min. transmission	0.966 and 0.771	0.985 and 0.876	0.975 and 0.896
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	6307 / 0 / 388	11986 / 0 / 794	8787 / 0 / 488
Goodness-of-fit on F^2	1.025	1.008	1.121
Final R indices [$I>2\sigma(I)$]	R1 = 0.0410 wR2 = 0.0905	R1 = 0.0897 wR2 = 0.1495	R1 = 0.0491 wR2 = 0.1243
R indices (all data)	R1 = 0.0711 wR2 = 0.1011	R1 = 0.2611 wR2 = 0.1937	R1 = 0.0777 wR2 = 0.1333
Largest diff. peak and hole (e.Å^{-3})	0.444 and -0.336	0.815 and -0.431	0.400 and -0.539