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Supporting Information

Supramolecular Assemblies of Ru(II) Organometallic Half-Sandwich Complexes

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Supporting Information

Syntheses of complexes

*[(η^6-p-cymene)$RuCl_2$(4-aminobenzonitrile)].**(1)***

Complex **1** was obtained from [Ru(η^6-*p*-cymene)Cl_2]$_2$ (0.04g,0.065mmol) and 4-aminobenzonitrile (0.016g, 0.13mmol). Yield: 49mg, 0.12mmol (90%). (m.p=227-229^{o}C). Anal. Calcd for $C_{17}H_{20}Cl_2N_2Ru$: C, 48.12; H, 4.75; N, 6.60. Found (%): C, 47.92; H, 4.84; N, 6.56. ^{1}H-NMR (500MHz,d_6-DMSO) δ7.39 (2H,d,*J* = 8.5Hz,C_6H_4); 6.60 (2H,d,*J*=8.5Hz,C_6H_4); 6.15 (2H,S,NH_2); 5.81 (4H,dd,*J*=20.0,6.0Hz,C_6H_4); 2.84 (1H,hept,*CH*); 2.09 (3H,S,*Me*); 1.19 (6H,d,*J*=6.5Hz,Me_2). ^{13}C-NMR (126MHz,d_6-DMSO) δ152.9 (Ar-C-NH_2); 133.4 (Ar-C-i_{pr}); 120.7 (Ar-C-CH_3); 113.4, 86.3 (Ar-C); 106.3, 100.1 (Ar-C); 95.5 (CN); 85.5(Ar-C-CN); 29.9 (CH); 21.5 (Me_2); 17.8 (Me). IR (KBr, cm^{-1}): 3421.16 ν_{N-H}; 3134.37, 3043.44 ν_{CH-Ph}; 2957.00 ν_{CH_3}; 2229.09 $\nu_{C\equiv N}$; 1487.29, 1241.07 ν_{C-N}; 1101.87 $\nu_{C=C}$; 837.71 $\nu_{Ru=N}$. Crystals suitable for X-ray analysis were collected by slow evaporation of a saturated methanol/ dichloromethane (1:2) mixture of **1**.

*[(η^6-p-cymene)$RuCl_2$(4-aminobenzyl cyanide)]. **(2)***

Complex **2** was obtained from [Ru(η^6-*p*-cymene)Cl_2]$_2$ (0.04g,0.065mmol) and 4-aminobenzyl cyanide (0.018g, 0.13mmol). Yield: 49.2mg, 0.11mmol (86%). (m.p=231-233^{o}C). Anal. Calcd for $C_{18}H_{22}Cl_2N_2Ru$: C, 49.32; H, 5.06; N, 6.39. Found (%): C, 49.06; H, 5.17; N, 6.28. ^{1}H-NMR (500MHz,d_6-DMSO) δ6.98 (2H,d,*J*=8.5Hz,C_6H_4); 6.56 (2H,d,*J*=8.5Hz,C_6H_4); 5.81 (4H,dd, *J*=20.5, 6.5Hz,C_6H_4); 5.25(2H,S,NH_2); 3.78 (2H,S,CH_2); 2.83 (1H,hept,*CH*); 2.09 (3H,S,*Me*); 1.19 (6H,d,*J*=7.0

Hz,Me_2). ^{13}C-NMR(126MHz, d_6-DMSO) δ147.9(Ar-C-NH_2); 128.7(Ar-C-i_{pr}); 119.9(Ar-C-CH_3); 117.5, 86.3 (Ar-C); 114.2, 100.1 (Ar-C); 105.3(CN); 85.5(Ar-C-CH_2CN); 77.1(CH_2CN); 29.9 (CH); 21.5 (Me_2); 17.8 (Me). IR (KBr, cm^{-1}): 3432.78 ν_{N-H}; 3221.61, 3126.90 ν_{CH-Ph}; 2964.10 ν_{CH_3}; 2227.63 $\nu_{C\equiv N}$; 1241.07 ν_{C-N}; 1081.80 $\nu_{C=C}$; 877.43 $\nu_{Ru=N}$. Crystals suitable for X-ray analysis were collected by slow evaporation of a saturated methanol/ dichloromethane (1:1) mixture of **2**.

*[(η^6-p-cymene)$RuCl_2$(4-aminophenylacetic acid)]. **(3)***

Complex **3** was obtained from [Ru(η^6-*p*-cymene)Cl_2]$_2$ (0.02g,0.032mmol) and 4-aminophenylacetic acid (0.01g, 0.064mmol). Yield: 11.9mg, 0.03mmol (80%). (m.p= 207-209^{o}C). Anal. Calcd for $C_{18}H_{23}Cl_2NO_2Ru$: C, 47.27; H, 5.07; N, 3.06. Found (%): C, 47.38; H, 5.01; N, 2.76. ^{1}H-NMR (500MHz,d_6-DMSO) ^{1}H NMR (500MHz,d_6-DMSO) δ12.1 (1H,S,OH); 6.89 (2H,d,*J*=8.5

Hz,C_6H_4); 6.49 (2H,d,*J*=8.5Hz,C_6H_4); 5.81 (4H,dd,*J*=20.0,6.0Hz,C_6H_4); 4.96 (2H,S,NH_2); 3.17 (2H,d, *J*=5.0 Hz,CH_2); 2.85 (1H,hept,CH); 2.09 (3H,S,Me); 1.19 (6H,d,*J*=7.0Hz,Me_2). ^{13}C-NMR (126MHz, d_6-DMSO) δ173.4 (COOH); 147.2(Ar-C-NH_2); 129.7(Ar-C-i_{pr}); 121.7(Ar-C-CH_3); 113.7, 86.3 (Ar-C); 106.3, 100.1(Ar-C); 85.5(Ar-C-CH_2); 36.1(CH_2);29.9(CH); 21.5 (Me_2); 17.8 (Me). IR (KBr, cm^{-1}): 3430.66 ν_{N-H}; 3216.90, 3123.39 ν_{CH-Ph}; 2966.37 ν_{CH_3}; 1708.52 $\nu_{C=O}$; 1377.26 ν_{O-H}; 1231.24 ν_{C-N}; 1049.81 $\nu_{C=C}$; 879.89 $\nu_{Ru=N}$. Crystals suitable for X-ray analysis were collected by slow diffusion of diethyl ether into a MeOH: DCM (3 : 2) mixture of **3**.

*[(η^6-p-cymene)$RuCl_2$(methyl 4-aminobenzoate)]. **(4)***

Complex **4** was obtained from [Ru(η^6-*p*-cymene)Cl_2]$_2$ (0.04g,0.065mmol) and methyl 4-aminobenzoate (0.02g, 0.13mmol). Yield: 23.8mg, 0.06mmol (81%). (m.p= 187-189^{o}C). Anal. Calcd for $C_{18}H_{23}Cl_2NO_2Ru$: C, 47.27; H, 5.07; N, 3.06. Found (%): C, 47.24; H, 5.12; N, 3.09.

^{1}H-NMR (500MHz,d_6-DMSO) ^{1}H NMR (500MHz,d_6-DMSO) δ7.63 (2H,d,*J*=8.5Hz,C_6H_4); 6.56 (2H,d,*J*=8.5 Hz,C_6H_4); 5.99 (2H,S,NH_2); 5.81 (4H,dd,*J*=20.5,6.5Hz,C_6H_4); 3.70 (3H,S,OCH_3); 2.84 (1H,hept,*CH*);2.09(3H,S,*Me*); 1.19(6H,d,*J*=7.0Hz,Me_2). ^{13}C-NMR(126MHz,d_6-DMSO) δ166.3 ($COOCH_3$); 153.5(Ar-C-NH_2); 131.0(Ar-C-i_{pr}); 115.7(Ar-C-CH_3); 112.6 , 86.3(Ar-C); 106.3,100.1(Ar-C); 85.5(Ar-C-COO); 51.1(OCH_3);29.9 (CH); 21.5 (Me_2); 17.8 (Me). IR (KBr, cm^{-1}): 3419.12 ν_{N-H} ; 3288.07, 3186.51 ν_{CH-Ph} ; 2970.29 ν_{CH_3} ; 1717.20 $\nu_{C=O}$; 1284.57 ν_{C-O} ; 1109.04 ν_{C-N} ; 1057.02 $\nu_{C=C}$; 882.71 $\nu_{Ru=N}$. Crystals suitable for X-ray analysis were collected by slow evaporation of a saturated methanol mixture of **4**.

[(η^6-p-cymene)$RuCl_2$(ethyl 4-aminobenzoate)]. ***(5)***

Complex **5** was obtained from [Ru(η^6-*p*-cymene)Cl_2]$_2$ (0.04g,0.065mmol) and ethyl 4-aminobenzoate (0.022g, 0.13mmol). Yield: 46.8mg, 0.1mmol (76%). (m.p= 194-196^{o}C). Anal. Calcd for $C_{19}H_{25}Cl_2NO_2Ru$: C, 48.45; H, 5.35; N, 2.97. Found (%): C, 48.28; H, 4.86; N, 2.66. ^{1}H-NMR (500MHz,d_6-DMSO) δ7.63 (2H,d,*J*=8.5Hz,C_6H_4); 6.55 (2H,d,*J*=8.5Hz,C_6H_4); 5.98 (2H,S,NH_2); 5.81(4H,dd,*J*=20.0,6.0Hz,C_6H_4); 4.19 (2H,dd, *J*=7.5, 14.5Hz,CH_2); 2.84 (1H,hept,*CH*); 2.09 (3H,S,*Me*); 1.27(3H,t,*J*=7.5,Hz,CH_2CH_3); 1.19 (6H,d,*J*=7.0Hz,Me_2). ^{13}C-NMR (126MHz,d_6-DMSO) δ165.8(COOCH$_2$); 153.4(Ar-C-NH_2); 130.9(Ar-C-i_{pr}); 115.9(Ar-C-CH_3); 112.6, 86.3(Ar-C); 106.3,100.1(Ar-C); 85.5(Ar-C-COO); 59.4(OCH_2); 29.9 (CH); 21.5 (Me_2); 17.8 (Me);14.3 (OCH_2CH_3). IR (KBr, cm^{-1}): 3439.04 ν_{N-H} ; 3274.16, 3204.13 ν_{CH-Ph} ; 3114.41 ν_{CH_3} ;2967.19 ν_{CH_2} ; 1709.31 $\nu_{C=O}$; 1277.66 ν_{C-O} ;1113.43 ν_{C-N} ; 1055.94 $\nu_{C=C}$; 861.91 $\nu_{Ru=N}$. Crystals suitable for X-ray analysis were collected by slow evaporation of a saturated methanol mixture of **5**.

[(η^6-p-cymene)$RuCl_2$(Butyl 4-aminobenzoate)]. ***(6)***

Complex **6** was obtained from [Ru(η^6-*p*-cymene)Cl_2]$_2$ (0.04g,0.065mmol) and ethyl 4-aminobenzoate (0.022g, 0.13mmol). Yield: 46.8mg, 0.1mmol (76%). (m.p= 186-188^{o}C). Anal. Calcd for $C_{21}H_{29}Cl_2NO_2Ru$: C, 50.54; H, 5.86; N, 2.81. Found (%): C, 50.19; H, 5.76; N, 2.84. ^{1}H-NMR (500MHz,d_6-DMSO) ^{1}H NMR (500MHz,d_6-DMSO) δ7.63 (2H,d,*J*=8.5Hz,C_6H_4); 6.56 (2H,d,

J=8.5 Hz,C_6H_4); 5.90 (2H,S,NH_2); 5.81(4H,dd,*J*=20.5,6.5Hz,C_6H_4); 4.20 (2H,t,*J*=6.5Hz,CH_2); 2.84 (1H,hept,*CH*); 2.09 (3H,S,*Me*); 1.64 (2H,m,*J*=15.0,6.5,Hz,CH_2CH_2); 1.40 (2H,m,*J*=15.0,7.5,Hz, $CH_2CH_2CH_2$); 1.19 (6H,d,*J* = 7.0Hz,Me_2); 0.93 (3H,t,*J*=7.5,Hz,CH_2CH_3). ^{13}C-NMR (126MHz,d_6-DMSO) δ165.8(COOCH$_2$); 153.4(Ar-C-NH_2); 130.9(Ar-C-i_{pr}); 116.0(Ar-C-CH_3);112.6, 86.3 (Ar-C); 106.3, 100.1(Ar-C); 85.5(Ar-C-COO); 63.2 (OOCH$_2$); 30.4 (CH$_2$CH$_2$); 29.9 (CH); 21.5 (Me_2);18.8(CH$_2$CH$_3$); 17.8 (Me); 13.6(CH$_2$CH$_3$). IR (KBr, cm^{-1}): 3423.02 ν_{N-H} ;3202.04 ν_{CH-Ph} ; 3101.70 ν_{CH_3} ;2958.14 ν_{CH_2} ; 1717.17 $\nu_{C=O}$; 1275.52 ν_{C-O} ;1107.68 ν_{C-N} ; 1022.52 $\nu_{C=C}$; 870.22 $\nu_{Ru=N}$. Crystals suitable for X-ray analysis were collected by slow evaporation of a saturated methanol mixture of **6**.

[(η^6-C_6H_6)$RuCl_2$(ethyl 4-aminobenzoate)]. ***(7)***

Complex **7** was obtained from (η^6-C_6H_6)$RuCl_2$ (0.25g,0.5mmol) and ethyl 4-aminobenzoate (0.18g, 1.0mmol). Yield: 283.3mg, 0.68mmol (68%). (m.p= 198-200^{o}C). Anal. Calcd for $C_{15}H_{17}Cl_2NO_2Ru$: C, 43.42; H, 4.13; N, 3.38. Found (%): C, 43.28; H, 4.07; N, 3.19. ^{1}H-NMR (500MHz,d_6-DMSO) ^{1}H NMR (500MHz,d_6-DMSO) δ7.63 (2H,d,*J*=8.5Hz,C_6H_4); 7.37 (1H,S,*NH*); 6.55 (2H,d,*J*=8.5Hz,C_6H_4); 5.98 (6H,m, C_6H_6); 4.19 (3H,m,*NH*,OCH_2); 1.27 (3H,t,*J*=7.5Hz,CH_3); ^{13}C-NMR (126MHz,d_6-DMSO) δ153.4(COOCH$_2$); 130.9(Ar-C-NH_2) ; 128.3

,116.0, 112.6(Ar-C); 87.6(Ar-C-COO); 59.4($OOCH_2$), ; 14.3(CH_3). IR (KBr, cm^{-1}): 3431.73 ν_{N-H} ;3211.01,3134.25 ν_{CH-Ph} ; 2979.86 ν_{CH_3} ;2920.04 ν_{CH_2} ; 1709.27 $\nu_{C=O}$; 1275.77 ν_{C-O} ;1168.28 ν_{C-N} ; 1073.11 $\nu_{C=C}$; 846.75 $\nu_{Ru=N}$. Crystals suitable for X-ray analysis were collected by slow diffusion of diethyl ether into a MeOH: DCM (1:3) mixture of **7**.

[(η^6-C_6H_6)$RuCl_2$(butyl 4-aminobenzoate)]. ***(8)***

Complex **8** was obtained from *(η^6-C_6H_6)$RuCl_2$* (0.25g,0.5mmol) and *butyl 4-aminobenzoate* (0.2g, 1.0mmol). Yield: 288.1mg, 0.65mmol (65%). (m.p= 194-196°C). Anal. Calcd for $C_{17}H_{21}Cl_2NO_2Ru$: C, 46.06; H, 4.77; N, 3.16. Found (%): C, 45.83; H, 4.61; N, 3.04.^{1}H-NMR (500MHz,d_6-DMSO) ^{1}H NMR (500MHz,d_6-DMSO) δ7.63 (2H,d,*J*=8.5Hz,C_6H_4); 7.38 (1H,S,*NH*); 6.55 (2H,d,*J*=8.5Hz,C_6H_4); 5.98 (6H,m, C_6H_6); 4.16 (3H,m,*NH*,OCH_2); 1.64 (2H,m, *J*=7.0,14.5Hz,OCH_2CH_2); 1.40 (2H,m, *J*= 7.5,14.5Hz,$OCH_2CH_2CH_2$); 0.93 (3H,t, *J*=7.5Hz,CH_3); ^{13}C-NMR (126MHz,d_6-DMSO) δ153.4(C$OOCH_2$); 130.9(Ar-C-NH_2); 128.5,116.0,112.6(Ar-C); 87.6(Ar-C-COO); 63.2($OOCH_2$); 30.4(C$H_2CH_{22}CH_3$); 18.7(CH_2CH_3); 13.6(CH_3). IR (KBr, cm^{-1}): 3429.92 ν_{N-H} ;3122.61 ν_{CH-Ph} ; 3062.01 ν_{CH_3} ;2956.19 ν_{CH_2} ; 1710.79 $\nu_{C=O}$; 1276.23 ν_{C-O} ;1111.16 ν_{C-N} ; 1073.11 $\nu_{C=C}$; 842.06 $\nu_{Ru=N}$. Crystals suitable for X-ray analysis were collected by slow diffusion of diethyl ether into a MeOH: DCM (1:3) mixture of **8**.

Complexes **1-8** are soluble in methanol, dimethylformamide, dimethysulfoxide; sparingly soluble in water, acetone, dichloromethane, chloroform, acetonitrile, benzene; while insoluble in petroleum ether and diethyl ether.

Ortep views

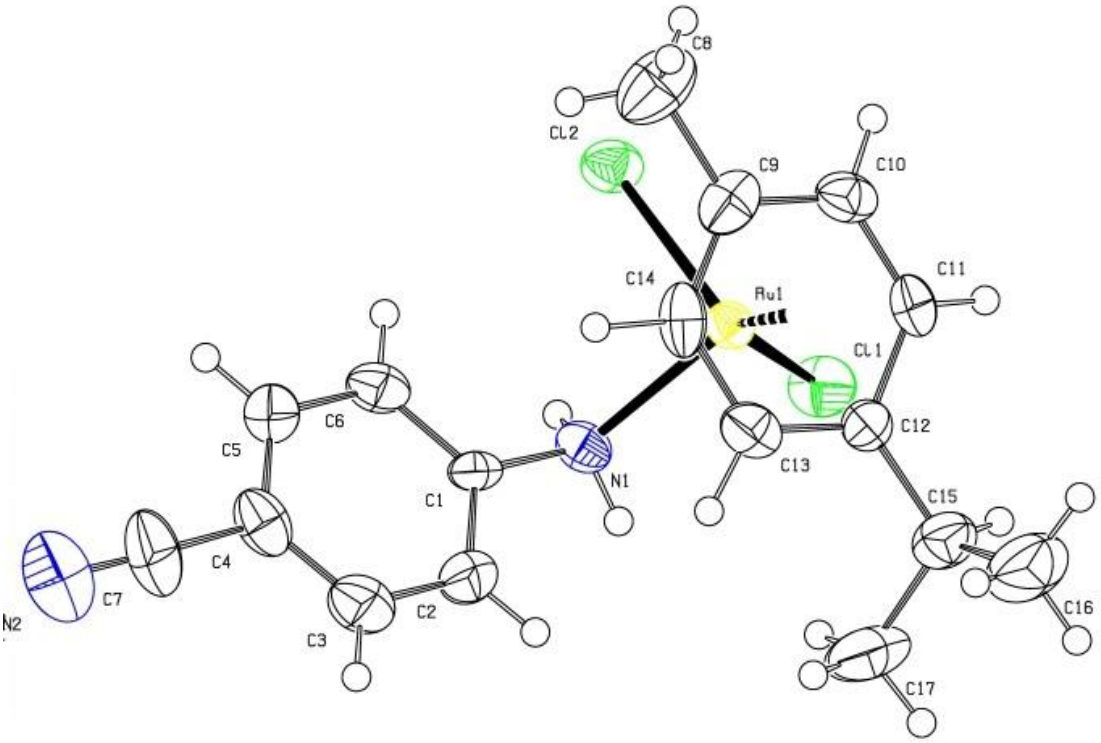


Figure S1 ORTEP view of compound **1**

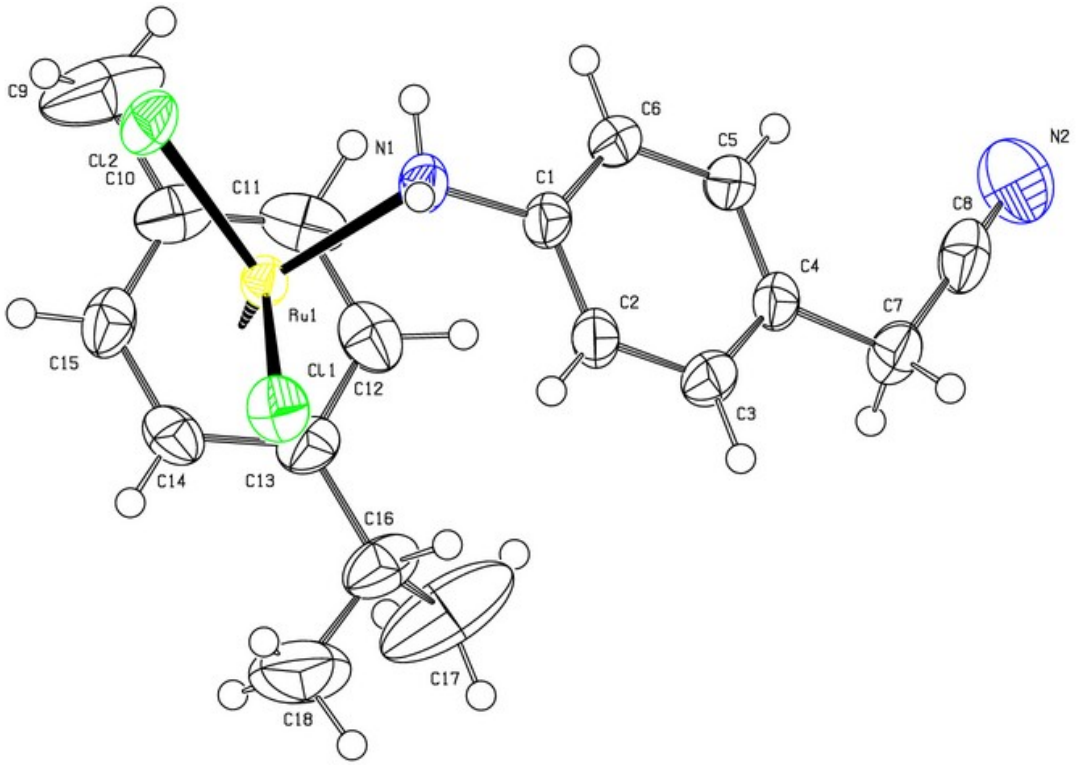


Figure S2 ORTEP view of compound **2**

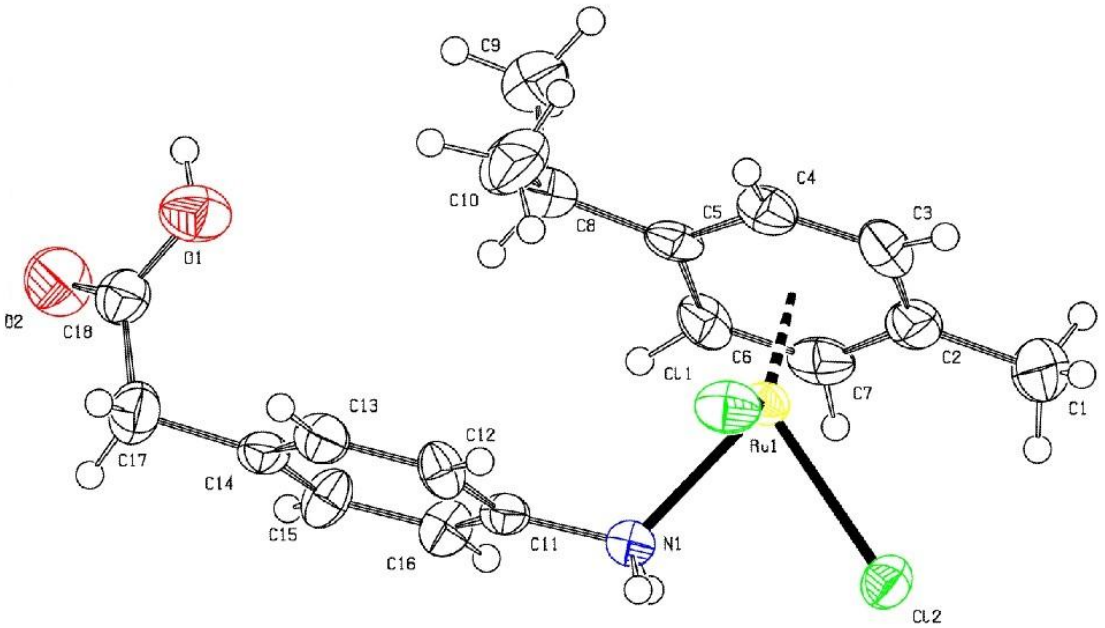


Figure S3 ORTEP view of compound **3**

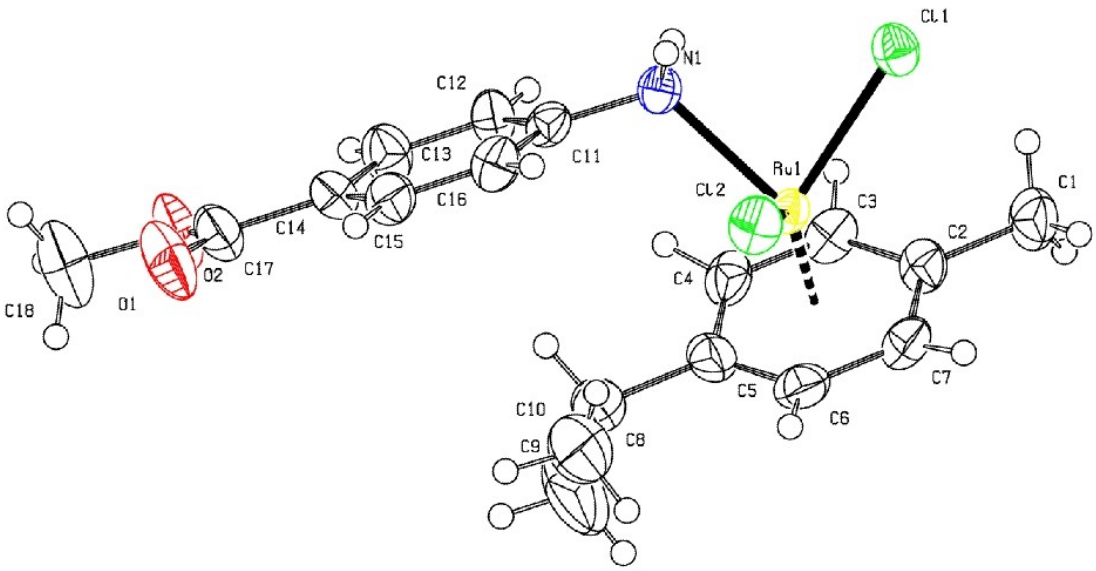


Figure S4 ORTEP view of compound **4**

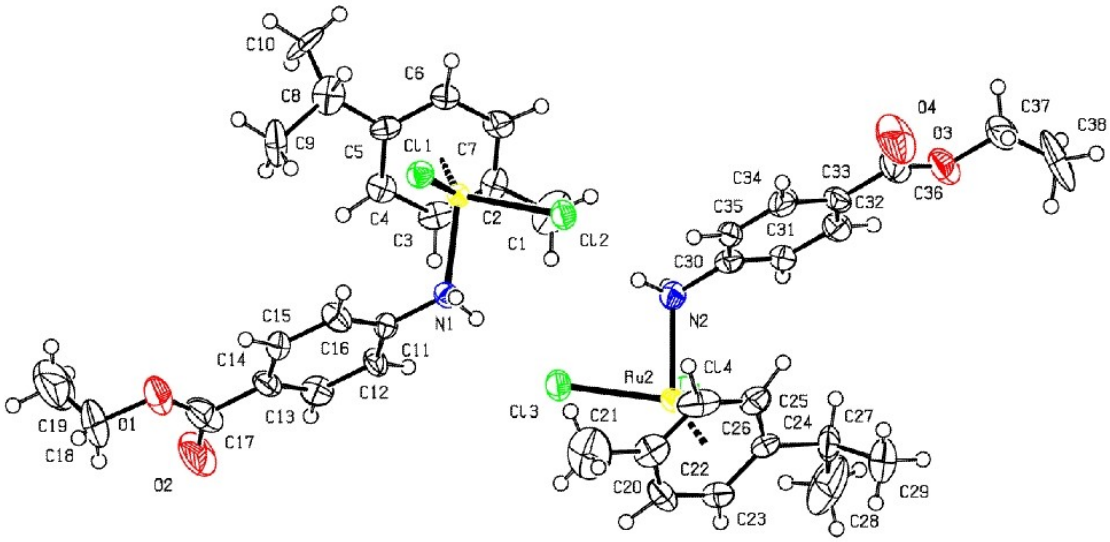


Figure S5 ORTEP view of compound **5**

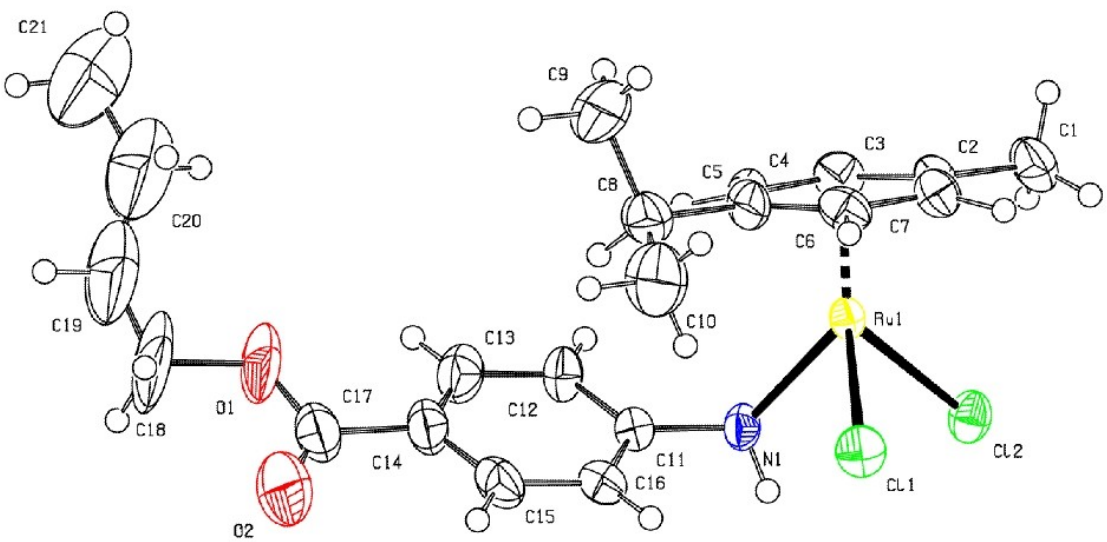


Figure S6 ORTEP view of compound **6**

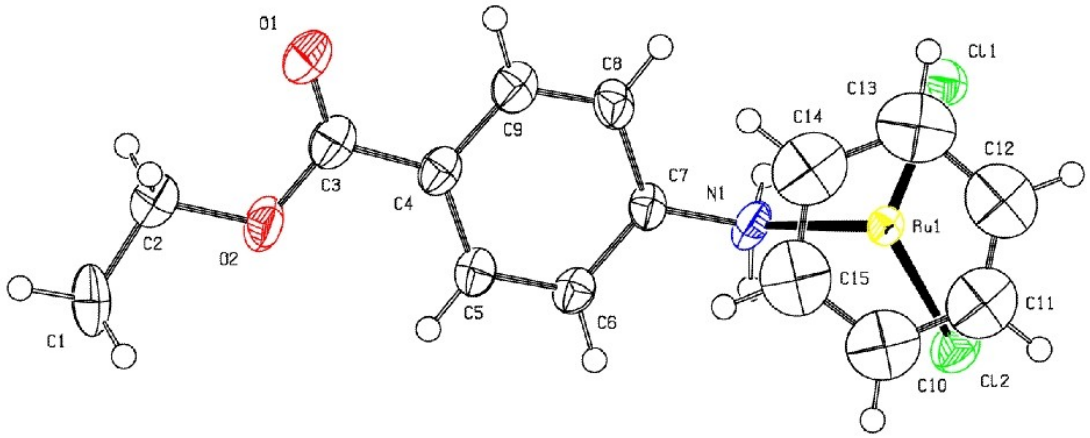


Figure S7 ORTEP view of compound **7**

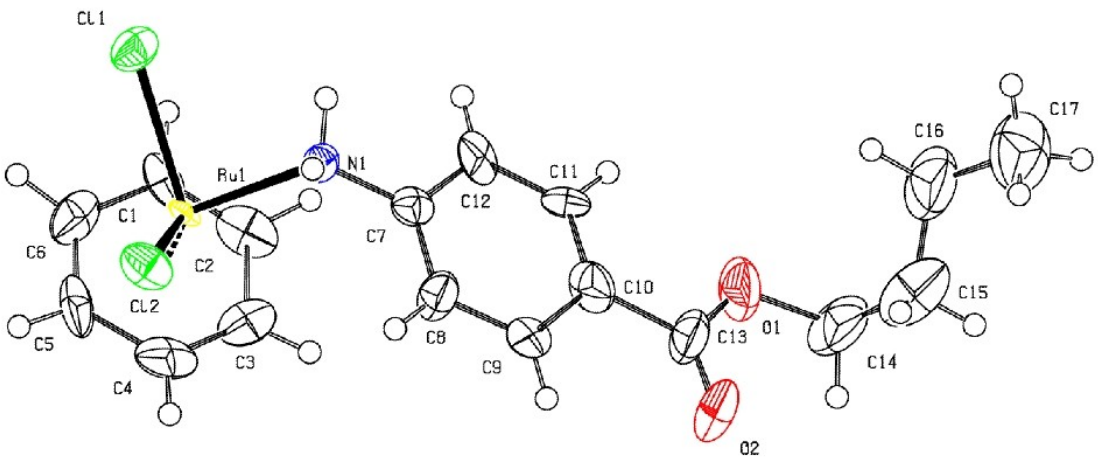
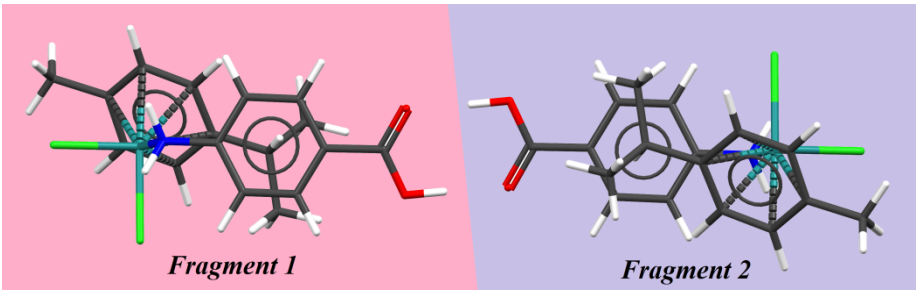
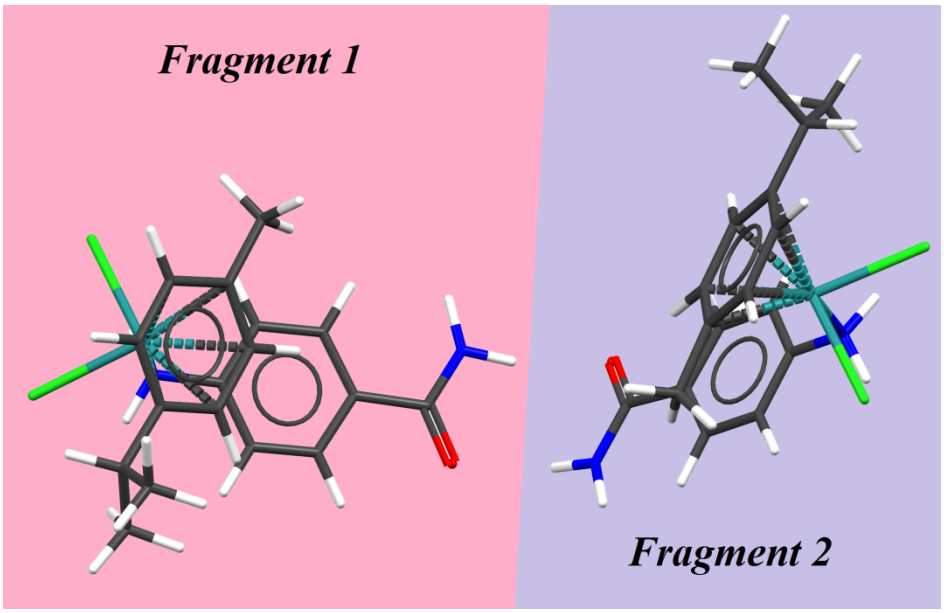


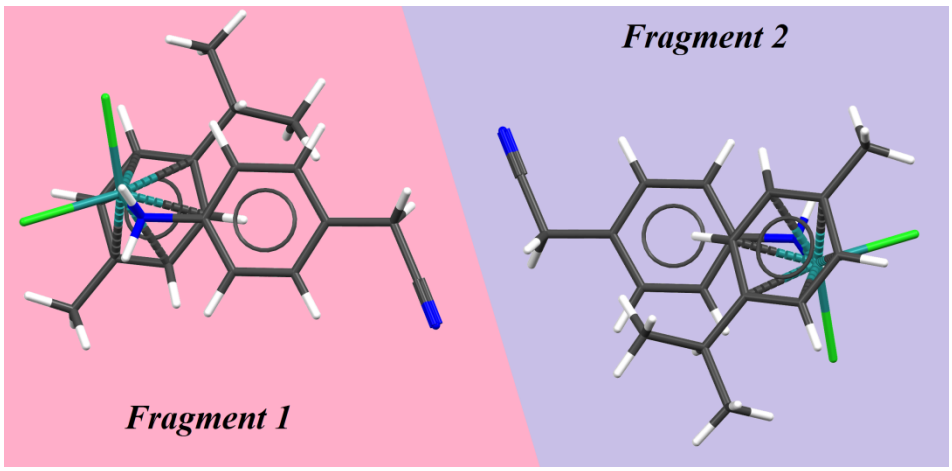
Figure S8 ORTEP view of compound **8**



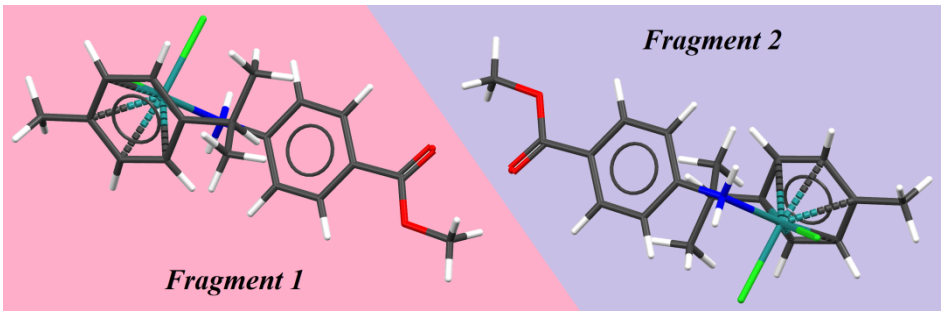
(a)



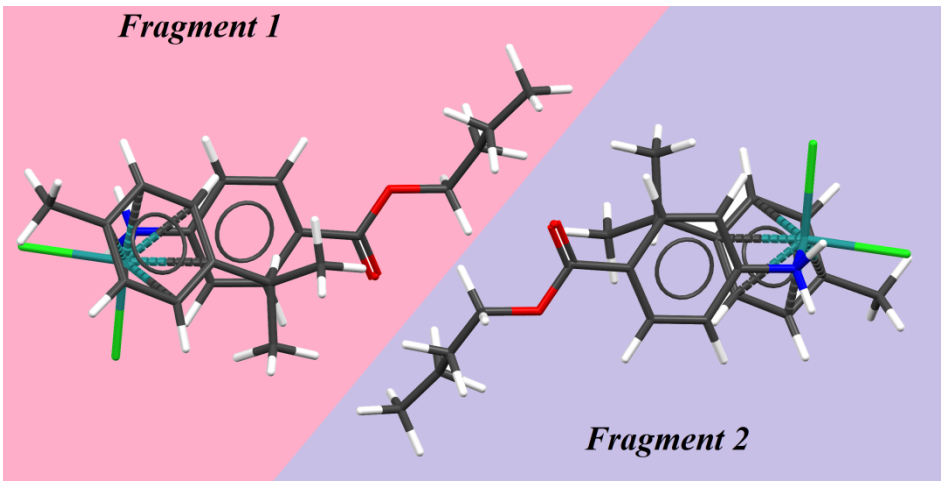
(b)



(c)

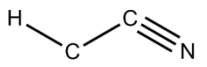


(d)

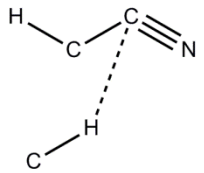


(e)

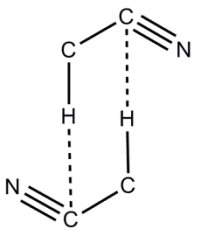
Figure S9. Fragments selected for hydrogen bonding interaction energy analysis in compounds [(Cymene)Ru(4-aminobenzoic acid)Cl_2] (a), [(Cymene)Ru(4-aminobenzamide)Cl_2] (b), [(Cymene)Ru(4-aminobenzylcyanide)Cl_2] (c), [(Cymene)Ru(methyl 4-aminobenzoate)Cl_2] (d) and [(Cymene)Ru(butyl 4-aminobenzoate)Cl_2] (e). Calculations were performed with the experimental structures (X-H bond normalized) as the starting point, at the BLYP-D3-ZORA/TZP level.



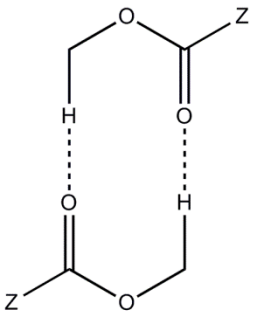
Search query for potential hits



Search query for C-H···C_{CN} observed hits

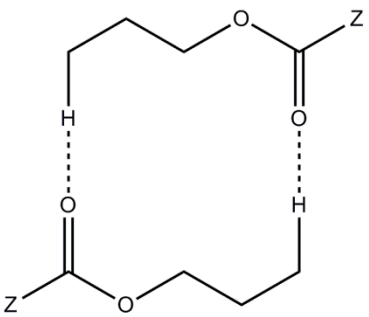


Search query for finding $R_2^2(6)$ C-H···C_{CN}



Search query for finding $R_2^2(10)$ C-H···O_{CO}

Z= not hydrogen



Search query for finding $R_2^2(14)$ C-H···O_{CO}

Figure S10. CSD searching queries for analysing C-H···C_{CN} interaction (search criteria: C-H···C contact within van der Waals distance + 0.0 Å and no disorder no error). The CSD searches have been done using Cambridge Structural Database, version 5.35 (Last update may 2014); CCDC: Cambridge, U.K., November 2013.

Table S1. Selected bond distances (Å) and angles (°) for complexes **1-8**.

		Complex							
		1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Bond distance	Ru1-Cl1	2.427(3)	2.418(2)	2.425(2)	2.422(2)	2.407(3)	2.407(2)	2.409(4)	2.412(5)
	Ru1-Cl2	2.426(2)	2.425(1)	2.420(2)	2.402(2)	2.407(3)	2.423(2)	2.407(4)	2.418(5)
	Ru1-N1	2.18(1)	2.172(4)	2.168(6)	2.184(5)	2.171(9)	2.187(5)	2.16(1)	2.18(1)
	Ru2-Cl3	-	-	-	-	2.435(3)	-	-	-
	Ru2-Cl4	-	-	-	-	2.401(4)	-	-	-
	Ru2-N2	-	-	-	-	2.18(1)	-	-	-
Bond angle	Cl1-Ru1-Cl2	88.96(9)	88.49(6)	86.92(7)	87.36(6)	88.5(1)	87.30(7)	87.9(1)	88.5(2)
	Cl1-Ru1-N1	80.3(2)	82.0(1)	85.9(2)	80.1(1)	82.8(2)	84.0(2)	82.6(4)	81.0(4)
	Cl2-Ru1-N1	82.7(2)	80.5(1)	79.2(2)	83.7(1)	80.6(2)	80.0(2)	81.9(4)	83.1(4)
	Cl3-Ru2-Cl4	-	-	-	-	85.9(1)	-	-	-
	Cl3-Ru2-N2	-	-	-	-	81.9(3)	-	-	-
	Cl4-Ru2-N2	-	-	-	-	81.7(3)	-	-	-

Table S2. Hydrogen bond geometries for compounds **1-8**.

Compound	**D-H…A**	**d(D-H)/Å**	**d(H…A)/Å**	**d(D…A)/Å**	**<D-H…A/°**	**Sym. Code**
1	C10-H10…Cl1	0.980	2.807(3)	3.74(1)	159.6(6)	1-x,-y,1-z
	C11-H11…Cl2	0.980	2.922(3)	3.63(1)	129.8(6)	1-x,-y,1-z
	N1-H1B…N2	0.90	2.40(2)	3.24(2)	155.9(6)	2-x,-1/2+y,1/2-z
	N1-H1A…Cl2	0.90	2.548(2)	3.365(7)	151.2(5)	2-x,-y, 1-z
	C17-H17C…N2	0.960	2.72(2)	3.48(2)	136.3(9)	2-x,-1/2+y,1/2-z
	C13-H13…Cl1	0.980	2.934(3)	3.55(1)	121.6(6)	1-x,1/2+y,1/2-z
2	C15-H15…Cl1	0.980	2.770(2)	3.657(7)	150.9(4)	-x,2-y,1-z
	C14-H14…Cl2	0.980	3.036(2)	3.892(8)	146.6(4)	-x,2-y,1-z
	N1-H1A…Cl2	0.90	2.802(2)	3.673(7)	162.2(3)	1-x,2-y,1-z
	C6-H6….Cl2	0.930	2.792(2)	3.658(7)	155.4(4)	1-x,2-y,1-z
	N1-H1B…N2	0.90	2.703(7)	3.572(9)	162.5(4)	X,1.5-y, ½+z
	C7-H7B…C8	0.970	2.881(6)	3.675(8)	139.7(5)	1-x,1-y, 1-z
3	C4-H4…O1	0.980	2.577(7)	3.45(1)	148.1(5)	-1/2+x,1/2-y, 1/2+z
	N1-H1A…Cl2	0.90	2.477(2)	3.349(7)	163.3(4)	1-x,-y,1-z
	N1-H1B…O2	0.90	2.123(6)	3.004(8)	166.0(4)	-1+x,y,z
	C16-H16…Cl2	0.93	2.880(2)	3.671(9)	143.8(5)	1-x,-y,1-z

4	C7-H7…Cl1	0.980	2.924(2)	3.853(8)	158.3(4)	1-x,2-y,1-z
	C1-H1D…Cl2	0.960	2.966(2)	3.691(8)	133.3(5)	1-x,2-y,1-z
	N1-H1B…Cl1	0.90	2.411(2)	3.294(6)	166.8(3)	1-x,1-y,1-z
	N1-H1A…Cl2	0.90	2.503(2)	3.356(5)	158.3(3)	2-x,1-y,1-z
	C12-H12…Cl1	0.930	2.863(2)	3.622(7)	139.6(4)	1-x,1-y,1-z
	C16-H16…Cl1	0.930	2.817(2)	3.529(8)	134.3(4)	2-x,1-y,1-z
	C18-H18A…O1	0.960	2.561(7)	3.42(1)	149.5(7)	3-x,-y,-z
5	C35-H35…Cl2	0.930	2.807(3)	3.50(1)	131.8(7)	x,y,z
	N2-H2B…Cl2	0.90	2.455(3)	3.33(1)	165.5(6)	x,y,z
	N1-H1A…Cl3	0.90	2.502(3)	3.40(1)	179.2(6)	x,y,z
	N11-H1B…Cl1	0.90	2.461(3)	3.32(1)	159.4(6)	1-x,1-y,-z
	C22-H22…Cl1	0.980	2.618(2)	3.57(1)	163.2(8)	-1+x,y, z
	C23-H23…Cl2	0.980	2.843(3)	3.51(1)	125.6(8)	-1+x,y, z
	C3-H3…O2	0.980	2.52(1)	3.23(1)	128.7(7)	-x,-y,-z
6	C7-H7…Cl2	0.980	2.892(2)	3.820(8)	158.3(5)	1-x,2-y,-z
	C1-H1E…Cl1	0.960	3.003(2)	3.722(8)	132.7(5)	1-x,2-y,-z
	C12-H12…Cl2	0.930	2.875(2)	3.609(9)	136.7(5)	1-x,1-y,-z
	C16-H16…Cl2	0.930	2.811(2)	3.565(8)	139.0(5)	2-x,1-y,-z
	N1-H1A…Cl2	0.90	2.388(2)	3.282(7)	172.0(4)	1-x,1-y,-z
	N1-H1B…Cl1	0.90	2.477(2)	3.344(5)	161.9(4)	2-x,1-y,-z
	C20-H20B…O2	0.960	2.74(1)	3.59(3)	147.0(1)	2-x, -y,1-z
7	C11-H11…Cl1	0.980	2.801(4)	3.68(3)	150.0 (1)	-x,1/2+y,1/2-z
	C12-H12…Cl2	0.980	2.733(4)	371(3)	175.0(2)	-x,1/2+y,1/2-z
	N1-H1A...Cl2	0.90	2.692(4)	3.46(1)	144.7(9)	3-x,1-y,-z
	N1-H1B…Cl1	0.90	2.926(4)	3.48(1)	121.1(9)	3-x,1-y,-z
	C14-H14…O1	0.980	2.65(1)	3.49(3)	145.0(2)	1-x,1/2+y, 1/2-z
8	C5-H5…Cl1	0.980	2.868(5)	3.80(2)	157.0(1)	2-x,-1-y,1-z
	N6-H6…N2	0.980	2.688(6)	3.61(2)	161.0(1)	2-x,-1-y,1-z
	N1-H1A…Cl2	0.90	2.773(4)	3.38(1)	125.7(9)	2-x,-y,1-z
	N1-H1B…Cl1	0.90	2.525(5)	3.37(1)	157.8(9)	2-x,-y,1-z

Table S3. Details of calculated hydrogen bonding interaction energies (BLYP-D3-ZORA/TZP) of different complexes.

Complex	Fragmants	Basis-Set	Energy(KJ/mol)
[(Cymene)Ru(4-aminobenzoic acid)Cl_2]	Fragment 1	BLYP-D3-ZORA/TZP	-24310.24
	Fragment 2	BLYP-D3-ZORA/TZP	-24310.46
	Fragment 1… Fragment 2	BLYP-D3-ZORA/TZP	-48717.54
	dimeric synthon	BLYP-D3-ZORA/TZP	-96.84 KJ/mol
[(Cymene)Ru(4-aminobenzamide)Cl_2]	Fragment 1	BLYP-D3-ZORA/TZP	-24815.17
	Fragment 2	BLYP-D3-ZORA/TZP	-24815.51
	Fragment 1… Fragment 2	BLYP-D3-ZORA/TZP	- 49682.87
	dimeric synthon	BLYP-D3-ZORA/TZP	-52.19 KJ/mol
[(Cymene)Ru(4-aminobenzylcyanide)Cl_2]	Fragment 1	BLYP-D3-ZORA/TZP	-24912.64
	Fragment 2	BLYP-D3-ZORA/TZP	-24912.78
	Fragment 1… Fragment 2	BLYP-D3-ZORA/TZP	-49842.79
	dimeric synthon	BLYP-D3-ZORA/TZP	-17.37 KJ/mol
[(Cymene)Ru(methyl 4-aminobenzoate)Cl_2]	Fragment 1	BLYP-D3-ZORA/TZP	-25818.02
	Fragment 2	BLYP-D3-ZORA/TZP	-25817.32
	Fragment 1… Fragment 2	BLYP-D3-ZORA/TZP	-51652.88
	dimeric synthon	BLYP-D3-ZORA/TZP	-17.54 KJ/mol
[(Cymene)Ru(butyl 4-aminobenzoate)Cl_2]	Fragment 1	BLYP-D3-ZORA/TZP	-30127.52
	Fragment 2	BLYP-D3-ZORA/TZP	-30127.21
	Fragment 1… Fragment 2	BLYP-D3-ZORA/TZP	-60302.22
	dimeric synthon	BLYP-D3-ZORA/TZP	-47.49 KJ/mol