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Supporting Information for

Unusual Dimer Formation of Cyclometalated Ruthenium NHC *p*-Cymene Complexes.

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EXPERIMENTAL

General

The reactions involving transition metals were carried out employing standard Schlenk techniques. Solvents used throughout this study were of high purity, dichloromethane and tetrahydrofuran were dried in an MBraun Solvent Purification System prior to use. Ruthenium(III)-chloride was purchased from Pressure Chemicals Co. and used as received. All other chemicals are commercially available from common suppliers and used without further purification. The dichloro(*p*-cymene)ruthenium(II) dimer was prepared according to the literature.[1] Phenylimidazoles and their respective imidazolium salts were prepared according to published procedures.[2] Sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate was prepared *via* a method published by the group of Smith.[3] ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC 300 P, a Bruker DRX 500 P or a Bruker ACS 600 spectrometer at 298 K. ^{1}H and ^{13}C spectra were referenced internally using the resonances of the solvent (^{1}H: 7.26, ^{13}C: 77.0 for $CDCl_3$; ^{1}H: 2.50, ^{13}C: 39.43 for DMSO-d_6; ^{1}H: 1.94, ^{13}C: 118.26 for CD_3CN; ^{1}H: 7.16, ^{13}C: 128.06 for C_6D_6). Shifts δ are given in ppm downfield from tetramethylsilane, coupling constants *J* in Hz. Elemental analyses were performed on a Eurovector Hekatech EA3000 by the microanalytical laboratory of our institute. Melting points have been determined on a hot stage microscope and are not corrected.

X-ray Crystallography

Preliminary examination and data collection for single crystals of compounds **1** and **2** were carried out on a NONIUS κ-CCD diffraction system (FR590) equipped with an Oxford Cryosystem cooling system at the window of a fine-focus sealed tube using graphite-monochromated Mo K_α radiation (λ = 0.71073 Å). The reflections were merged and corrected from Lorentz, polarization and decay effects. Absorption correction was applied using SADABS.[4] The structures were solved by a combination of direct methods[5] with the aid of difference Fourier synthesis and were refined against all data using SHELXL-97.[6] Hydrogen atoms were assigned to ideal positions using the SHELXL-97 riding model. All non-hydrogen atoms were refined with anisotropic displacement parameters. Full-matrix least-squares refinements were carried out by minimizing $\Sigma w(F_o^2 - F_c^2)^2$ with the SHELXL-97 weighting scheme. Details of the structure determinations are given in the Supporting Information. Neutral-atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from the International Tables for Crystallography.[7] All calculations were performed with the programs COLLECT[8], DIRAX[9], EVALCCD[10], SIR92[5a], SIR97[5b], SADABS[4], the SHELXL-97 package[6, 11], and PLATON[12]. Images of the solid state structures were generated with ORTEP-3[13] and MERCURY.[14]

Preliminary examination and data collection for single crystals of compound **6** were carried out on a RIGAKU AFC7 diffraction system (Saturn 724+ CCD detector) equipped with a sealed x-ray tube using graphite-monochromated Mo K_α radiation (λ = 0.71073 Å). Intensity data were extracted using the CRYSTALCLEAR program package.[15] The reflections were merged and corrected from Lorentz, polarization and decay effects and absorption correction was applied based on multiple scans. The structure was solved by a combination of direct methods[16] with the aid of difference Fourier synthesis and were refined against all data using SHELXL-97.[6] Hydrogen atoms were assigned to ideal positions using the SHELXL-97 riding

model. All non-hydrogen atoms were refined with anisotropic displacement parameters. Full-matrix least-squares refinements were carried out by minimizing $\Sigma w(F_o^2 - F_c^2)^2$ with the SHELXL-97 weighting scheme. Neutral-atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from the International Tables for Crystallography.[7] All calculations were performed with the CRYSTALCLEAR program package[15-16], the SHELX-97 program package[6, 11], PLATON[12] and WINGX.[17] Images of the solid state structures were generated with ORTEP-3[13] and MERCURY.[14]

For compound **6** one level-A alert and level-C alerts are suggested by the PLATON/CIF check program: These alerts are attributed to the strong disorder of the CF_3-groups in the BAr^F_4 anion. All disordered groups were treated with the DFIX and ISOR command as implemented in the SHELX program package[6, 11] to properly describe all disordered atoms.

Chloro[1-methyl-3-(phenyl-κC^2)imidazol-2-ylidene-κC^2][η^6-1-methyl-4-(1-methylethyl) benzene] ruthenium(II) ***1***

1.43 g (5 mmol) of 1-methyl-3-phenylimidazolium iodide, 1.53 g (2.5 mmol) of [$RuCl_2$(η^6-*p*-cymene)]$_2$ were placed in a Schlenk tube. 100 ml of CH_2Cl_2 and (under vigorous stirring) 1.17 g (5 mmol) of Ag_2O were added. The resulting deep red suspension was stirred at room temperature under exclusion of light for 24 h and the suspension was filtered through a cannula. The solvent was evaporated *in vacuo* and the crude product was dissolved in little amounts of THF (approx. 60 ml) and filtered over basic Al_2O_3. The analytically pure product precipitated upon slow addition of pentane as bright yellow to orange crystals. (1.36 g, 64 %, dec. > 215 °C).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 – 8.08 (m, 1H, $C_{ar}H$), 7.33 (d, *J* = 2.0 Hz, 1H, $C_{im}H$), 7.08 – 7.03 (m, 1H, $C_{ar}H$), 6.99 – 6.93 (m, 3H, $C_{ar}H$), 5.59 (d, *J* = 6.0 Hz, 1H, $C_{ar}H$(cym)), 5.56 (d, *J* = 5.4 Hz, 1H, $C_{ar}H$(cym)), 5.47 (d, *J* = 6.0 Hz, 1H, $C_{ar}H$(cym)), 5.39 (d, *J* = 5.8 Hz, 1H, $C_{ar}H$(cym)), 4.15 (s, 3H, NCH_3), 2.17 (hept, *J* = 6.9 Hz, 1H, $CH(CH_3)_2$), 2.06 (s, 3H, $C_{ar}CH_3$(cym)), 0.89 (d, *J* = 6.9 Hz, 3H, $CH(CH_3)_2$), 0.74 (d, *J* = 6.9 Hz, 3H, $CH(CH_3)_2$)

^{13}C NMR (126 MHz, $CDCl_3$) δ 188.3 ($C_{carbene}$), 162.9 (*C*Ru), 145.6 (C_{ar}N), 141.5 (C_{ar}H), 124.4 (C_{ar}H), 122.2 (C_{ar}H), 121.9 (C_{im}H), 114.2 (*C4*H), 110.9 (C_{im}H), 104.6 ($C_{ar}CH_3$(cym)), 98.8 (C_{ar}*i*-Pr(cym)), 92.6 (C_{ar}H(cym)), 89.7 (C_{ar}H(cym)), 87.7 (C_{ar}H(cym)), 84.1 (C_{ar}H(cym)), 37.8 (NCH_3), 31.0 ($CH(CH_3)_2$), 23.0 ($CH(CH_3)_2$), 21.7 ($CH(CH_3)_2$), 18.9 ($C_{ar}CH_3$(cym))

Anal. Calc. for $C_{20}H_{23}ClN_2Ru$ (M = 428.06 g/mol): C: 56.13, H: 5.42, N: 6.55, Found: C: 56.04, H: 5.34, N: 6.37 %

Chloro[1-(4-methoxyphenyl-κC^2)-3-methylimidazol-2-ylidene-κC^2][η^6-1-methyl-4-(1-methylethyl)benzene] ruthenium(II) ***2***

948 mg (3 mmol) of 1-(4-methoxyphenyl)-3-methylimidazolium iodide, 919 mg (1.5 mmol) of $[RuCl_2(\eta^6\text{-}p\text{-cymene})]_2$ and 702 mg (3 mmol) of Ag_2O were placed in a Schlenk tube and 80 ml of CH_2Cl_2 were added. The resulting deep red suspension was stirred at room temperature under exclusion of light for 16 h, then heated to 40 °C for 4 h and again stirred at room temperature overnight. The crude product was subsequently purified by column chromatography (SiO_2; CH_2Cl_2/MeOH 10:1; $R_f = 0.95$). The solvent of the collected yellow band was evaporated *in vacuo*, the residue was dissolved in little amounts of THF (approx. 50 ml) and filtered over basic Al_2O_3. The analytically pure product precipitated upon slow addition of pentane as bright yellow to orange crystals. (1.06 g, 77.2 %; Slow dec. > 190 °C).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72 (d, *J* = 2.6 Hz, 1H, C5*H*), 7.26 ([signal obscured by solvent residual signal], 1H, C2*H*), 6.98 (d, *J* = 8.3 Hz, 1H, C3*H*), 6.95 (d, *J* = 2.0 Hz, 1H, C1*H*), 6.49 (dd, *J* = 8.3, 2.6 Hz, 1H, C4*H*), 5.57 (d, *J* = 6.0 Hz, 1H, C6*H*), 5.53 (d, J = 5.9 Hz, 1H, C8*H*), 5.46 (d, J = 5.9 Hz, 1H, C7*H*), 5.39 (d, J = 5.9 Hz, 1H, C9*H*), 4.13 (s, 3H, NC*H$_3$*), 3.85 (s, 3H, OC*H$_3$*), 2.18 (hept, *J* = 6.9 Hz, 1H, C*H*$(CH_3)_2$), 2.06 (s, 3H, $C_{ar}CH_3$(cym)), 0.89 (d, J = 6.9 Hz, 3H, CH(C*H$_3$*)$_2$), 0.75 (d, J = 6.9 Hz, 3H, CH(C*H$_3$*)$_2$)

^{13}C NMR (151 MHz, $CDCl_3$) δ 186.9 ($C_{carbene}$), 164.9 (*C*Ru), 155.9 (C_{ar}N), 140.0 (C_{ar}O), 127.4 (*C5*H), 121.9 (*C1*H), 114.2 (*C2*H), 111.0 (*C3*H), 106.9 (*C4*H), 104.8 ($C_{ar}CH_3$(cym)), 98.9 (C_{ar}*i*-Pr(cym)), 92.6 (*C6*H), 89.6 (*C8*H), 87.9 (*C7*H), 84.4 (*C9*H), 55.6 (O*C*H$_3$), 37.9 (N*C*H$_3$), 31.1 (*C*H$(CH_3)_2$), 23.2 (CH(*C*H$_3$)$_2$), 21.9 (CH(*C*H$_3$)$_2$), 19.1 ($C_{ar}CH_3$(cym))

Anal. Calc. for $C_{21}H_{25}ClN_2ORu$ (M = 458.07 g/mol): C: 55.08, H: 5.50, N: 6.12, Found: C: 55.35, H: 5.75, N: 6.12%

Chloro[1-(4-bromophenyl-κC^2)-3-methylimidazol-2-ylidene-κC^2][η^6-1-methyl-4-(1-methylethyl)benzene] ruthenium(II) ***3***

5.48 g (15 mmol) of 1-(4-bromophenyl)-3-methylimidazolium iodide, 4.58 g (7.5 mmol) of $[RuCl_2(\eta^6\text{-}p\text{-cymene})]_2$ and 3.51 g (15 mmol) of Ag_2O were placed in a Schlenk tube and 300 ml of CH_2Cl_2 were added. The resulting deep red suspension was stirred at room temperature under exclusion of light for 60 h and the suspension was filtered through a cannula. The solvent was evaporated *in vacuo* and the remaining solids were dissolved in THF (approx. 150 ml) and filtered over basic Al_2O_3. After evaporation the crude product was then dissolved in 200 ml of THF/DCM 5:1 and again slowly filtered over basic Al_2O_3. The filtrate was evaporated to approx. 2/3 and the analytically pure product precipitated upon slow addition of pentane as yellow microcrystals. (5.9 g, 77.6 %; dec. > 205 °C).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.22 (d, *J* = 2.0 Hz, 1H, C5*H*), 7.28 (d, *J* = 2.0 Hz, 1H, C2*H*), 7.07 (dd, *J* = 8.1, 2.1 Hz, 1H, C4*H*), 6.98 (d, *J* = 2.0 Hz, 1H, C1*H*), 6.92 (d, *J* = 8.1 Hz, 1H, C3*H*), 5.58 (2x dd [overlain], 5.9, 1.3 Hz, 2H, 2x $C_{ar}H$(cym)), 5.50 (dd, *J* = 6.0, 1.3 Hz, 1H, $C_{ar}H$(cym)), 5.43 (dd, *J* = 5.9, 1.2 Hz, 1H, C_{ar}(cym)*H*), 4.14 (s, 3H, NCH_3), 2.17 (hept, *J* = 6.9 Hz, 1H, C*H*$(CH_3)_2$), 2.08 (s, 3H, $C_{ar}CH_3$(cym)), 0.88 (d, *J* = 6.9 Hz, 3H, CH$(CH_3)_2$), 0.75 (d, *J* = 6.9 Hz, 3H, $(CH_3)_2$CH)

^{13}C NMR (151 MHz, $CDCl_3$) δ 188.3 ($C_{carbene}$), 166.4 (*C*Ru), 144.8 (C_{ar}N), 143.2 (*C5*H), 125.1 (*C4*H), 122.4 (*C1*H), 117.7 (C_{ar}Br), 114.5 (*C2*H), 112.4 (*C3*H), 105.8 ($C_{ar}CH_3$(cym)), 99.3 (C_{ar}*i*-Pr(cym)), 92.7 (C_{ar}H(cym)), 90.0 (C_{ar}H(cym)), 88.2 (C_{ar}H(cym)), 84.8 (C_{ar}H(cym)), 38.0 (NCH_3), 31.2(*C*H$(CH_3)_2$), 23.2 (CH(*C*$H_3)_2$), 22.0 (CH(*C*$H_3)_2$), 19.1 ($C_{ar}CH_3$(cym))

Anal. Calc. for $C_{20}H_{22}BrClN_2Ru$ (M = 505.97 g/mol): C: 47.40, H: 4.38, N: 5.53, Found: C: 47.50, H: 4.36, N: 5.54 %

Chloro[1-methyl-3-(4-nitrophenyl-κC^2)imidazol-2-ylidene-κC^2][η^6-1-methyl-4-(1-methylethyl)benzene] ruthenium(II) ***4***

530 mg (1.6 mmol) of 1-methyl-3-(4-nitrophenyl)imidazolium iodide, 490 mg (0.8 mmol) of $[RuCl_2(\eta^6\text{-}p\text{-cymene})]_2$ and 375 mg (1.6 mmol) of Ag_2O were placed in a Schlenk tube and 25 ml of CH_2Cl_2 were added. The resulting deep red suspension was stirred at room temperature under exclusion of light for 24 h and the suspension was filtered through a cannula. The solvent was evaporated *in vacuo* and the remaining solids were dissolved in THF/DCM 5:1 (approx. 20 ml) and filtered over basic Al_2O_3. After evaporation the crude product was then dissolved in 20 ml of DCM and again slowly filtered over basic Al_2O_3. The filtrate was evaporated to approx. 1/4 and the analytically pure product precipitated upon slow addition of diethyl ether as orange microcrystals. (420 mg, 55.5 %; dec. > 220 °C).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.98 (d, *J* = 2.4 Hz, 1H, C5*H*), 7.89 (dd, *J* = 8.5, 2.4 Hz, 1H, C4*H*), 7.37 (d, *J* = 2.1 Hz, 1H, C2*H*), 7.12 (d, *J* = 8.5 Hz, 1H, C3*H*), 7.03 (d, *J* = 2.1 Hz, 1H, C1*H*), 5.68 (dd, *J* = 6.0, 1.2 Hz, 1H, $C_{ar}H$(cym)), 5.65 (dd, *J* = 5.8, 1.3 Hz, 1H, $C_{ar}H$(cym)), 5.61 (dd, *J* = 6.1, 1.3 Hz, 1H, $C_{ar}H$(cym)), 5.47 (dd, *J* = 6.0, 1.2 Hz, 1H, $C_{ar}H$(cym)), 4.17 (s, 3H, NCH_3), 2.18 (m, 1H, $CH(CH_3)_2$), 2.11 (s, 3H, $C_{ar}CH_3$(cym)), 0.89 (d, *J* = 6.9 Hz, 3H, $CH(CH_3)_2$), 0.74 (d, *J* = 6.9 Hz, 3H, $CH(CH_3)_2$).

^{13}C NMR (126 MHz, $CDCl_3$) δ 190.6 ($C_{carbene}$), 165.3 (*C*Ru), 151.2 ($C_{ar}N$), 144.0 ($C_{ar}NO_2$), 136.0 (*C5*H), 123.3 (*C1*H), 119.6 (*C4*H), 114.9 (*C2*H), 110.6 (*C3*H), 106.5 ($C_{ar}CH_3$(cym)), 100.2 (C_{ar}(*i*-Pr)(cym)), 93.3 (C_{ar}H(cym)), 90.6 (C_{ar}H(cym)), 88.9 (C_{ar}H(cym)), 85.1 (C_{ar}H(cym)), 38.2 (NCH_3), 31.3 ($CH(CH_3)_2$), 23.2 ($CH(CH_3)_2$), 21.9 ($CH(CH_3)_2$), 19.2 ($C_{ar}CH_3$(cym)).

Anal. Calc. for $C_{20}H_{22}ClN_3O_2Ru$ (M = 473.04 g/mol): C: 50.79, H: 4.69, N: 8.88, Found: C: 50.45, H: 4.54, N: 8.79 %

μ-Chloro-bis{[1-(4-methoxyphenyl-κC^2)-3-methylimidazol-2-ylidene-κC^2][η^6-1-methyl-4-(1-methylethyl)benzene] ruthenium(II)}(1+) tetrakis[3,5-bis(trifluoromethyl)phenyl]borate ***5***

114 mg (0.25 mmol) of complex **2** and 122 mg (0.14 mmol) of sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate were placed in a Schlenk tube and 10 ml of CH_2Cl_2 were added. The resulting yellow to orange solution was stirred at room temperature for 5 h and the solvent was removed *in vacuo*. The solids were dissolved in little amounts of diethyl ether and filtered over Celite and afterwards over basic Al_2O_3. The filtrate was evaporated to dryness and thoroughly dried to give the analytically pure product as an orange solid. (190 mg, 85 %, dec. >133 °C).

^{1}H NMR (500 MHz, C_6D_6) δ 8.55 (s, 4H, C_{ar}(BArF)*H*), 8.19 (d, *J* = 2.7 Hz, 1H, C5*H*), 7.80 (s, 2H, C_{ar}(BArF)*H*), 6.82 (d, *J* = 8.4 Hz, 1H, C3*H*), 6.70 (d, *J* = 2.0 Hz, 1H, C_{im}*H*), 6.67 (dd, *J* = 8.4, 2.6 Hz, 1H, C4*H*), 6.23 (d, *J* = 2.0 Hz, 1H, C_{im}*H*), 5.46 (dd, *J* = 6.0, 1.3 Hz, 1H, C_{ar}*H*(cym)), 5.22 (d, *J* = 5.8 Hz, 1H, C_{ar}*H*(cym)), 3.86 (s + d [overlain], 4H, C_{ar}*H*(cym) + OC*H*$_3$), 3.60 (dd, *J* = 6.1, 1.3 Hz, 1H, C_{ar}*H*(cym)), 3.27 (s, 3H, NC*H*$_3$), 1.58 (hept, *J* = 6.9 Hz, 1H, C*H*(CH_3)$_2$), 1.04 (s, 3H, C_{ar}C*H*$_3$(cym)), 0.66 (d, *J* = 7.0 Hz, 3H, CH(C*H*$_3$)$_2$), 0.37 (d, *J* = 6.9 Hz, 3H, CH(C*H*$_3$)$_2$).

^{13}C NMR (126 MHz, C_6D_6) δ 184.1 (*C*$_{carbene}$), 167.3 (*C*Ru), 156.7 (*C*$_{ar}$O), 140.7 (*C*$_{ar}$N), 135.5 (*C*$_{ar}$(BArF)H), 130.4 (*C*$_{ar}$H), 130.1 ([partially obscured by solvent signal] m, *C*$_{ar}$(BArF)(CF_3)), 125.3 (q, *J* = 271 Hz, C_{ar}(BArF)(*C*F_3)), 122.8 (*C*$_{ar}$H), 118.1 (*C*$_{ar}$(BArF)H), 113.5 (*C*$_{ar}$H), 110.7 (*C*$_{ar}$H), 106.4 (*C*$_{ar}$H), 104.9 (weak, *C*$_{ar,ipso}$(cym)), 94.7 (weak, *C*$_{ar}$H(cym)), 93.9 (weak, *C*$_{ar}$H(cym)), 85.2 (weak, *C*$_{ar}$H(cym)), 79.8 (weak, *C*$_{ar}$H(cym)), 55.5 (OCH_3), 36.8 (NCH_3), 30.4 (*C*H(CH_3)$_2$), 22.2 (CH(*C*H_3)$_2$), 20.8 (CH(*C*H_3)$_2$), 17.5 (C_{ar}CH_3(cym)); [second *C*$_{ar,ipso}$(cym) and *C*$_{ar}$(BArF)B not detectable].

Anal. Calc. for $C_{74}H_{62}BClF_{24}N_4O_2Ru_2$ (M = 1744.24 g/mol): C: 50.97, H: 3.58, N: 3.24, Found: C: 51.35, H: 3.63, N: 3.19 %

μ-Chloro-bis{[1-(4-bromophenyl-κC^2)-3-methylimidazol-2-ylidene-κC^2][η^6-1-methyl-4-(1-methylethyl)benzene] ruthenium(II)}(1+) tetrakis[3,5-bis(trifluoromethyl)phenyl]borate ***6***

101 mg (0.2 mmol) of complex **3** and 98 mg (0.11 mmol) of sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate were placed in a Schlenk tube and 10 ml of CH_2Cl_2 were added. The resulting yellow to orange solution was stirred at room temperature for 3 h and the solvent was removed *in vacuo*. The solids were dissolved in small amounts of diethyl ether (approx. 5 ml) and filtered over Celite and afterwards over basic Al_2O_3. An excess of pentane was slowly added to the filtrate and the solution was left to stand in a refrigerator for 3 days, where the analytically pure product slowly crystallized as orange crystals. (80 mg, 44 %, slow dec. > 145 °C).

^{1}H NMR (600 MHz, C_6D_6) δ 8.59 (d, *J* = 2.1 Hz, 1H, C5*H*), 8.43 (s, 4H, C_{ar}(BArF)*H*), 7.68 (s, 2H, C_{ar}(BArF)*H*), 7.21 (dd, *J* = 8.2, 2.1 Hz, 1H, C4*H*), 6.45 (d, *J* = 2.1 Hz, 1H, C2*H*), 6.39 (d, *J* = 8.2 Hz, 1H, C3*H*), 6.08 (d, *J* = 2.1 Hz, 1H, C1*H*), 5.37 (dd, *J* = 6.2, 1.3 Hz, 1H, C_{ar}*H*(cym)), 5.12 (dd, *J* = 6.0, 1.3 Hz, 1H, C_{ar}*H*(cym)), 3.72 (dd, *J* = 5.9, 1.3 Hz, 1H, C_{ar}*H*(cym)), 3.45 (dd, *J* = 6.1, 1.3 Hz, 1H, C_{ar}*H*(cym)), 3.13 (s, 3H, NC*H*$_3$), 1.30 (hept, *J* = 6.9 Hz, 1H, C*H*(CH_3)$_2$), 0.81 (s, 3H, C_{ar}C*H*$_3$(cym)), 0.48 (d, *J* = 6.9 Hz, 3H, CH(C*H*$_3$)$_2$), 0.21 (d, *J* = 6.9 Hz, 3H, CH(C*H*$_3$)$_2$).

^{13}C NMR (151 MHz, C_6D_6) δ 185.3 ($C_{carbene}$), 169.0 (*C*Ru), 162.8 (weak, m, C_{ar}(BArF)B), 145.6 (C_{ar}N), 144.9 (*C5*H), 135.5 (C_{ar}(BArF)H), 128.9 (weak, m, C_{ar}(BArF)(CF_3)), 126.2 (*C4*H), 124.4 (q, *J* = 272 Hz, C_{ar}(BArF)(*C*F$_3$)), 123.3 (*C1*H), 118.2 (*C*$_{ar}$(BArF)H), 117.8 (C_{ar}Br), 113.8 (*C2*H), 112.2 (*C3*H), 102.5$^{\#}$ (C_{ar}*i*-Pr(cym)), 100.8$^{\#}$ (C_{ar}CH$_3$(cym)), 94.6* (C_{ar}H(cym)), 94.0* (C_{ar}H(cym)), 85.2* (C_{ar}H(cym)), 80.3* (C_{ar}H(cym)), 36.8 (N*C*H$_3$), 30.5 (*C*H(CH_3)$_2$), 21.9 (CH(*C*H$_3$)$_2$), 20.9 (CH(*C*H$_3$)$_2$), 17.4 (C_{ar}*C*H$_3$(cym)) *only visible in HSQC spectrum; $^{\#}$only visible in HMBC spectrum.

Anal. Calc. for $C_{72}H_{56}BBr_2ClF_{24}N_4Ru_2$ (M = 1840.04 g/mol): C: 46.96, H: 3.07, N: 3.04, Found: C: 46.79, H: 2.84, N: 3.00 %

μ-Chloro-bis{[1-(4-nitrophenyl-κC^2)-3-methylimidazol-2-ylidene-κC^2][η^6-1-methyl-4-(1-methylethyl)benzene] ruthenium(II)}(1+) tetrakis[3,5-bis(trifluoromethyl)phenyl]borate **7**

236 mg (0.5 mmol) of complex **4** and 244 mg (0.275 mmol) of sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate were placed in a Schlenk tube and 20 ml of CH_2Cl_2 were added. The resulting orange solution was stirred at room temperature for 4.5 h and the solvent was removed *in vacuo*. The solid material was dissolved in small amounts of diethyl ether and filtered over Celite and afterwards over basic Al_2O_3. Evaporation of the volatiles and drying in vacuo gave the product as an orange powder. (95 mg, 21 %, mp 85-98 °C; slow dec. > 170 °C). [Letters A and B indicating the different NMR shifts of the two metal centers]

^{1}H NMR (600 MHz, CD_3CN) δ 8.89 (d, *J* = 2.5 Hz, 1H, C5*H* [B]), 8.84 (d, *J* = 2.4 Hz, 1H, C5*H* [A]), 7.98 (dd, *J* = 8.5, 2.4 Hz, 1H, C4*H* [A]), 7.85 (dd, *J* = 8.5, 2.5 Hz, 1H, C4*H* [B]), 7.72 (d, *J* = 2.2 Hz, 1H, C2*H* [A]), 7.71–7.68 (m, 8H, C_{ar}(BArF)*H*), 7.67 (s, 4H, C_{ar}(BArF)*H*), 7.61 (d, *J* = 2.1 Hz, 1H, C2*H* [B]), 7.42 (d, *J* = 8.6 Hz, 1H, C3*H* [A]), 7.33 (d, *J* = 2.1 Hz, 1H, C1*H* [A]), 7.31 (d, *J* = 8.5 Hz, 1H, C3*H* [B]), 7.25 (d, *J* = 2.1 Hz, 1H, C1*H* [B]), 6.09–6.07 (m, 2H, C_{ar}(cym)*H* [B,A]), 5.94 (dd, *J* = 6.2, 1.4 Hz, 1H, C_{ar}(cym)*H* [A]), 5.90 (dd, *J* = 6.1, 1.4 Hz, 1H, C_{ar}(cym)*H* [B]), 5.77 (dd, *J* = 6.1, 1.3 Hz, 1H, C_{ar}(cym)*H* [B]), 5.75 (dd, *J* = 6.0, 1.4 Hz, 1H, C_{ar}(cym)*H* [A]), 5.63 (2x dd [overlain], *J* = 6.0, 1.3 Hz, 2H, C_{ar}(cym)*H* [B,A]), 4.11 (s, 3H, NC*H*$_3$ [A]), 4.09 (s, 3H, NC*H*$_3$ [B]), 2.20–2.15 (m, 1H, C*H*$(CH_3)_2$ [B]), 2.13–2.07 (m, 1H, C*H*$(CH_3)_2$ [A]), 2.04 (s, 3H, C_{ar}(cym)C*H*$_3$ [B]), 2.02 (s, 3H, C_{ar}(cym)C*H*$_3$ [A]), 0.86 (d, *J* = 6.9 Hz, 3H, CH(C*H*$_3$)$_2$ [B]), 0.82 (d, *J* = 6.9 Hz, 3H, CH(C*H*$_3$)$_2$ [A]), 0.74 (d, *J* = 6.9 Hz, 3H, CH(C*H*$_3$)$_2$ [B]), 0.68 (d, *J* = 6.9 Hz, 3H, CH(C*H*$_3$)$_2$ [A]).

^{13}C NMR (151 MHz, CD_3CN) δ 191.4 ($C_{carbene}$ [B]), 185.0 ($C_{carbene}$ [A]), 167.6 (*C*Ru [B]), 162.6 (q, *J* = 45 Hz, C_{ar}(BArF)B), 160.4 (*C*Ru [A]), 152.7 (C_{ar}N [B]), 152.6 (C_{ar}N [A]), 145.0$^{\#}$ ($C_{ar}NO_2$ [A]), 144.4$^{\#}$ ($C_{ar}NO_2$ [B]), 136.7 (*C5*H [A]), 136.5 (*C5*H [B]), 135.6

(C_{ar}(BArF)H), 129.8 (m, C_{ar}(BArF)(CF_3)), 125.8 (*C1*H [A]), 125.4 (q, *J* = 272 Hz, C_{ar}(BArF)(*C*F_3)), 124.9 (*C1*H [B]), 121.3 (*C4*H [A]), 119.7 (*C4*H [B]), 118.3 *(*C_{ar}(BArF)H), 116.9 (*C2*H [A]), 115.8 (*C2*H [B]), 112.3 (*C3*H [A]), 111.4 (*C3*H [B]), 108.0 (C_{ar}(cym)CH_3 [B]), 107.8 (C_{ar}(cym)CH_3 [A]), 105.3[#] (C_{ar}(cym)*i*-Pr [B]), 100.3 (C_{ar}(cym)*i*-Pr [A]), 97.2 (C_{ar}(cym)H [B]), 94.6 (C_{ar}(cym)H [B]), 93.6 (C_{ar}(cym)H [A]), 91.3 (C_{ar}(cym)H [A]), 90.8 (C_{ar}(cym)H [A]), 90.0 (C_{ar}(cym)H [B]), 89.4 (C_{ar}(cym)H [B]), 86.0 (C_{ar}(cym)H [A]), 38.8 (N*C*H_3 [A]), 38.5 (N*C*H_3 [B]), 31.9 (2x *C*H(CH_3)$_2$ [A,B]), 23.1 (CH(*C*H_3)$_2$ [A]), 22.9 (CH(*C*H_3)$_2$ [B]), 22.0 (CH(*C*H_3)$_2$ [B]), 21.9 (CH(*C*H_3)$_2$ [A]), 19.1 (C_{ar}(cym)*C*H_3 [B]), 19.0 (C_{ar}(cym)*C*H_3 [A]) [#]only visible in HMBC spectrum

Anal. Calc. for $C_{72}H_{56}BClF_{24}N_6O_4Ru_2$ (M = 1774.18 g/mol): C: 48.76, H: 3.18, N: 4.74, Found: C: 49.02, H: 3.30, N: 4.68 %

Table S1. Crystallographic details for complex **1**.

Chemical formula	$C_{20}H_{23}ClN_2Ru$
M_r	427.92
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Temperature (K)	198
a, b, c (Å)	10.982 (2), 12.1790 (14), 13.450 (3)
V (Å^3)	1798.9 (6)
Z	4
F(000)	872
D_x (Mg m^{-3})	1.580
Radiation type	Mo $K\alpha$
μ (mm^{-1})	1.02
Crystal size (mm)	0.51 × 0.30 × 0.28
Absorption correction	Multi-scan *SADABS* 2.10
T_{min}, T_{max}	0.624, 0.763
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	40661, 3699, 3412
R_{int}	0.047
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.626
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.023, 0.066, 1.26
No. of reflections	3699
No. of parameters	222
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.57, −0.65

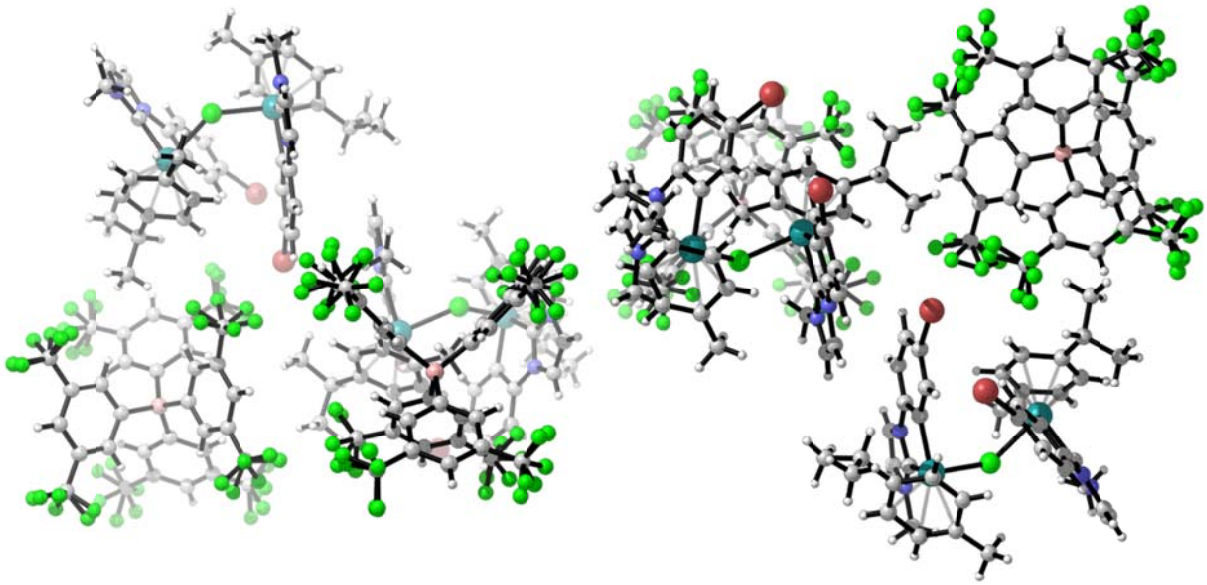
Table S2. Crystallographic details for complex **2**.

Chemical formula	$C_{21}H_{25}ClN_2ORu$
M_r	457.95
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	198
a, b, c (Å)	17.260 (3), 7.8530 (9), 14.921 (3)
β (°)	106.611 (14)
V (Å^3)	1938.0 (6)
Z	4
F(000)	936
D_x (Mg m^{-3})	1.570
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.96
Crystal size (mm)	0.46 × 0.16 × 0.15
Absorption correction	Multi-scan *SADABS* 2.10
T_{min}, T_{max}	0.667, 0.871
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	44467, 3972, 3104
R_{int}	0.065
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.626
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.027, 0.066, 1.12
No. of reflections	3972
No. of parameters	240
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.44, −0.60

Table S3. Crystallographic details for complex **6**.

Chemical formula	$C_{72}H_{56}BBr_2ClN_4F_{24}Ru_2$
M_r	1841.42
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	295
a, b, c (Å)	13.8063 (3), 13.2266 (3), 41.5510 (11)
β (°)	97.253 (1)
V (Å^3)	7526.9 (3)
Z	4
F(000)	3648
D_x (Mg m^{-3})	1.625
Radiation type	Mo $K\alpha$
μ (mm $^{-1}$)	1.60
Crystal size (mm)	0.46 × 0.39 × 0.17
Diffractometer	Rigaku Saturn724+ CCD (2x2 bin mode) diffractometer
Absorption correction	Multi-scan
T_{min}, T_{max}	0.587, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	138680, 16437, 14732
R_{int}	0.034
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.639
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.052, 0.143, 1.11
No. of reflections	16437
No. of parameters	1197
No. of restraints	384
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.18, −1.02

Figure S1: Crystal packing in structure **6**:



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