

Extending Ligand Field Molecular Mechanics to Modelling Organometallic π -Bonded Systems: Applications to Ruthenium-Arenes

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Table S1: Complexes used for KS-DFT calculations, symmetry of examined conformers and reference number.
 Ru = Ru(II); bz = benzene;

Compound	symmetry	ref. number
[RuH ₆] ⁴⁺	<i>O_h</i>	1
[RuCl ₆] ⁴⁺	<i>O_h</i>	2
[Ru(NH ₂) ₆] ⁴⁺	<i>S₆</i>	3
[Ru(NH ₃) ₆] ²⁺	<i>S₆</i>	4
[Ru(py) ₆] ²⁺	<i>D₃</i>	5
[Ru(H ₂ O) ₆] ²⁺	<i>S₆, T_h</i>	6
[Ru(en) ₃] ²⁺	<i>D₃</i>	7
Ru(bz) ₂ ²⁺	<i>D_{6h}, D_{6d}</i>	8
[RuH ₃ (bz)]	<i>C₃</i>	9
[RuCl ₃ (bz)]	<i>C_{3v}</i>	10
[Ru(NH ₂) ₃ (bz)] ⁻	<i>C₃</i>	11
[Ru(NH ₃) ₃ (bz)] ²⁺	<i>C₃</i>	12
[Ru(py) ₃ (bz)] ²⁺	<i>C₁, C₃</i>	13
[Ru(H ₂ O) ₃ (bz)] ²⁺	<i>C₃</i>	14
[RuH ₂ (NH ₃)(bz)]	<i>C_s</i>	15
[RuH ₂ (NH ₂)(bz)] ⁻	<i>C₁</i>	16
[RuH ₂ (H ₂ O)(bz)]	<i>C_s</i>	17
[RuH ₂ Cl(bz)] ⁻	<i>C_s</i>	18
[RuCl ₂ H(bz)] ⁻	<i>C_s</i>	19
[RuCl ₂ (NH ₂)(bz)] ⁻	<i>C_s</i>	20
[RuCl ₂ (NH ₃)(bz)]	<i>C_s</i>	21
[RuCl ₂ (H ₂ O)(bz)]	<i>C_s</i>	22
[Ru(NH ₂) ₂ H(bz)] ⁻	<i>C₁, C_s</i>	23
[Ru(NH ₂) ₂ (NH ₃)(bz)] ⁻	<i>C_s</i>	24
[Ru(NH ₂) ₂ (H ₂ O)(bz)]	<i>C₁</i>	25
[Ru(NH ₂) ₂ Cl(bz)] ⁻	<i>C₁</i>	26
[Ru(NH ₃) ₂ H(bz)] ⁺	<i>C_s</i>	27
[Ru(NH ₃) ₂ (NH ₂)(bz)] ⁺	<i>C_s</i>	28
[Ru(NH ₃) ₂ (H ₂ O)(bz)] ²⁺	<i>C₁</i>	29
[Ru(NH ₃) ₂ Cl(bz)] ⁺	<i>C₁</i>	30
[Ru(H ₂ O) ₂ H(bz)] ⁺	<i>C₁</i>	31
[Ru(H ₂ O) ₂ (NH ₂)(bz)] ⁺	<i>C₁</i>	32
[Ru(H ₂ O) ₂ (NH ₃)(bz)] ²⁺	<i>C₁</i>	33
[Ru(H ₂ O) ₂ Cl(bz)] ⁺	<i>C₁, C_s</i>	34

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Table S2: Charge Scheme 1 (CS1): Computed Hirshfeld charges from ADF calculations

Compound	Ru	H	Cl	N(NH2)	H(NH2)	N(NH3)	H(NH3)	N(py)	C(py)	H(py)	O(H2O)	H(H2O)	N(en)	HN(en)	C(en)	HC(en)	C(bz)	H(bz)	bz	Total	
[RuH ₆] ²⁺	-1.084	-0.486																			-4
[RuCl ₆] ⁴⁺	-0.082		-0.653																		-4
[Ru(NH ₂) ₆] ⁴⁺	-0.112			-0.546	-0.051																-4
[Ru(NH ₃) ₆] ²⁺	0.194					-0.152	0.151														2
[Ru(py) ₆] ²⁺	0.254							-0.069	0.007	0.065											2
[Ru(H ₂ O) ₆] ²⁺	0.308										-0.15	0.216									2
[Ru(en) ₃] ²⁺	0.188												-0.11	0.137	-0.002	0.07					2
Ru(bz) ₂ ²⁺	0.392																0.024	0.11	0.804		2
[RuH ₃ (bz)]	0.044	-0.186															-0.101	0.02	-0.486		-1
[RuCl ₃ (bz)]	0.293		-0.385														-0.067	0.044	-0.138		-1
[Ru(NH ₂) ₃ (bz)]	0.338			-0.424	0.025												-0.094	0.058	-0.216		-1
[Ru(NH ₃) ₃ (bz)] ²⁺	0.377					-0.131	0.162										-0.003	0.096	0.558		2
[Ru(py) ₃ (bz)] ²⁺	0.347							-0.063	0.018	0.074							-0.01	0.087	0.462		2
[Ru(H ₂ O) ₃ (bz)] ²⁺	0.44										-0.148	0.218					0.011	0.105	0.696		2
[RuH ₂ (NH ₃)(bz)]	0.163	-0.138				-0.157	0.13										-0.067	0.047	-0.12		0
[RuH ₂ (NH ₂)(bz)]	0.168	-0.167		-0.402	0.018												-0.099	0.021	-0.468		-1
[RuH ₂ (H ₂ O)(bz)]	0.184	-0.139									-0.182	0.168					-0.061	0.051	-0.06		0
[RuH ₂ Cl(bz)]	0.14	-0.146	-0.464														-0.091	0.027	-0.384		-1
[RuCl ₂ H(bz)]	0.225	-0.123	-0.419														-0.08	0.036	-0.264		-1
[RuCl ₂ (NH ₂)(bz)]	0.314		-0.388	-0.376	0.024												-0.074	0.039	-0.21		-1
[RuCl ₂ (NH ₃)(bz)]	0.325		-0.294			-0.166	0.111										-0.046	0.062	0.096		0
[RuCl ₂ (H ₂ O)(bz)]	0.336		-0.266								-0.202	0.118					-0.04	0.067	0.162		0
[Ru(NH ₂) ₂ H(bz)]	0.267	-0.155		-0.387	0.022												-0.095	0.024	-0.426		-1
[Ru(NH ₂) ₂ (NH ₃)(bz)]	0.212			-0.175	0.055	-0.325	0.101										-0.062	0.052	-0.06		0
[Ru(NH ₂) ₂ (H ₂ O)(bz)]																					
[Ru(NH ₂) ₂ Cl(bz)]	0.344		-0.4	-0.375	0.025												-0.083	0.034	-0.294		-1
[Ru(NH ₃) ₂ H(bz)] ⁺	0.275	-0.101				-0.142	0.147										-0.034	0.072	0.228		1
[Ru(NH ₃) ₂ (NH ₂)(bz)] ⁺	0.35			-0.3	0.082	-0.144	0.137										-0.032	0.074	0.252		1
[Ru(NH ₃) ₂ (H ₂ O)(bz)] ²⁺	0.382					-0.128	0.164				-0.154	0.219					0.002	0.099	0.606		2
[Ru(NH ₃) ₂ Cl(bz)] ⁺	0.337		-0.207			-0.147	0.138										-0.024	0.08	0.336		1
[Ru(H ₂ O) ₂ H(bz)] ⁺	0.31	-0.102									-0.158	0.199					-0.026	0.078	0.312		1
[Ru(H ₂ O) ₂ (NH ₂)(bz)] ⁺																					
[Ru(H ₂ O) ₂ (NH ₃)(bz)] ²⁺	0.413					-0.127	0.164				-0.152	0.218					0.007	0.102	0.654		2
[Ru(H ₂ O) ₂ Cl(bz)] ⁺	0.378		-0.168								-0.165	0.175					-0.016	0.086	0.42		1

Table S3: Charge Scheme 2 (CS2): Averaged charges (not including homoleptic species)

Ru	H	Cl	N(NH2)	H(NH2)	N(NH3)	H(NH3)	N(py)	C(py)	H(py)	O(H2O)	H(H2O)	C(bz)	H(bz)	bz
0.287	-0.143	-0.336	-0.352	0.035	-0.163	0.139	-0.065	0.015	0.072	-0.166	0.188	-0.049	0.061	0.070

Table S4: AOM parameterisation details

CL-:

Since $[\text{RuCl}_6]^{4-}$ (**2**) is octahedral, independent values for e_σ and e_π cannot be determined. Therefore, as we have done previously, we performed a PES scan for D_{4h} $[\text{RuCl}_4]^{2-}$ (using the same internuclear distances and the same method as in the PES scan for **2**). From the usual AOM formalism for square planar complexes, the e_σ and e_π parameters for the tetrachlororuthenate can be obtained, as well as the e_{ds} mixing parameter. The ratio e_σ/e_π (≈ 4) in $[\text{RuCl}_4]^{2-}$ was then used to calculate the e_σ and e_π parameters of **2**. The e_{ds} parameter was used unmodified.

N:

For the AOM parameters of the atom type “N” we studied compound **4**. Although its lowest energy conformer is S_6 symmetric, the distortion of its Ru-N₆ nuclear frame from O_h symmetry is very small. From the rigid PES scan (keeping the S_6 symmetry and using the ADC procedure) the distance dependence of Δ_{oct} , and, because NH₃ is a σ -only donor, also the distance dependence of e_σ can be obtained. At each point the arithmetic mean of the orbitals 17–18 a_g, which form the e_g -like set and the 14–16 a_g orbitals, which form the t_{2g} -like set, were used in the e_σ calculation.

(exp. Δ_{oct} in $[\text{Ru}(\text{en})_3]^{2+}$ 25450 cm⁻¹)

Du:

In the AOM parameterisation of the benzene ligand all carbon centres were treated as one virtual atom positioned at the carbon atoms' centroid. In the rigid PES scan using the ADC procedure we used the eclipsed, D_{6h} symmetric conformation of **8**, which is the minimum on all hypersurfaces we examined. The e_σ and e_π parameters were calculated from the KS-MO energy differences using the AOM formalism for linear ML_2 systems without δ -bonding and we omitted the estimation of an e_{ds} parameter.

OH2:

For the AOM parameterisation of the “OH2” atom type we examined compound **6**. The lowest energy conformer of **6** is S_6 symmetric, but the deviation of its Ru-O₆ nuclear frame from O_h symmetry is too large so we proceeded to use a T_h symmetric conformation of **6** in the rigid PES scan and got from this the distance dependence of Δ , which only yields the distance dependence of the ratio $e_\sigma/e_{\pi\perp}$. The parameter $e_{\pi\perp}$ is the AOM parameter for the π -type interaction between the lone-pair on the water molecule's oxygen atom and the ruthenium's d-AOs. From a rigid PES scan (using the ADC approximation and the same internuclear distances as for the PES scan of the hexaquo complex) of a D_{2h} symmetric conformation of **6** we could fix e_σ and e_π and calculate e_σ and $e_{\pi\perp}$ in **6**'s T_h symmetric conformation.

HYDR:

To estimate the AOM parameters of the “HYDR” atom type we examined compound **1**. Its lowest energy conformer is O_h symmetric. Interestingly, all Ru d-AOs are used in the occupied bonding MOs. Nevertheless, we obtained the distance dependency of the e_σ parameter using the usual AOM formalism for octahedral complexes from the distance dependence of the energy difference of the d-AO dominated occupied MOs $1e_g^2$ and $1t_{2g}^6$ in a normal PES scan (no ADC procedure).

“NIDO” and “NM” atom type:

The AOM parameters of the “NIDO” atom type were obtained following a similar procedure as for the “OH2” atom type using a T_h symmetric conformer of compound **3**. (The lowest energy conformer of **3** is S_6 symmetric but similarly to **6**, the Ru-N nuclear frame deviates significantly from O_h symmetry.) Although the amide anion is isoelectronic with water and therefore also capable of forming a π -bond to Ru, which gives rise to an $e_{\pi\perp}$ parameter, in the LFMM parameter optimisation the latter turned out to be superfluous. Therefore only the e_σ parameter is part of the final parameter set.

Because of their chemical similarity, the LFMM parameter set for “NIDO” and “NM” atom types are the same. However, in order to be able to distinguish these donors in the non-LFMM region (which is parameterised by the MMFF94 FF) they are assigned different type names.

NPYR:

For the AOM parameterisation of the “NPYR” atom type we examined compound **5** whose lowest energy conformer is D_2 symmetric. We proceeded as already described for the “CL-” atom type; $[\text{RuCl}_4]^{2-}$ has to be substituted by $[\text{Ru}(\text{py})_4]^{2+}$. Because of the steric demands of the pyridine ligands a completely square planar complex is not accomplishable. Instead, we used a D_{4h} symmetric conformation of $[\text{Ru}(\text{py})_4]^{2+}$ in which the pyridine ring normals lie in the Ru-N plane.

Interestingly also in the optimization of the molecular mechanics LFMM parameter of the “NPYR” atom type the $e_{\pi\perp}$ parameter turned out to be a source of difficulty in that the sign of $e_{\pi\perp}$ changes during the PES scan. This, combined with its relatively small value led us to discarded π bonding. Therefore only the e_{σ} and the e_{ds} parameter are part of the final parameter set.

Table S5: LFMM parameter values

```
# Latest version of LFMM parameter file for Ru(II)-arene complexes
[Morse]
# DFT-optimised
#Ru+2 CL- 2.44986 49.9539 1.52463
#Ru+2 Du 1.96747 125.113 1.26661
Ru+2 HYDR 1.77451 100 0.92886
#Ru+2 N 2.34732 80.036 1.14342
Ru+2 NIDO 2.12741 150.036 1.31545
Ru+2 NM 2.12741 150.036 1.31545
Ru+2 NPYD 2.27033 150 1.09853
#Ru+2 OH2 2.35756 170 0.697935
# Structure refined
Ru+2 Du 1.9300 125.113 1.26661
Ru+2 N 2.3000 80.036 1.14342
Ru+2 OH2 2.23 170.0 0.8
Ru+2 CL- 2.50 49.9539 1.52463
%
[ll]
Ru+2 CL- 7310.55 6
Ru+2 Du 0 6
Ru+2 HYDR 250 6
Ru+2 N 1606.99 6
Ru+2 NIDO 661.009 6
Ru+2 NM 661.009 6
Ru+2 N5B 100 6
Ru+2 OH2 775.289 6
%
[esig]
Ru+2 CL- 0 0 0 0 0 1.52292e+006 -2.2473e+006
Ru+2 Du 891 0 0 13032 0 0 0
Ru+2 HYDR 0 0 29276 0 0 0 0
Ru+2 N 0 0 0 0 91921 267451 0
Ru+2 NIDO 0 0 0 -1.81012e+006 1.08361e+007 -2.03018e+007 1.23141e+007
Ru+2 NM 0 0 0 -1.81012e+006 1.08361e+007 -2.03018e+007 1.23141e+007
Ru+2 N5B 0 0 -179272 843858 -671272 0 0
Ru+2 OH2 0 0 0 -209022 918562 -677107 0
%
[epix]
Ru+2 CL- 0 1354.96 -500805 2.82704e+006 -5.32132e+006 3.25777e+006 0
Ru+2 Du -5123 0 72332 0 0 0 0
Ru+2 HYDR 0 0 0 0 0 0 0
Ru+2 N 0 0 0 0 0 0 0
Ru+2 NIDO 0 0 0 0 0 0 0
Ru+2 NM 0 0 0 0 0 0 0
Ru+2 NPYD 0 0 0 0 0 0 0
Ru+2 OH2 0 0 0 0 0 0 0
%
[epiy]
Ru+2 CL- 0 1354.96 -500805 2.82704e+006 -5.32132e+006 3.25777e+006 0
Ru+2 Du -5123 0 72332 0 0 0 0
Ru+2 HYDR 0 0 0 0 0 0 0
Ru+2 N 0 0 0 0 0 0 0
Ru+2 NIDO 0 0 0 0 0 0 0
Ru+2 NM 0 0 0 0 0 0 0
```

```
Ru+2 NPYD -7038.09 0 121185 -156909 0 0 0
Ru+2 OH2 0 0 0 554544 -3.61027e+006 7.96321e+006 -5.74335e+006
%
[exds]
Ru+2 CL- 0 0 0 0 0 0 406901
Ru+2 Du 0 0 0 0 0 0 0
Ru+2 N 0 0 0 0 0 0 300000
Ru+2 NIDO 0 0 0 0 0 0 300000
Ru+2 NM 0 0 0 0 0 0 300000
Ru+2 HYDR 0 0 0 0 0 0 0
Ru+2 NPYD 0 0 0 -52433.5 222321 -166430 0
#Ru+2 OH2 0 0 0 0 0 0 300000
Ru+2 OH2 0 0 0 0 0 0 0
%
```

Table S6: Full comparison of bond length difference (obs-calc, Å), M-L rms values and heavy-atom overlay rmsds for each half-sandwich complex.

Refcode	Du	N	N	NM	NM	NIDO	NIDO	NPYD	OH2	CL-	HYDR	M-L(rms)	Heavy Atom rmsd
CAFPOP	-0.01	0.00	-0.02							-0.01		0.013	0.32
CAFQAC	-0.01	0.00	0.01							0.02		0.011	1.05
CEKDIG	-0.01	-0.02	-0.02							0.02		0.017	0.14
CEKDOM	-0.01	0.02	-0.01							0.02		0.014	0.17
CEKFII	-0.02	-0.02	-0.03					0.02				0.021	0.18
CIJFEH	-0.01	-0.01	-0.03							0.00		0.016	1.24
CIJFIL	0.00	0.00	0.01							0.02		0.011	0.87
CIJFOR	0.00	-0.01	-0.01							0.02		0.014	2.07
DOMTAB	0.01	0.00		-0.06	-0.02							0.034	0.60
FEEGUT	-0.01	0.02		-0.03						-0.02		0.020	0.46
INUNAG	-0.01	0.02	0.04						-0.06			0.037	0.95
INUNEK	-0.01	0.02	0.02						0.02			0.018	0.17
INUNIO	-0.02	0.01	0.02						-0.05			0.027	0.40
INUNOU	0.00	0.02	0.03						-0.02			0.019	0.15
IPAKOZ	-0.01	0.01	-0.01							0.02		0.015	0.21
IPAKUF	-0.01	0.01	-0.01							0.04		0.022	0.37
IVEMOL	-0.02	-0.03	0.02							0.03		0.024	0.14
IVEMUR	0.00	-0.02	0.02							0.03		0.020	0.12
IVENAY	-0.01	0.01	0.01							0.02		0.013	0.22
IVENEC	-0.01	0.01	0.01							0.02		0.013	0.22
IVENIG	0.00	-0.02	-0.03							0.00		0.017	0.33
KEYJUT	0.04	0.07				0.04				0.09		0.065	1.03
LARYEI	-0.01	-0.05	-0.02							0.05		0.039	0.76
LAZZIW	-0.02	0.01	0.03						-0.08			0.045	0.44
LAZZOC	-0.01	0.00	-0.02							0.03		0.017	0.12
MIDMOC	0.00	0.02	0.01							0.00		0.009	0.06
MIDMUI	-0.01	0.00	-0.01							0.02		0.010	0.24
MIDNET	-0.01	-0.01	-0.01							0.02		0.014	0.11
MIMRUV	-0.02	-0.01	-0.01							0.03		0.017	0.46

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MIMSAC	0.00	-0.01	-0.01						0.02		0.015	0.74
MISPEK	-0.01	-0.02	-0.03					0.02			0.021	0.13
OKAMIW	-0.04	-0.02		-0.05					0.00		0.031	1.20
OKAMOC	-0.01	0.01		-0.02					0.02		0.015	0.78
PEWCID	-0.02	-0.01				0.02			0.02		0.016	0.15
QASJAW	-0.01	0.00	0.01						0.02		0.013	1.13
RIHFOD	-0.04			0.02		0.18					0.109	0.51
RIHFUJ	-0.03	0.02		-0.03						0.18	0.093	0.58
SECKOB	-0.04	0.00				0.05			-0.02		0.031	0.66
TANROQ	-0.01	-0.01		-0.04					0.00		0.023	0.59
TAXFON10	-0.01	0.01		-0.04					0.00		0.020	0.33
TOBTOT	-0.01	-0.01				0.05			-0.01		0.027	0.51
TOBVAH	-0.01	-0.03				0.00	0.04				0.027	0.44
TOBVEL	-0.02	0.02				-0.02			-0.06		0.035	1.14
WOCMUW	0.00	0.03	-0.06						0.01		0.031	0.48
XEBTUU	-0.01	0.00	-0.01						0.03		0.017	0.41
ZALWIS	0.00	0.02		-0.03					-0.03		0.024	0.67
ZUKGER	-0.04	0.02		0.01					0.01		0.023	0.33