New Insights into $Re_3(\mu\text{-}Cl)_3Cl_6$ Aromaticity. Evidence of σ- and π-Diatropicity

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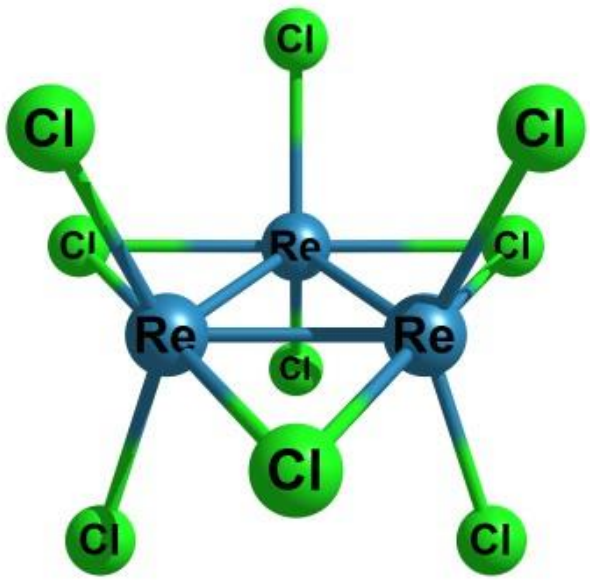

Re	0.694185055	1.202364091	0.000000000
Re	0.694185055	-1.202364091	0.000000000
Re	-1.388370105	0.000000000	0.000000000
Cl	2.808039214	0.000000000	0.000000000
Cl	-1.404019110	-2.431833185	0.000000000
Cl	-1.404019110	2.431833185	0.000000000
Cl	-2.244072170	0.000000000	2.091401158
Cl	-2.244072170	0.000000000	-2.091401158
Cl	1.122036085	1.943424148	2.091401158
Cl	1.122036085	1.943424148	-2.091401158
Cl	1.122036085	-1.943424148	2.091401158
Cl	1.122036085	-1.943424148	-2.091401158

Figure SI-1. Structure and Cartesian coordinates of the $Re_3(\mu\text{-}Cl)_3Cl_6$ cluster optimized at the PW91/TZVP level of theory. Spin-orbit relativistic corrections were incorporated via the Zeroth Order Regular Approximation using the ADF2012.01 package.

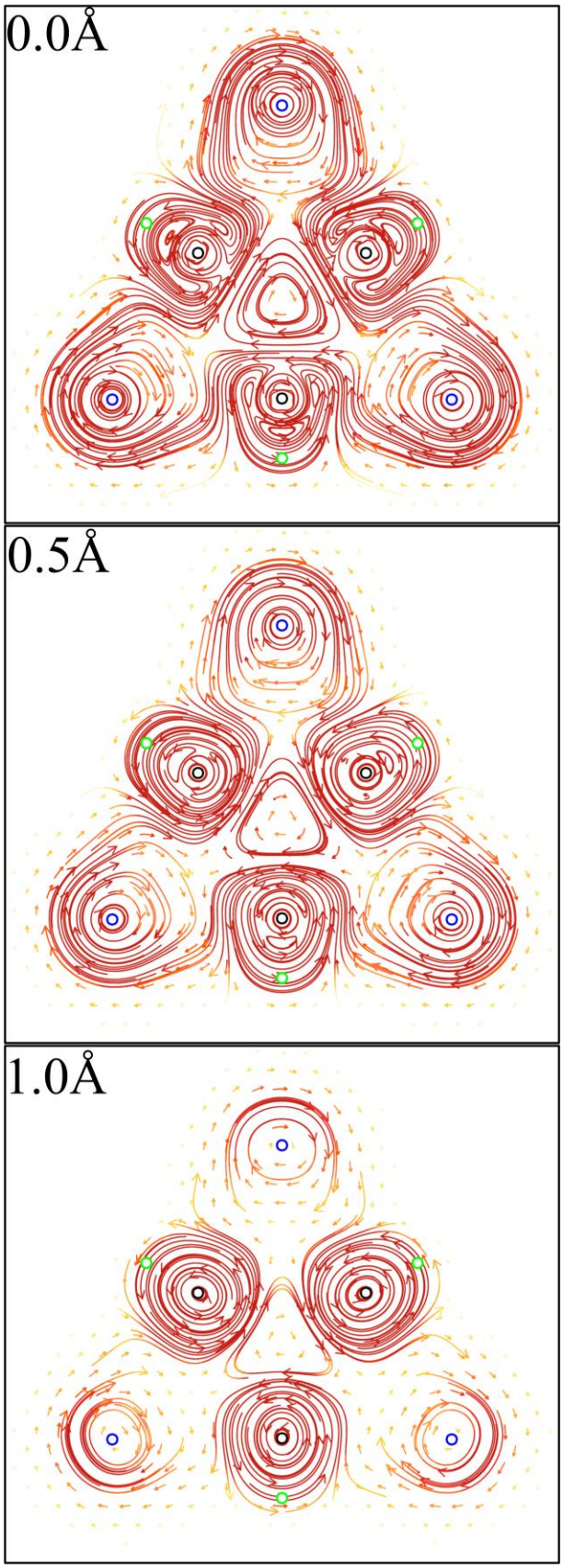

Figure SI-2. MICD plots for $Re_3(\mu\text{-}Cl)_3Cl_6$ at the molecular plane, at 0.5 Å and at 1.0 Å above the molecular plane. The intensity of the color of the vector arrow is proportional to the current strength. Clockwise vectors represent diatropic currents and the anticlockwise vectors paratropic currents

Table SI-1: NICS and B^{ind}_z values of $Re_3(\mu\text{-}Cl)_3Cl_6$ obtained with the ADF package (2-component spin-orbit relativistic corrections) and with Gaussian 09 program (using the effective core potential included in the Def2-TZVP basis set)

	ADF calculations (using TZ2P basis set)	Gaussian 09 calculations (using Def2-TZVP basis set)
	PW91/TZVP	PW91/Def2-TZVP
NICS(0)	-54.77	-51.46
NICS(1)	-27.24	-27.27
$B^{ind}_z(0)$	-121.13	-117.69
$B^{ind}_z(1)$	-40.68	-38.32

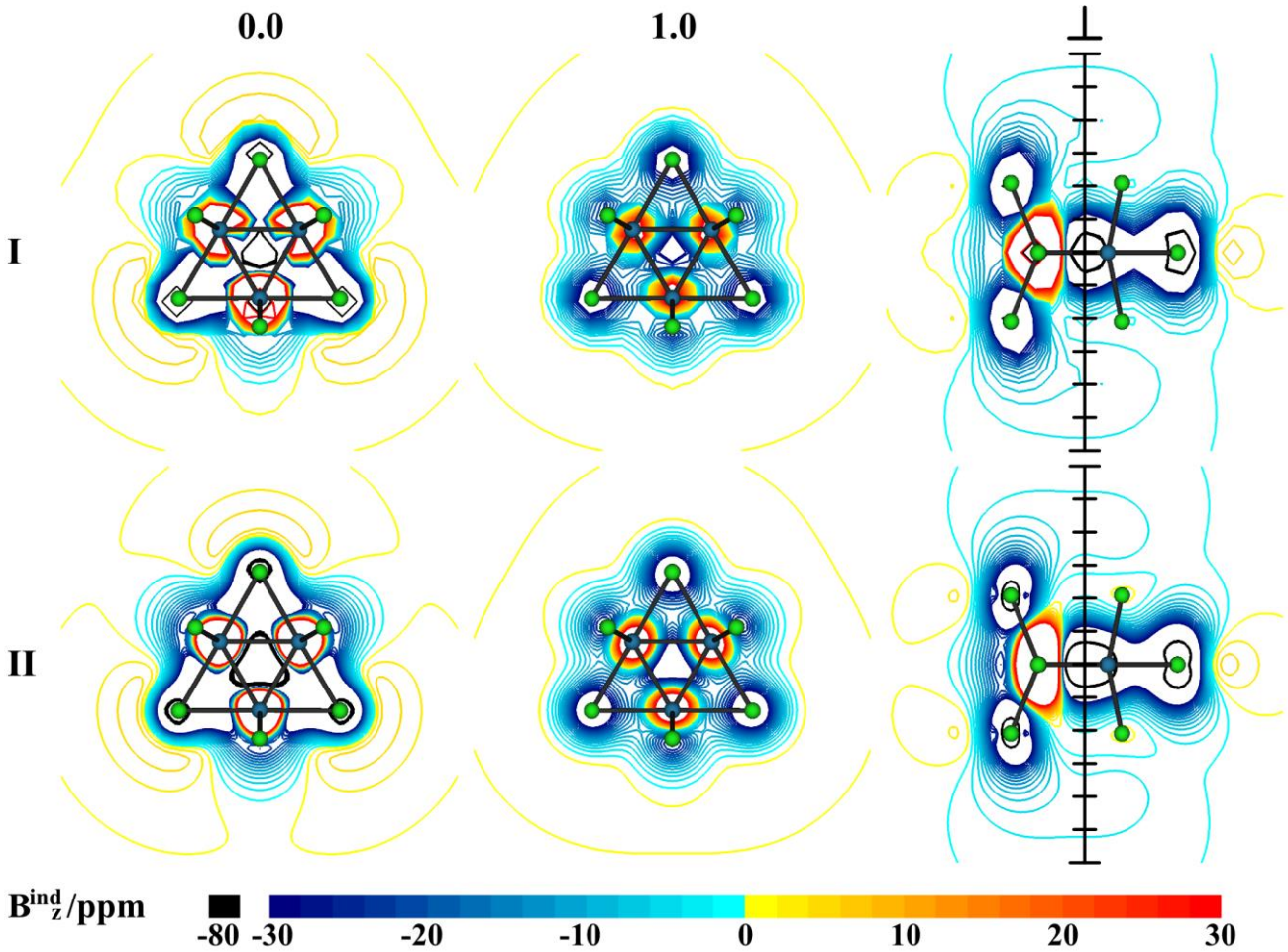

Figure SI-3. Plots of B^{ind}_z isolines for the $Re_3(\mu\text{-}Cl)_3Cl_6$ cluster, the I row shows B^{ind}_z isolines calculated with 2-component spin-orbit relativistic corrections using ADF package, II row shows B^{ind}_z isolines calculated using the effective core potential included in the Def2-TZVP basis set with the Gaussian 09 program.

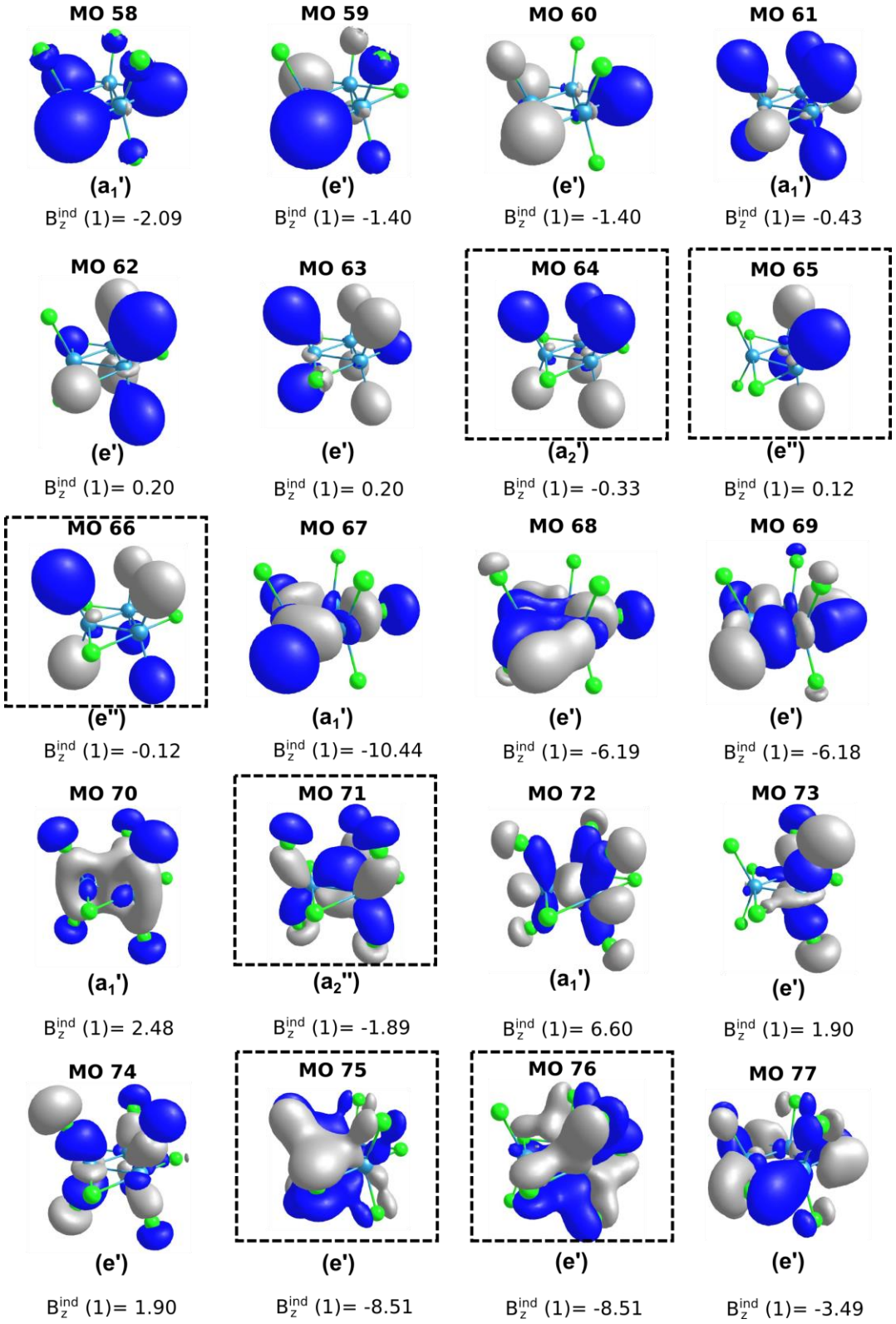

Figure SI-4. Occupied valence molecular orbitals, their symmetries and their contributions to B^{ind}_z (1). The π molecular orbitals are enclosed in dashed squares. Total σ and π valence molecular orbitals contributions to $B^{ind}_z(1)$ are -6.59 and -16.47 respectively.

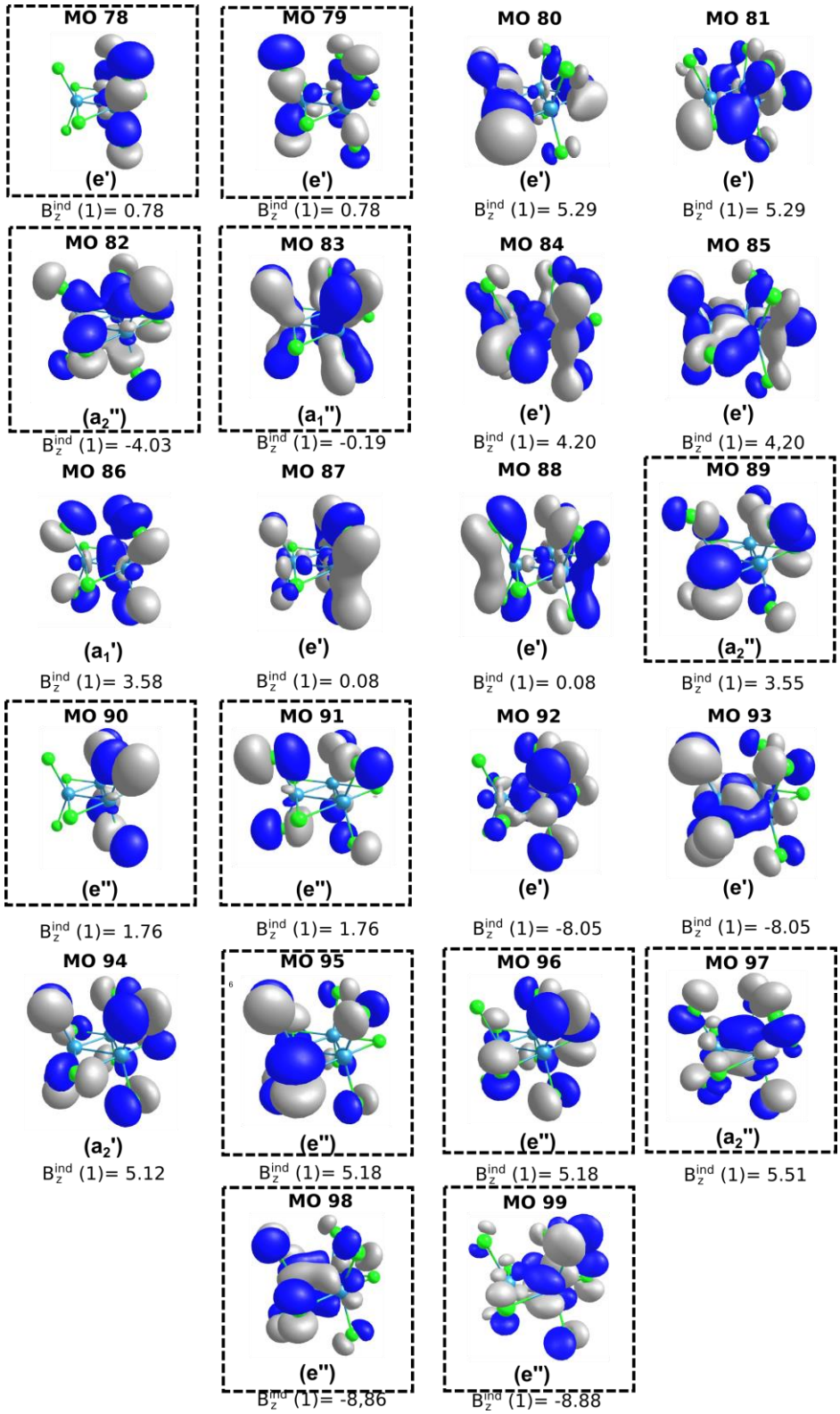

Figure SI-4 (continuation). Occupied valence molecular orbitals, their symmetries and their contributions to B^{ind}_z (1). The π molecular orbitals are enclosed in dashed squares. Total σ and π valence molecular orbitals contributions to B^{ind}_z(1) are -6.59 and -16.47 respectively.