Occurrence of Double Bond in π−Aromatic Rings: An Easy Way to Design Doubly Aromatic Carbon−Metal Structures

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Supporting Information

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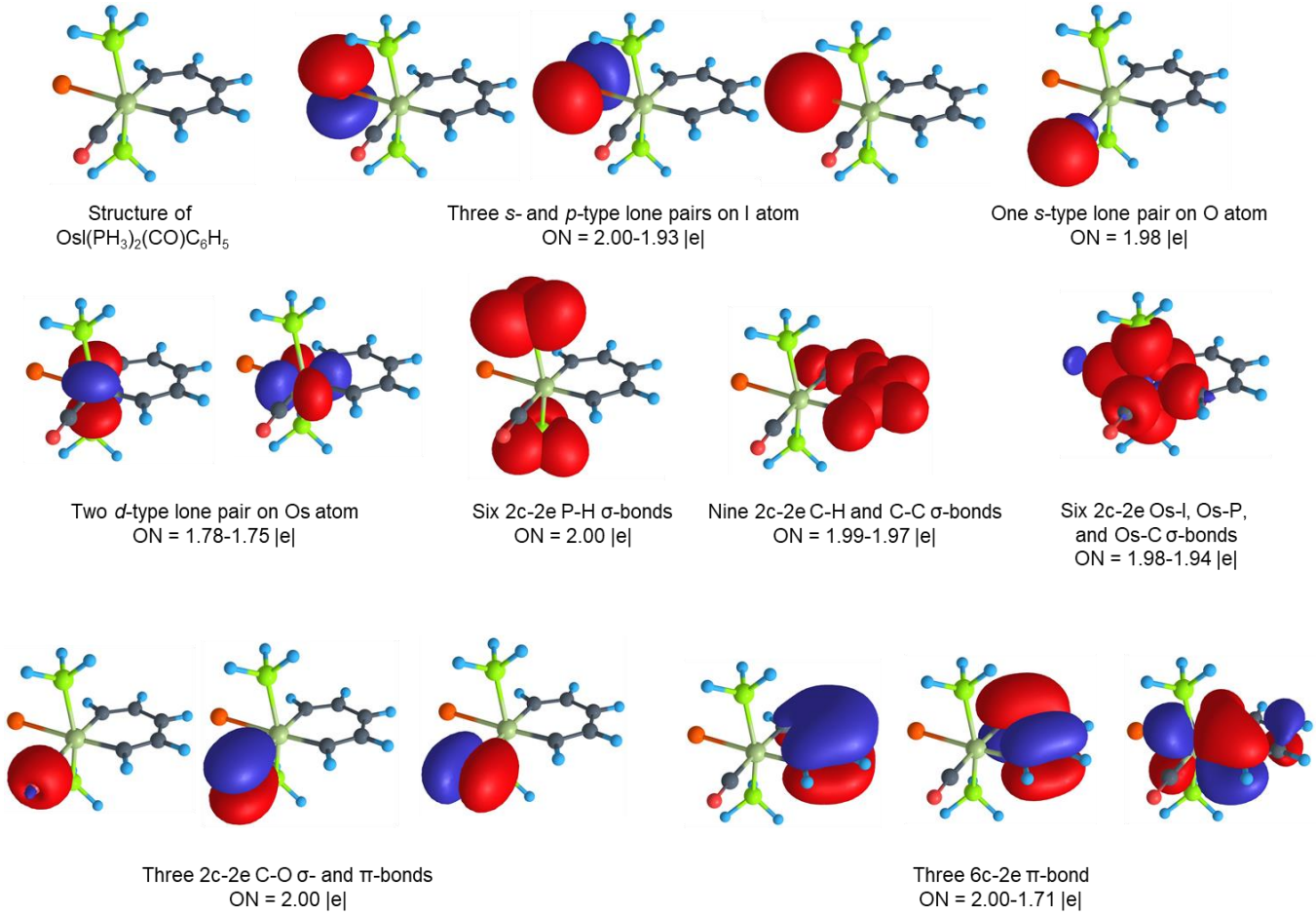

Figure S1. Chemical bonding pattern of [**Os**]C_5H_5.

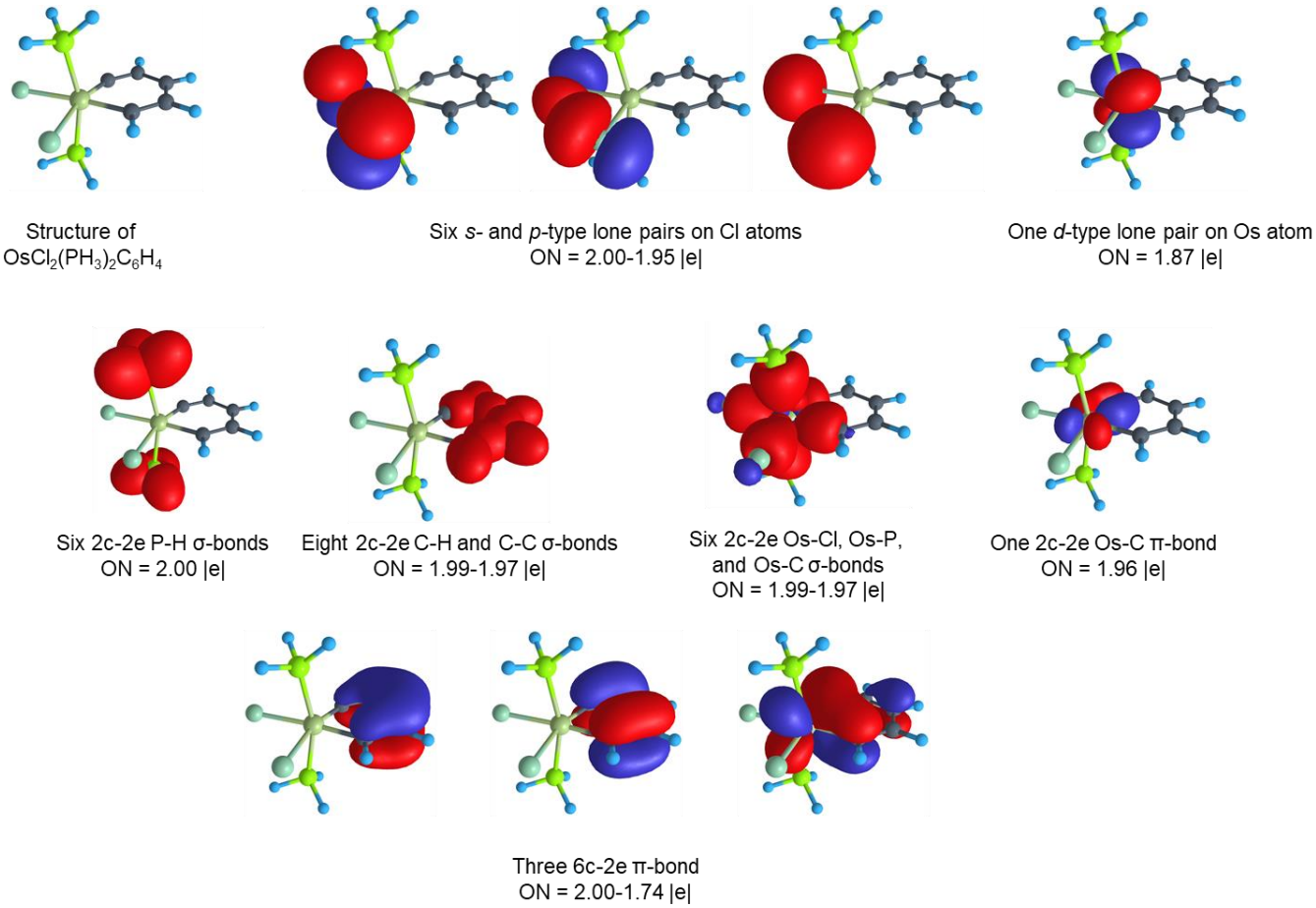

Figure S2. Chemical bonding pattern of [**Os**]C_5H_4.

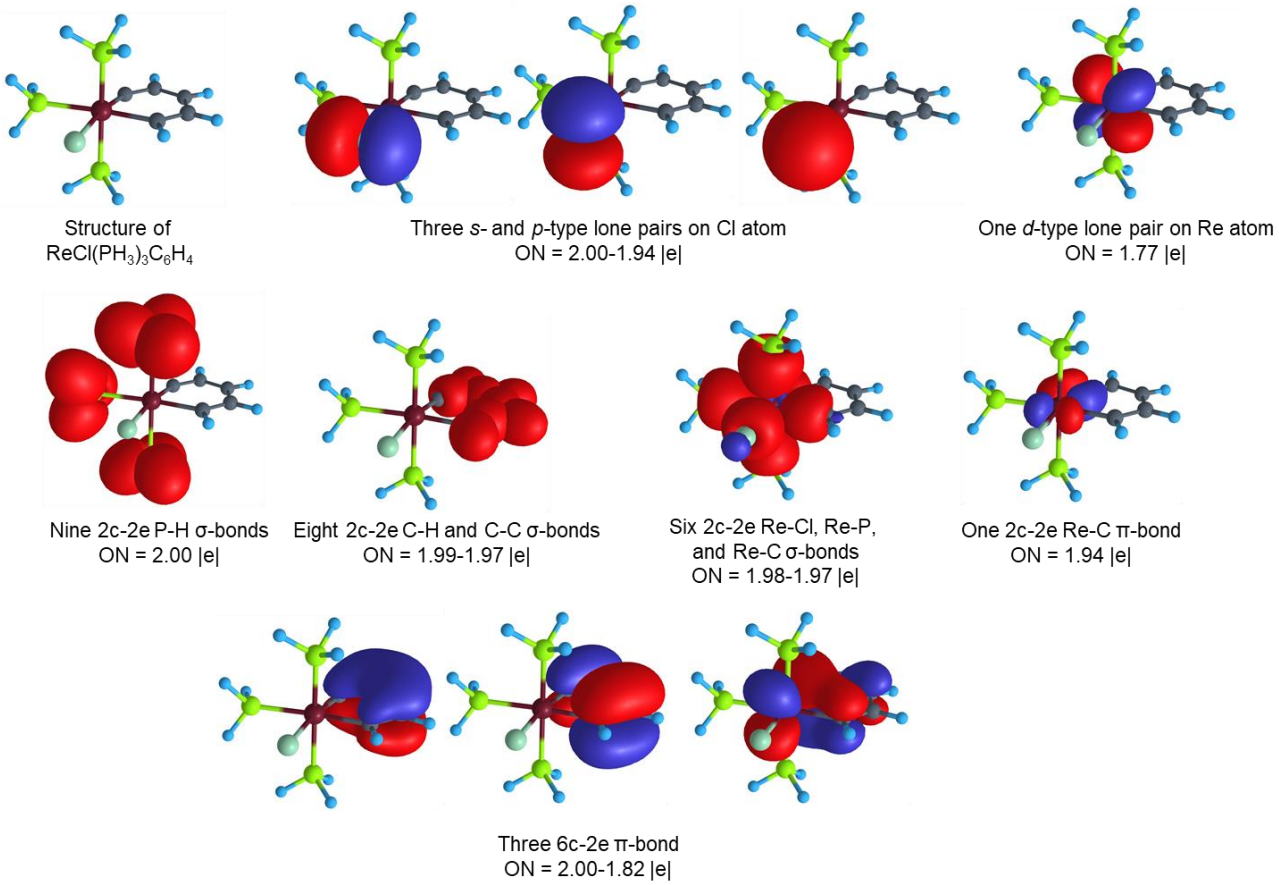

Figure S3. Chemical bonding pattern of [**Re**]C_5H_4.

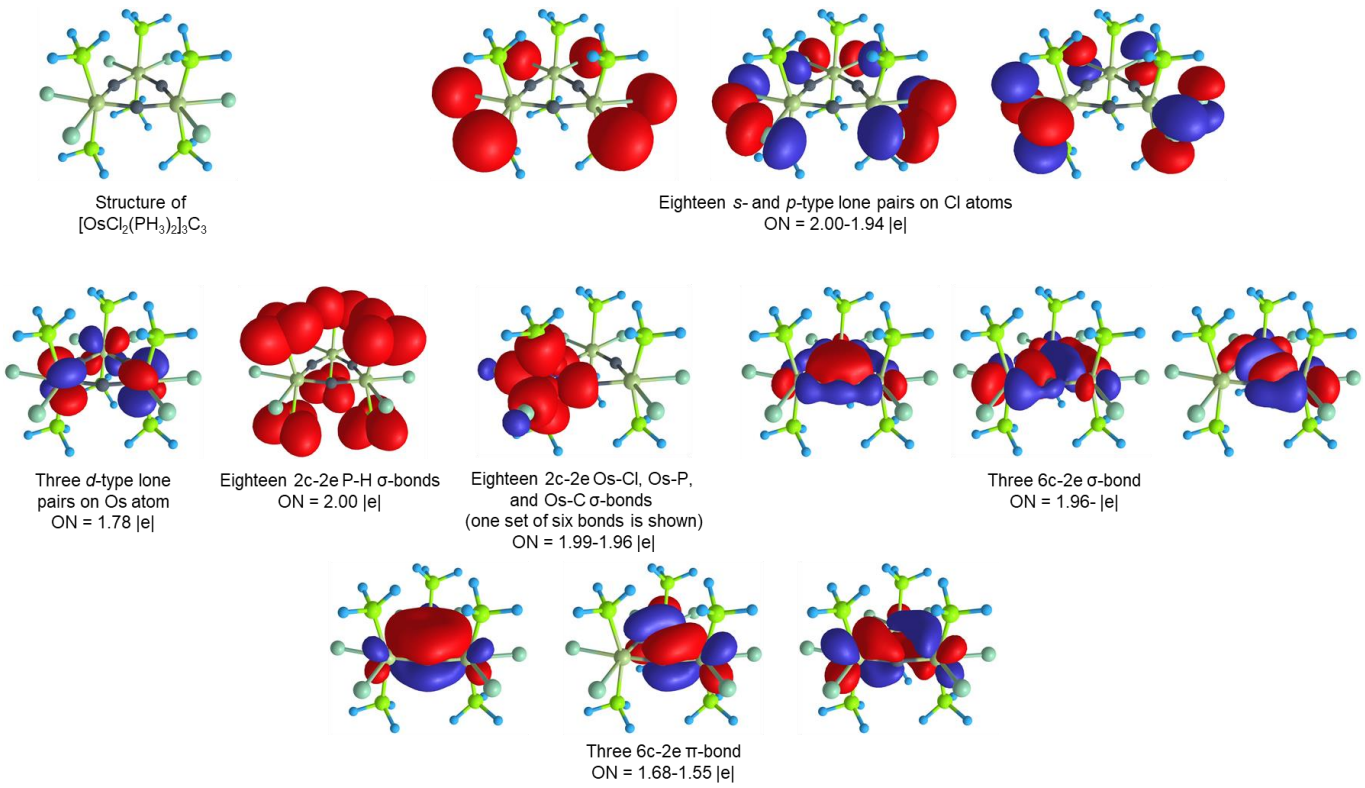

Figure S4. Chemical bonding pattern of [**Os**]$_3$C$_3$.

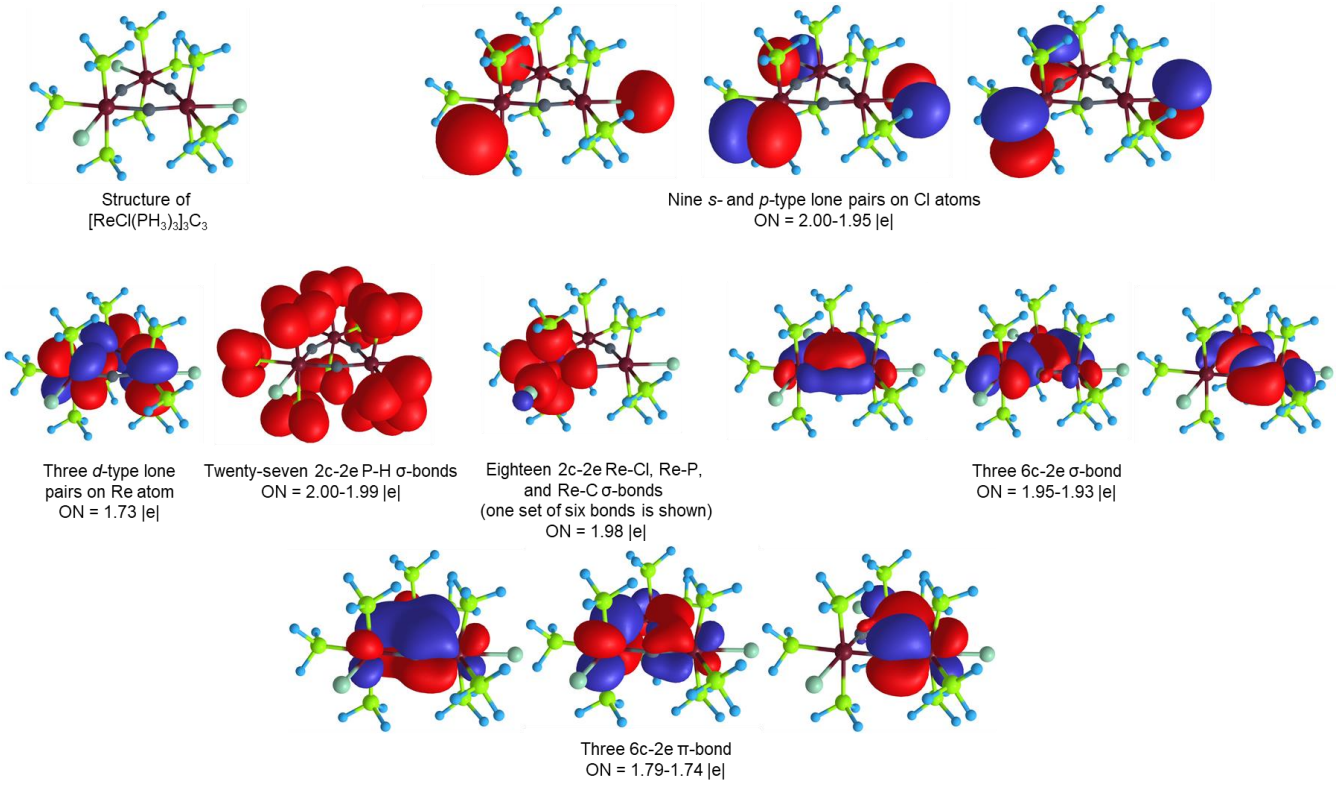

Figure S5. Chemical bonding pattern of [**Re**]$_3$C$_3$.

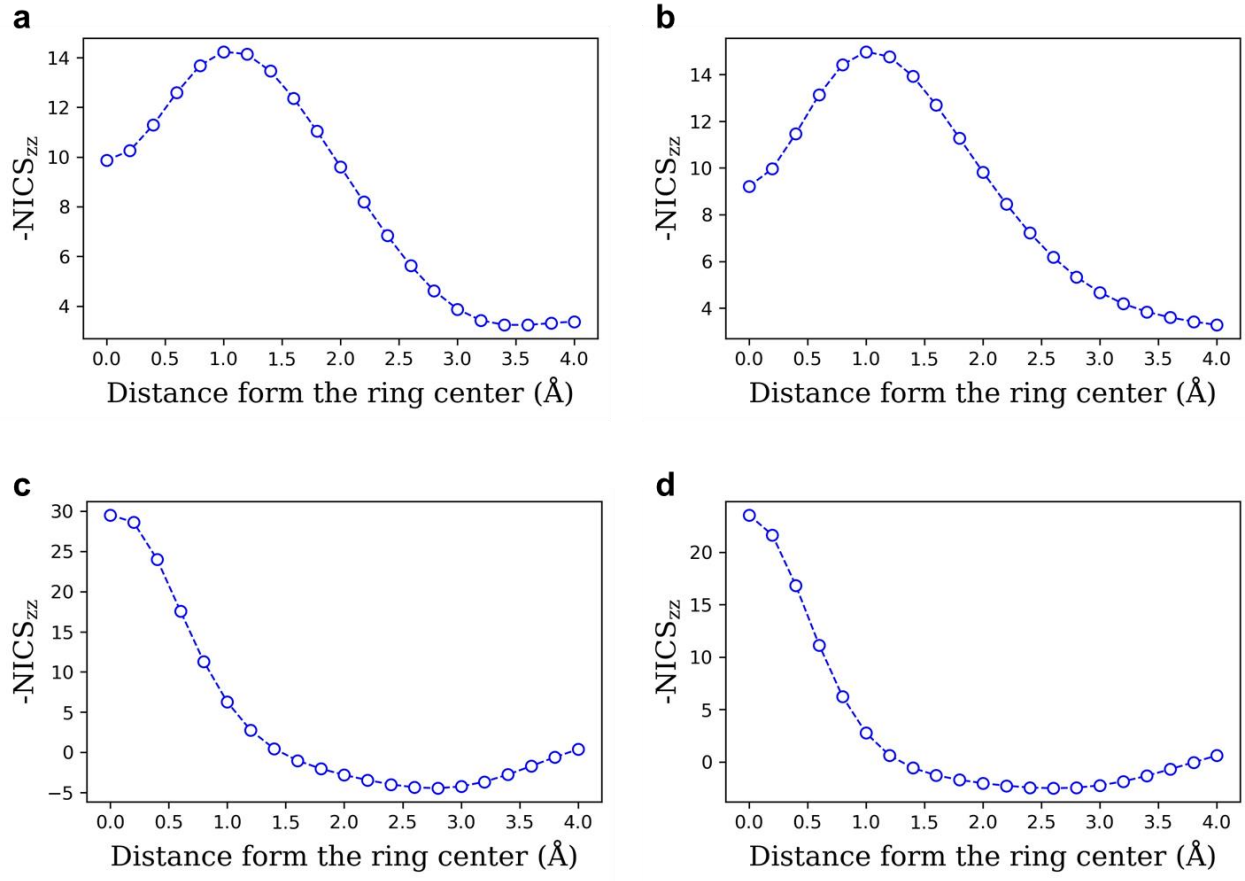

Figure S6. The NICS$_{zz}$ values calculated at different distances from the ring center: [**Re**]C_5H_4 (**a**), [**Os**]C_5H_4 (**b**), [**Re**]C_3 (**c**), [**Os**]C_3 (**d**).

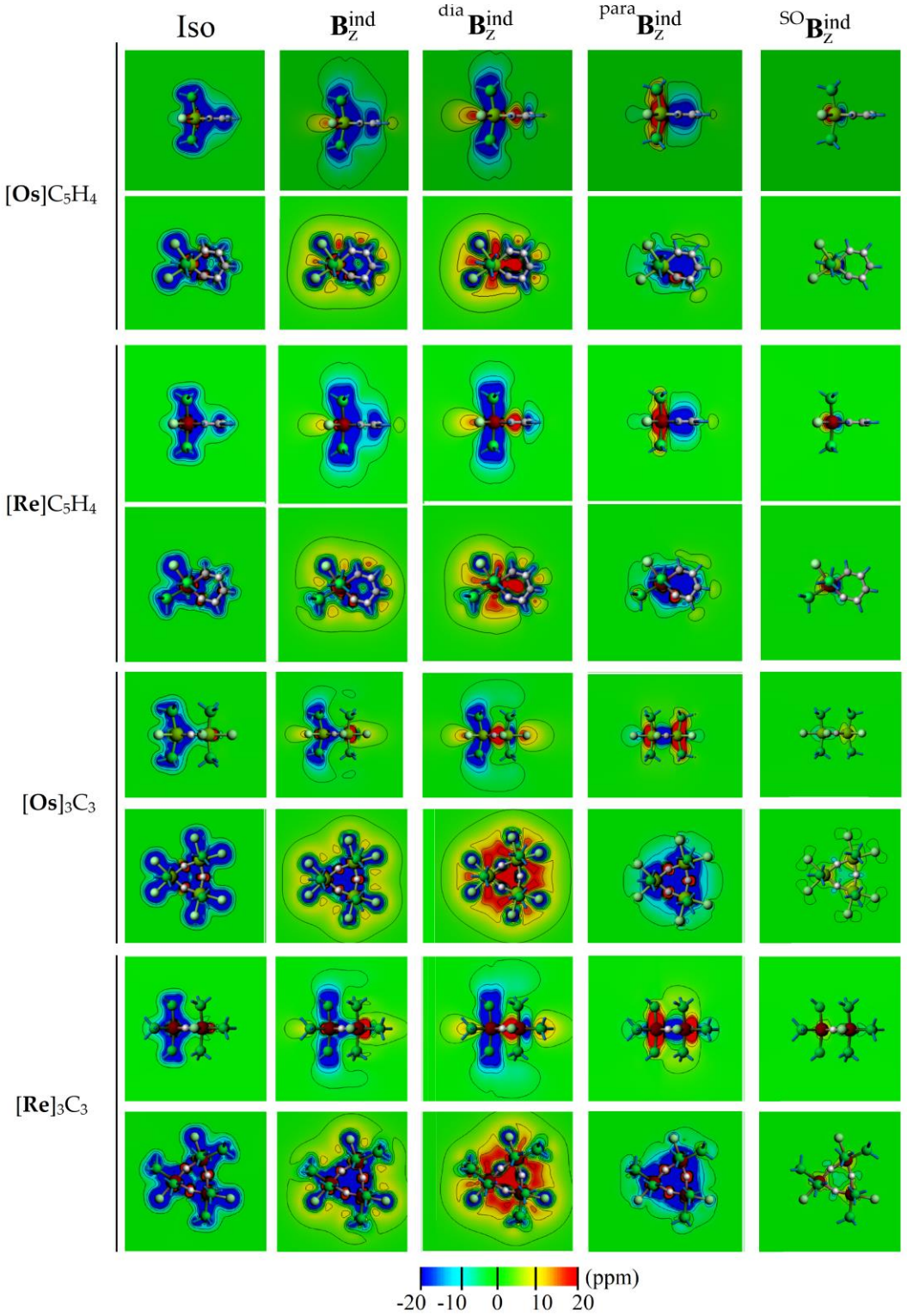

Figure S7. The induced magnetic field for investigated complexes, given as contour plot and its contribution from diamagnetic ($^{dia}B_z^{ind}$), paramagnetic ($^{para}B_z^{ind}$), and spin–orbit ($^{SO}B_z^{ind}$) terms.

Table S1. Optimized structures of investigated complexes.

[Os]C_5H_5	PBE0/def2tzvp, 0 Imaginary Frequencies			
	76	−0.016377000	0.510429000	0.000000000
	6	1.978674000	−0.093854000	0.000000000
	6	0.653674000	2.366970000	0.000000000
	1	−0.074399000	3.184241000	0.000000000
	6	3.116042000	0.664446000	0.000000000
	6	1.963773000	2.856527000	0.000000000
	1	4.093176000	0.185347000	0.000000000
	1	2.107521000	3.934684000	0.000000000
	6	3.098304000	2.072589000	0.000000000
	1	4.058259000	2.584156000	0.000000000
	53	−0.786554000	−2.224369000	0.000000000
	15	−0.016377000	0.098443000	2.293886000
	15	−0.016377000	0.098443000	−2.293886000
	1	0.833143000	−0.931161000	−2.733990000
	1	−1.224690000	−0.297518000	−2.895292000
	1	0.370275000	1.117437000	−3.194957000
	1	0.833143000	−0.931161000	2.733990000
	1	−1.224690000	−0.297518000	2.895292000
	1	0.370275000	1.117437000	3.194957000
	1	2.168296000	−1.172740000	0.000000000
	6	−1.815920000	1.187062000	0.000000000
	8	−2.856776000	1.666256000	0.000000000
[**Os**]C_5H_4	PBE0/def2tzvp, 0 imaginary frequencies			
	76	0.057262000	−0.018753000	−0.087455000
	6	−1.345279000	−0.272567000	−1.124134000
	6	−1.429875000	0.250012000	1.266407000
	1	−1.094521000	0.475854000	2.278966000
	6	−2.700536000	−0.330860000	−1.309748000
	6	−2.795036000	0.186883000	1.092826000
	1	−3.175186000	−0.540349000	−2.259646000
	1	−3.447335000	0.358006000	1.944353000
	6	−3.410720000	−0.090924000	−0.141615000
	1	−4.496263000	−0.118858000	−0.186055000
	17	2.097236000	−0.354440000	−1.395549000
	17	1.507082000	0.517560000	1.835950000
	15	0.381145000	2.278237000	−0.438918000
	15	0.497784000	−2.279395000	0.360778000
	1	0.607676000	−3.134701000	−0.749295000
	1	1.729813000	−2.479110000	1.001468000
	1	−0.361658000	−3.038300000	1.183799000
	1	−0.263203000	2.929735000	−1.511558000
	1	1.721405000	2.611664000	−0.688507000
	1	0.058692000	3.150372000	0.615917000

[**Re**]C_5H_4	PBE0/def2tzvp, 0 imaginary frequencies
	75 −0.083604000 −0.000001000 −0.121317000
	6 1.311462000 −0.000040000 −1.225144000
	6 1.474551000 −0.000068000 1.281708000
	1 1.194326000 −0.000004000 2.339765000
	6 2.687335000 −0.000068000 −1.423624000
	6 2.824570000 −0.000064000 1.044917000
	1 3.163564000 −0.000076000 −2.397324000
	1 3.517918000 −0.000056000 1.883419000
	6 3.410784000 −0.000054000 −0.253136000
	1 4.495927000 −0.000058000 −0.320386000
	17 −1.708853000 0.000042000 1.811478000
	15 −0.209051000 −2.348941000 0.219419000
	15 −0.208857000 2.348945000 0.219431000
	1 −1.398180000 3.063042000 −0.057110000
	1 −0.009341000 2.795688000 1.541614000
	1 0.698718000 3.204069000 −0.441353000
	1 0.698394000 −3.204154000 −0.441430000
	1 −1.398466000 −3.062909000 −0.057053000
	1 −0.009495000 −2.795717000 1.541585000
	1 −3.044141000 1.053907000 −1.412807000
	1 −1.970206000 0.000043000 −2.916906000
	1 −3.044241000 −1.053680000 −1.412778000
	15 −2.103837000 0.000067000 −1.511778000
[**Os**]$_3C_3$	PBE0/def2tzvp, 0 imaginary frequencies
	76 0.000000000 2.103220000 −0.000108000
	6 1.183242000 0.683137000 −0.000277000
	6 −1.183235000 0.683149000 −0.000277000
	6 −0.000007000 −1.366286000 −0.000277000
	17 1.710170000 3.877612000 0.096341000
	17 −1.710185000 3.877631000 −0.095748000
	15 −0.148940000 2.563993000 −2.306385000
	15 0.149220000 2.562665000 2.306355000
	1 1.428475000 2.503150000 2.883775000
	1 −0.255791000 3.870791000 2.607823000
	1 −0.593270000 1.832276000 3.262586000
	1 0.594889000 1.835124000 −3.262706000
	1 0.254883000 3.872752000 −2.606656000
	1 −1.427798000 2.503637000 −2.884612000
	76 1.821442000 −1.051610000 −0.000108000
	1 1.291820000 −1.432751000 −3.262706000
	1 3.226460000 −2.157111000 −2.606656000
	1 2.882112000 −0.015309000 −2.884612000
	1 1.453554000 −2.488671000 2.883775000
	1 3.480099000 −1.713874000 2.607823000

	1 1.883433000 −0.402351000 3.262586000 15 2.144723000 −1.410561000 2.306355000 17 4.213219000 −0.457752000 −0.095748000 17 2.503025000 −3.419856000 0.096341000 15 2.294953000 −1.153010000 −2.306385000 76 −1.821442000 −1.051610000 −0.000108000 1 −1.886709000 −0.402373000 −3.262706000 1 −3.481343000 −1.715641000 −2.606656000 1 −1.454314000 −2.488328000 −2.884612000 1 −2.882029000 −0.014479000 2.883775000 1 −3.224307000 −2.156917000 2.607823000 1 −1.290162000 −1.429925000 3.262586000 15 −2.293943000 −1.152104000 2.306355000 17 −2.503034000 −3.419879000 −0.095748000 17 −4.213195000 −0.457755000 0.096341000 15 −2.146013000 −1.410983000 −2.306385000
[**Re**]$_3$C$_3$	PBE0/def2tzvp, 0 imaginary frequencies
	75 0.488616000 −2.112701000 0.027325000 6 −0.970561000 −1.014492000 0.046660000 6 1.363927000 −0.333281000 0.046650000 6 −0.393283000 1.347878000 0.046299000 17 2.512902000 −3.678693000 −0.161736000 15 0.859504000 −2.263191000 −2.323218000 15 0.785945000 −2.275262000 2.371450000 1 −0.177257000 −2.840369000 3.243127000 1 1.892743000 −3.055001000 2.773192000 1 1.056312000 −1.123606000 3.146294000 1 0.084050000 −1.555896000 −3.273557000 1 0.796501000 −3.531743000 −2.940866000 1 2.134856000 −1.880390000 −2.784573000 1 −0.591603000 −5.205598000 1.004299000 1 −2.169290000 −4.232527000 −0.032315000 1 −0.565268000 −5.140735000 −1.101074000 15 −0.757515000 −4.245088000 −0.021914000 75 1.585427000 1.479532000 0.027194000 17 1.929900000 4.015593000 −0.162669000 15 1.531263000 1.875468000 −2.323473000 15 1.576136000 1.818733000 2.371193000 15 4.055261000 1.466443000 −0.020538000 1 1.307782000 0.849853000 −3.273730000 1 2.661280000 2.455976000 −2.940459000 1 0.561537000 2.787591000 −2.785622000

	1	2.546867000	1.267869000	3.243642000
	1	1.696966000	3.167224000	2.772870000
	1	0.443247000	1.476449000	3.145252000
	1	4.803575000	2.092104000	1.005017000
	1	4.750136000	0.237450000	−0.028387000
	1	4.735552000	2.078756000	−1.100365000
	75	−2.073936000	0.633253000	0.027166000
	17	−4.442560000	−0.336476000	−0.161612000
	15	−2.390017000	0.386736000	−2.323310000
	15	−2.363042000	0.457194000	2.371266000
	15	−3.298160000	2.778285000	−0.022026000
	1	−1.389801000	0.704475000	−3.273791000
	1	−3.457233000	1.075253000	−2.941088000
	1	−2.696057000	−0.909320000	−2.784241000
	1	−2.371463000	1.574023000	3.242804000
	1	−3.591336000	−0.112102000	2.773248000
	1	−1.500330000	−0.352189000	3.146152000
	1	−2.581884000	3.994936000	−0.032592000
	1	−4.170356000	3.059218000	−1.100937000
	1	−4.212763000	3.114396000	1.004492000

Table S2. Coordinates of chosen points for NICS calculation.

[**Os**]C_5H_4	76	0.054040000	−0.099087000	−0.119586000
	6	−1.363000000	−0.049669000	−1.166392000
	6	−1.413437000	−0.076443000	1.281397000
	1	−1.063813000	−0.099986000	2.313846000
	6	−2.720237000	−0.004018000	−1.340739000
	6	−2.780744000	−0.037769000	1.117828000
	1	−3.207986000	0.027529000	−2.306446000
	1	−3.420892000	−0.034143000	1.995366000
	6	−3.413713000	−0.002240000	−0.138427000
	1	−4.499544000	0.029074000	−0.172306000
	17	2.070798000	−0.221871000	−1.499042000
	17	1.535089000	−0.075665000	1.854000000
	15	0.483578000	2.201174000	0.050372000
	15	0.390153000	−2.419934000	−0.198145000
	1	0.455453000	−3.006885000	−1.473728000
	1	1.614063000	−2.813811000	0.363255000
	1	−0.500521000	−3.305744000	0.445270000
	1	−0.133909000	3.105904000	−0.838651000
	1	1.836950000	2.522106000	−0.137119000
	1	0.206517000	2.826453000	1.279004000
	Point 1	−1.937000000	0.000000000	−0.051000000
	Point 2	−1.937000000	1.000000000	−0.051000000

[**Re**]C_5H_4	75 −0.083604000 −0.000001000 −0.121317000 6 1.311462000 −0.000040000 −1.225144000 6 1.474551000 −0.000068000 1.281708000 1 1.194326000 −0.000004000 2.339765000 6 2.687335000 −0.000068000 −1.423624000 6 2.824570000 −0.000064000 1.044917000 1 3.163564000 −0.000076000 −2.397324000 1 3.517918000 −0.000056000 1.883419000 6 3.410784000 −0.000054000 −0.253136000 1 4.495927000 −0.000058000 −0.320386000 17 −1.708853000 0.000042000 1.811478000 15 −0.209051000 −2.348941000 0.219419000 15 −0.208857000 2.348945000 0.219431000 1 −1.398180000 3.063042000 −0.057110000 1 −0.009341000 2.795688000 1.541614000 1 0.698718000 3.204069000 −0.441353000 1 0.698394000 −3.204154000 −0.441430000 1 −1.398466000 −3.062909000 −0.057053000 1 −0.009495000 −2.795717000 1.541585000 1 −3.044141000 1.053907000 −1.412807000 1 −1.970206000 0.000043000 −2.916906000 1 −3.044241000 −1.053680000 −1.412778000 15 −2.103837000 0.000067000 −1.511778000 Point 1 1.937516000 −0.000049000 −0.116099000 Point 2 1.938000000 1.000000000 −0.116000000
[**Os**]$_3C_3$	76 0.000000000 2.103220000 −0.000108000 6 1.183242000 0.683137000 −0.000277000 6 −1.183235000 0.683149000 −0.000277000 6 −0.000007000 −1.366286000 −0.000277000 17 1.710170000 3.877612000 0.096341000 17 −1.710185000 3.877631000 −0.095748000 15 −0.148940000 2.563993000 −2.306385000 15 0.149220000 2.562665000 2.306355000 1 1.428475000 2.503150000 2.883775000 1 −0.255791000 3.870791000 2.607823000 1 −0.593270000 1.832276000 3.262586000 1 0.594889000 1.835124000 −3.262706000 1 0.254883000 3.872752000 −2.606656000 1 −1.427798000 2.503637000 −2.884612000 76 1.821442000 −1.051610000 −0.000108000 1 1.291820000 −1.432751000 −3.262706000 1 3.226460000 −2.157111000 −2.606656000 1 2.882112000 −0.015309000 −2.884612000 1 1.453554000 −2.488671000 2.883775000 1 3.480099000 −1.713874000 2.607823000 1 1.883433000 −0.402351000 3.262586000

	15 2.144723000 −1.410561000 2.306355000 17 4.213219000 −0.457752000 −0.095748000 17 2.503025000 −3.419856000 0.096341000 15 2.294953000 −1.153010000 −2.306385000 76 −1.821442000 −1.051610000 −0.000108000 1 −1.886709000 −0.402373000 −3.262706000 1 −3.481343000 −1.715641000 −2.606656000 1 −1.454314000 −2.488328000 −2.884612000 1 −2.882029000 −0.014479000 2.883775000 1 −3.224307000 −2.156917000 2.607823000 1 −1.290162000 −1.429925000 3.262586000 15 −2.293943000 −1.152104000 2.306355000 17 −2.503034000 −3.419879000 −0.095748000 17 −4.213195000 −0.457755000 0.096341000 15 −2.146013000 −1.410983000 −2.306385000 Point 1 0.000000000 0.000000000 −0.000193000 Point 2 0.000000000 0.000000000 1.000000000
[**Re**]$_3$C$_3$	75 0.488616000 −2.112701000 0.027325000 6 −0.970561000 −1.014492000 0.046660000 6 1.363927000 −0.333281000 0.046650000 6 −0.393283000 1.347878000 0.046299000 17 2.512902000 −3.678693000 −0.161736000 15 0.859504000 −2.263191000 −2.323218000 15 0.785945000 −2.275262000 2.371450000 1 −0.177257000 −2.840369000 3.243127000 1 1.892743000 −3.055001000 2.773192000 1 1.056312000 −1.123606000 3.146294000 1 0.084050000 −1.555896000 −3.273557000 1 0.796501000 −3.531743000 −2.940866000 1 2.134856000 −1.880390000 −2.784573000 1 −0.591603000 −5.205598000 1.004299000 1 −2.169290000 −4.232527000 −0.032315000 1 −0.565268000 −5.140735000 −1.101074000 15 −0.757515000 −4.245088000 −0.021914000 75 1.585427000 1.479532000 0.027194000 17 1.929900000 4.015593000 −0.162669000 15 1.531263000 1.875468000 −2.323473000 15 1.576136000 1.818733000 2.371193000 15 4.055261000 1.466443000 −0.020538000 1 1.307782000 0.849853000 −3.273730000 1 2.661280000 2.455976000 −2.940459000 1 0.561537000 2.787591000 −2.785622000 1 2.546867000 1.267869000 3.243642000 1 1.696966000 3.167224000 2.772870000 1 0.443247000 1.476449000 3.145252000 1 4.803575000 2.092104000 1.005017000

	1 4.750136000 0.237450000 −0.028387000 1 4.735552000 2.078756000 −1.100365000 75 −2.073936000 0.633253000 0.027166000 17 −4.442560000 −0.336476000 −0.161612000 15 −2.390017000 0.386736000 −2.323310000 15 −2.363042000 0.457194000 2.371266000 15 −3.298160000 2.778285000 −0.022026000 1 −1.389801000 0.704475000 −3.273791000 1 −3.457233000 1.075253000 −2.941088000 1 −2.696057000 −0.909320000 −2.784241000 1 −2.371463000 1.574023000 3.242804000 1 −3.591336000 −0.112102000 2.773248000 1 −1.500330000 −0.352189000 3.146152000 1 −2.581884000 3.994936000 −0.032592000 1 −4.170356000 3.059218000 −1.100937000 1 −4.212763000 3.114396000 1.004492000 Point 1 0.000000000 0.000000000 0.000000000 Point 2 0.000000000 0.000000000 1.000000000