Supporting Informations

Towards the first theoretical scale of the *trans* effect

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Contents

S1 Dual Descriptor formulations

As we mentioned in the main body of the article, the usual Dual Descriptor (DD)[1] is defined as:

$$\Delta f_{usual}(\mathbf{r}) = \left(\frac{\partial^2 \rho(\mathbf{r})}{\partial N^2}\right)_{v(\mathbf{r})} \tag{1}$$

with $\rho(\mathbf{r})$ the electron density, $v(\mathbf{r})$ the external potential and N the number of electrons. Direct computation of this descriptor is not implemented yet in most of the quantum chemistry programs, and usually different levels of approximations are used.

The first one is the finite difference approximation (FDA): the derivative in equation (1) is approximated as the difference in electron density upon the addition and subtraction of one electron at frozen geometry:

$$\Delta f_{FDA}(\mathbf{r}) \approx \left(\frac{\rho_{N+1}(\mathbf{r}) - \rho_N(\mathbf{r})}{(N+1) - (N)} - \frac{\rho_N(\mathbf{r}) - \rho_{N-1}(\mathbf{r})}{(N) - (N-1)}\right) = \rho_{N+1}(\mathbf{r}) + \rho_{N-1}(\mathbf{r}) - 2\rho_N(\mathbf{r}). \tag{2}$$

A further approximation relies on the frozen orbital hypothesis. If we assume that upon the addition or subtraction of one electron the orbital diagram remains unchanged, then the additional electron will be located in the LUMO, whereas the subtracted one will come from the HOMO:

$$(\rho_{N+1}(\mathbf{r}) - \rho_N(\mathbf{r})) - (\rho_N(\mathbf{r}) - \rho_{N-1}(\mathbf{r})) \approx \rho_{LUMO}(\mathbf{r}) - \rho_{HOMO}(\mathbf{r}) \approx \Delta f_{FMO}(\mathbf{r}) \tag{3}$$

in direct link with the frontier MO theory.

Yet, both these levels of approximation present some limitations. First, the FMO-like expression becomes ill-defined when either the HOMO or LUMO present some degeneracy. Problems can also be found when using the FDA with transition metals, since the spin states of the $N+1$ and $N-1$ forms are not trivial. Furthermore, sometimes the addition of one electron cannot be achieved, because of a self-ionisation (negative electron affinities). As such, some of the authors recently developed a different approach to compute the DD, based on the excited states: the state specific formulation[2].

In this case, the DD is expressed as a sum of electron density differences between the ground state ($\rho_0(\mathbf{r})$) and the excited states ($\rho_n(\mathbf{r})$):

$$\Delta f_{ext}(\mathbf{r}) = \sum_n \omega_n \left(\underbrace{\rho_n(\mathbf{r}) - \rho_0(\mathbf{r})}_{\Delta f_n(\mathbf{r})}\right) \tag{4}$$

with ω_n a weighting parameter, and $\Delta f_n(\mathbf{r})$ the so-called nth state specific dual descriptor. The challenge to determine the weights has not been overcome yet. Nevertheless, one generally assumes the higher in energy an excited state, the lesser it will contribute to reactivity in the perturbed ground state. As we have already shown elsewhere[3], it is often sufficient to restrain the study to the calculation of the very first excited states, hence one usually has:

$$\Delta f(\mathbf{r}) \approx \rho_1(\mathbf{r}) - \rho_0(\mathbf{r}) \tag{5}$$

The connection between this formulation and the FMO-like one can be easily deduced. Under a frozen orbital hypothesis, the first excitation will in general consist in the promotion of one electron from the HOMO to the LUMO. The electron density difference will then be reduced to the difference of orbital densities of equation (3).

S2 Grand Canonical Dual Descriptor

Equation (1) is formulated within the canonical ensemble, *i.e.* with a fixed number of electrons N. The Grand Canonical ensemble, on the other hand, takes N as a free parameter[4,5]. The associated Legendre transform links N, the electron energy E and the chemical potential μ in a grand potential Ω:

$$\Omega = E - \mu N. \tag{6}$$

It is possible to define a Grand Canonical Dual Descriptor (GC-DD) $\Delta s(\mathbf{r})$:

$$\Delta s(\mathbf{r}) = \left(\frac{\partial^2 \rho(\mathbf{r})}{\partial \mu^2}\right)_{v(\mathbf{r})} \tag{7}$$

which will be more suited to the comparison of systems with different number of electrons. The GC-DD can furthermore be quite easily linked to the canonical DD.

$$\Delta s(\mathbf{r}) = \left(\frac{\partial^2 \rho(\mathbf{r})}{\partial \mu^2}\right)_{v(\mathbf{r})} = \left(\frac{\partial}{\partial \mu} s(\mathbf{r})\right)_{v(\mathbf{r})} = \left(\frac{\partial}{\partial \mu} S f(\mathbf{r})\right)_{v(\mathbf{r})} \tag{8}$$

with $s(\mathbf{r})$ the local softness, $S = 1/\eta$ the global softness (with η the corresponding global hardness) and $f(\mathbf{r})$ the Fukui function.

Developing the partial derivative in μ yields

$$\Delta s(\mathbf{r}) = \left(\frac{\partial}{\partial \mu} S\right)_{v(\mathbf{r})} f(\mathbf{r}) + S\left(\frac{\partial}{\partial \mu} f(\mathbf{r})\right)_{v(\mathbf{r})}. \tag{9}$$

Let us focus on the first term. Using the chain rule we get

$$\left(\frac{\partial}{\partial \mu} S\right)_{v(\mathbf{r})} f(\mathbf{r}) = \left(\frac{\partial N}{\partial \mu}\frac{\partial}{\partial N} S\right)_{v(\mathbf{r})} f(\mathbf{r}) = \left(S\frac{\partial}{\partial N} S\right)_{v(\mathbf{r})} f(\mathbf{r}) \tag{10}$$

$$= \left(\frac{1}{\eta}\frac{\partial}{\partial N} 1/\eta\right)_{v(\mathbf{r})} f(\mathbf{r}) = \left(-\frac{1}{\eta^3}\frac{\partial \eta}{\partial N}\right)_{v(\mathbf{r})} f(\mathbf{r}) = -\frac{\gamma}{\eta^3} f(\mathbf{r}) \tag{11}$$

with γ being the global hyperhardness.

Let us now develop the second term. Using here also the chain rule we get

$$S\left(\frac{\partial}{\partial \mu} f(\mathbf{r})\right)_{v(\mathbf{r})} = \frac{1}{\eta}\left(\frac{\partial N}{\partial \mu}\frac{\partial}{\partial N} f(\mathbf{r})\right)_{v(\mathbf{r})} = \frac{1}{\eta^2}\left(\frac{\partial f(\mathbf{r})}{\partial N}\right)_{v(\mathbf{r})} = \frac{\Delta f(\mathbf{r})}{\eta^2}$$

Hence:

$$\Delta s(\mathbf{r}) = \frac{\Delta f(\mathbf{r})}{\eta^2} - \frac{\gamma}{\eta^3} f(\mathbf{r}) \approx \frac{\Delta f(\mathbf{r})}{\eta^2} \tag{12}$$

since the ratio $\frac{\gamma}{\eta^3}$ is usually very small.

S3 Complexes geometries

S3.1 Complex 1

Co	0.00905475	-0.27797310	0.00119806
C	0.02677002	-2.26894535	0.01628913
H	-0.44157619	-2.65963639	-0.89194889
H	-0.52666789	-2.64127711	0.88384983
H	1.05007711	-2.65677618	0.07206124
H	-2.18284610	0.73081918	-0.01499424
H	-2.28543505	-0.68449818	0.85862025
H	2.14347901	0.85131390	-0.01099207
H	2.32823120	-0.58023809	-0.84232424
H	-2.28685218	-0.71054323	-0.84493096
H	2.32145191	-0.55690085	0.86131112
N	-1.94556514	-0.26453994	-0.00015717
N	0.01424016	-0.35647020	1.97670933
N	0.01580017	-0.37398015	-1.97237220
N	1.96060806	-0.15541195	0.00220085
O	-1.05226420	-0.47461484	-2.59365645
O	1.08873298	-0.38603692	-2.59132595
O	-1.05486193	-0.44300603	2.59838941
O	1.08669194	-0.37284189	2.59672303
N	-0.04779794	1.80193902	-0.01136514
O	-1.13619594	2.39959604	-0.01739300
O	1.00465306	2.46014397	-0.01346915

S3.2 Complex 2

Nb	0.00016193	-0.00017410	-0.69610886
N	-0.00015399	-0.00012594	1.63252928
N	1.51379407	1.50049109	-0.49882682
N	1.50079430	-1.51380836	-0.49862520
N	-1.51363214	-1.50069905	-0.49902685
C	-2.34944115	-2.32889426	-0.45925812
C	2.32911704	-2.34947819	-0.45860988
C	-0.00031804	-0.00013494	2.80694028
C	2.34948931	2.32879530	-0.45894590
S	-3.51439417	-3.48188734	-0.41742983
S	3.48313514	-3.51339350	-0.41615028
S	-0.00137110	0.00078107	4.46554635
S	3.51424547	3.48198630	-0.41700702
O	0.00038683	-0.00035402	-2.43755340
N	-1.50039319	1.51361997	-0.49922582
C	-2.32860533	2.34941416	-0.45952324
S	-3.48249219	3.51347605	-0.41749016

S3.3 Complex 3 and its derivatives

S3.3.1 X=CH_3^-

Rh	0.04439000	0.01636600	0.00044600
N	0.02927100	0.03538400	2.12691600
H	0.69830300	-0.60829200	2.54790700
H	0.26279900	0.94493400	2.52407200
N	0.78128700	-1.98498900	0.01575500
H	0.49560400	-2.53749400	-0.79229800
H	1.80144000	-2.00773000	0.02175800
N	0.06840900	0.01401100	-2.12531900
H	-0.84062400	-0.23755500	-2.51359100
H	0.31626900	0.91816800	-2.52595300
N	-0.66043500	2.03206700	-0.01670000
H	-1.24118000	2.27319800	0.78612900
H	0.11016200	2.70029900	-0.01159000
H	-0.88535500	-0.21893500	2.50002800
H	0.48642100	-2.52839600	0.82662200
H	0.74064400	-0.63862400	-2.52694800
H	-1.22388900	2.26576100	-0.83393200
O	-2.21542300	-0.76876700	-0.01514100
H	-3.01903100	-0.23343000	-0.02473200
H	-2.50337200	-1.69045700	-0.01462200
H	2.50190900	0.29865000	0.90701700
H	2.51486700	0.29598500	-0.87034900
H	2.04136100	1.75522300	0.01278400
C	1.98996400	0.66450800	0.01403600

S3.3.2 X=CO

Rh	-0.10360200	0.00001000	0.00012400
N	-0.14870100	0.00599500	2.14137000
H	0.30124600	-0.80082500	2.58202700
H	0.29676500	0.81790600	2.57720100
N	-0.14031500	-2.15098700	0.00597400
H	-0.62461400	-2.54645900	-0.80462100
H	0.78199100	-2.59604100	0.00326000
N	-0.15227900	-0.00601800	-2.14094300
H	-1.12088300	-0.00500700	-2.47207200
H	0.29631600	0.80110300	-2.58242100
N	-0.14003300	2.15101900	-0.00583700
H	-0.62213100	2.54670000	0.80596400
H	0.78233200	2.59596000	-0.00564100
H	-1.11662200	0.00440700	2.47448500
H	-0.61776700	-2.54233000	0.82261100
H	0.29287300	-0.81764700	-2.57761700
H	-0.61960900	2.54228600	-0.82126700
O	-2.25873200	0.00009600	0.00097900
H	-2.83475400	0.78119200	-0.00085200
H	-2.83485800	-0.78092000	0.00373000
C	1.82051400	-0.00005700	-0.00122300
O	2.93973600	-0.00015800	-0.00185400

S3.3.3 X=NO_2^-

Rh	-0.28089600	-0.00013800	0.00001600
N	-0.23413800	-1.54156400	1.47085100
H	0.64780900	-2.05228700	1.38442000
H	-0.27821400	-1.23081500	2.44083800
N	-0.23434700	-1.54118300	-1.47122000
H	-0.27842400	-1.22993800	-2.44104100
H	0.64748100	-2.05214400	-1.38507100
N	-0.23534800	1.54134900	-1.47080400
H	-0.98614100	2.22354200	-1.36689600
H	0.64629100	2.05262800	-1.38452800
N	-0.23536600	1.54095700	1.47120900
H	-0.27913700	1.22977800	2.44106600
H	0.64605300	2.05260800	1.38496600
H	-0.98450700	-2.22425800	1.36717400
H	-0.98489900	-2.22370500	-1.36777800
H	-0.27944900	1.23064600	-2.44080400
H	-0.98647100	2.22287100	1.36774500
O	-2.56045000	-0.00026800	0.00001100
H	-3.13272600	-0.00177000	0.77811800
H	-3.13270400	0.00001000	-0.77811400
N	1.72690300	0.00049000	-0.00003000
O	2.27194300	-1.08535200	-0.00012300
O	2.27118800	1.08670800	0.00000500

S3.3.4 X=NH_3

Rh	-0.00217200	-0.01882900	-0.01592300
N	-0.31352500	-1.45321700	1.53892200
H	-1.20441300	-1.95361000	1.49879800
H	0.39202100	-2.19077200	1.60194700
N	-2.11411500	0.34168100	-0.12539400
H	-2.33974000	1.33447400	-0.22757700
H	-2.59257800	-0.11046000	-0.90823900
N	0.31569400	1.48523200	-1.50127700
H	0.43507600	2.39705900	-1.05232500
H	1.15008600	1.35839800	-2.07894700
N	2.12139500	-0.29888300	0.11448600
H	2.42983800	-0.75637200	0.97585600
H	2.53261300	-0.85557500	-0.63883000
H	-0.30400400	-0.99092800	2.45161900
H	-2.62931900	0.04038100	0.70545800
H	-0.44881000	1.61155700	-2.16883900
H	2.63627700	0.58500600	0.08884300
O	0.14719200	1.51871400	1.49055200
H	0.94857500	1.77164900	1.97383000
H	-0.58638800	2.03871000	1.85282400
N	-0.14807800	-1.52165800	-1.46321600
H	-1.03153200	-2.03640100	-1.42933900
H	-0.07128100	-1.17721500	-2.42345400
H	0.57419000	-2.24039900	-1.37416900

S3.3.5 X=Pyridine

Rh	0.88480300	0.00000000	0.00001200
N	0.92094800	1.46017100	-1.55776600
H	0.08522000	1.43273500	-2.14482300
H	1.00114900	2.43113400	-1.25120600
N	0.92106600	-1.46039200	-1.55755200
H	0.99980900	-2.43142200	-1.25083600
H	0.08605700	-1.43209800	-2.14559200
N	0.92097000	-1.46013300	1.55783000
H	1.71104500	-1.32160000	2.19135300
H	0.08536600	-1.43250900	2.14505600
N	0.92095100	1.46041100	1.55756900
H	1.00035300	2.43138800	1.25085000
H	0.08558800	1.43253900	2.14512500
H	1.71087100	1.32148900	-2.19144300
H	1.71189900	-1.32261300	-2.19029300
H	1.00090500	-2.43112600	1.25129200
H	1.71134400	1.32229700	2.19078500
O	3.07599200	-0.00000200	-0.00009600
H	3.64912200	0.78056300	-0.00051600
H	3.64916800	-0.78053400	0.00060600
C	-1.86921900	1.16646000	-0.00000800
C	-1.86919900	-1.16647800	-0.00000400
C	-3.25515300	1.19898700	-0.00002600
H	-1.30260400	2.08826300	0.00000200
C	-3.25513500	-1.19902700	-0.00002400
H	-1.30257400	-2.08827300	-0.00000300
C	-3.96754500	-0.00002700	-0.00003400
H	-3.76113100	2.15799700	-0.00003600
H	-3.76109600	-2.15804600	-0.00003100
H	-5.05242500	-0.00003300	-0.00004900
N	-1.17459700	-0.00000500	0.00000000

S3.3.6 X=Cl^-

Rh	0.00004974	0.00009419	0.17462690
N	-1.15772393	-1.78111537	0.09190221
N	-1.75516399	1.18943117	0.09913289
N	1.15736885	1.78144028	0.09044803
N	1.75531216	-1.18933592	0.10050399
H	-2.07819124	-1.73159496	0.52806016
H	-0.70579915	-2.60049395	0.49727209
H	-1.70927426	1.81514834	-0.70650084
H	-1.91223491	1.76361336	0.92736302
H	1.31465409	1.99983332	-0.89615585
H	2.07952001	1.73095995	0.52289486
H	1.71247737	-1.81012116	-0.70914196
H	1.90815019	-1.76858816	0.92598504
H	-1.31860228	-1.99807592	-0.89444132
H	-2.60945610	0.65114202	-0.04170075
H	0.70721999	2.60019602	0.49904325
H	2.61083725	-0.65109387	-0.03281587
Cl	0.00010478	-0.00083081	-2.12462708
O	-0.00018680	0.00062284	2.38311005
H	-0.64043994	-0.44672508	2.95079923
H	0.64002718	0.44777497	2.95100720

S3.3.7 X=H_2O

Rh	-0.00004400	0.00006400	-0.00001400
N	-1.50759900	-1.51332800	-0.02569600
H	-1.23765700	-2.39513100	0.41711700
H	-2.38759100	-1.24958700	0.42450600
N	1.51357000	-1.50734700	0.01868900
H	2.39147100	-1.23948800	-0.43306600
H	1.76655700	-1.75253800	0.97943600
N	1.50710500	1.51355400	-0.04189600
H	1.74283500	1.76179200	-1.00623900
H	1.24360000	2.39368400	0.40808100
N	-1.51318500	1.50736500	0.04891900
H	-2.39733300	1.24183300	-0.39190200
H	-1.75273200	1.74756000	1.01435400
H	-1.75713700	-1.75789000	-0.98750200
H	1.24579500	-2.38933200	-0.42518700
H	2.39349200	1.24815900	0.39461000
H	-1.25180100	2.39176500	-0.39399700
O	-0.01647500	0.00466800	-2.09473500
H	-0.57808900	0.56369300	-2.65412500
H	0.53707800	-0.55145400	-2.66495100
O	0.01688900	-0.00541400	2.09475800
H	-0.53737300	-0.56315300	2.66271200
H	0.57833800	0.55144800	2.65646700

S3.4 Complexes 4

S3.4.1 Complex 4-OH

Co	0.00748786	-0.01720514	-0.00135787
N	-0.55053114	-1.22854213	1.48457132
N	0.47269393	1.24804920	1.46619934
N	0.53500084	1.23831710	-1.45347527
N	-0.61405199	-1.19252686	-1.48942387
C	-0.67851001	-0.44867087	2.76249945
C	0.45443996	0.55997801	2.79475545
C	-0.05809996	-0.70304902	-2.79266096
C	-0.10347902	0.81083607	-2.74264525
H	0.17981284	-1.93218119	1.59262402
H	-1.41070188	-1.74820001	1.31616912
H	-0.65582101	-1.11233904	3.62854511
H	-1.64714621	0.05307383	2.75279645
H	1.41792091	0.06585188	2.93811909
H	0.32809307	1.27832290	3.60712031
H	-0.32101903	1.88773718	1.39377297
H	1.31414185	1.81529122	1.37333985
H	-1.61783614	-1.00985329	-1.48058926
H	-0.49568880	-2.20152023	-1.40823327
H	0.96576224	-1.07141512	-2.89053600
H	-0.63291504	-1.09696327	-3.63313202
H	0.40292879	1.26264920	-3.59708023
H	-1.13243614	1.16717504	-2.72076430
H	1.54458002	1.30999098	-1.57017526
H	0.19130022	2.16698189	-1.21551485
H	-2.30969412	0.47980395	0.43341416
O	-1.60468820	0.85346289	-0.11160877
O	1.88522200	-0.90976788	0.03704399
H	2.66745710	-0.55055707	0.47404015
H	2.17691931	-1.62052701	-0.54751430

S3.4.2 Complex 4-SO3

Co	-0.02585507	-0.47393379	0.00973898
N	-1.35671521	-0.50464618	1.49863685
N	1.33459719	-0.46787312	1.47599600
N	1.33722191	-0.47061902	-1.44348917
N	-1.34947395	-0.50760481	-1.49720437
C	-0.67966785	-0.29127186	2.81933626
C	0.70720094	-0.90606099	2.75488617
C	-0.66402431	-0.99853789	-2.72985821
C	0.69842824	-0.32679711	-2.78979494
H	-1.87510201	-1.37975295	1.50758629
H	-2.01833706	0.25926986	1.36811316
H	-1.26688632	-0.71543229	3.63630550
H	-0.61631316	0.78597480	2.96193048
H	0.65035302	-1.99758802	2.74704641
H	1.30938719	-0.61218188	3.61778429
H	1.66015497	0.50341320	1.52406593
H	2.16713906	-1.02174231	1.28846617
H	-1.59187788	0.47874084	-1.64210897
H	-2.21747228	-1.01681408	-1.34955227
H	-0.56299803	-2.08430800	-2.65968137
H	-1.25114488	-0.77486207	-3.62368515
H	1.32417505	-0.75932014	-3.57285820
H	0.58317079	0.73843298	-2.97883346
H	1.87092627	-1.33586986	-1.40711088
H	1.98615197	0.30065523	-1.28256531
S	-0.00672002	1.78102223	-0.02213019
O	-0.88130714	2.20161813	1.09953190
O	1.45014199	2.04668932	0.17547888
O	-0.52173120	2.12755819	-1.37667313
O	0.01775813	-2.81342905	0.01584886
H	0.58794609	-3.38424620	0.54416725
H	-0.58360419	-3.39278501	-0.46643006

S3.5 Complex 5 and its derivatives

S3.5.1 X=CH_3^-

Ru	0.0182 0.0008 -0.5058
N	-3.0265 2.7941 -0.3497
H	-2.5810 4.5619 -0.9659
H	-4.6481 2.3328 -1.2772
N	2.8069 3.0242 -0.2864
H	4.5613 2.5944 -0.9514
H	2.3349 4.6758 -1.1543
N	3.0353 -2.7934 -0.2869
H	2.7011 -4.4712 -1.1690
H	4.7572 -2.2246 -0.9323
N	-2.7929 -3.0238 -0.3489
H	-4.4550 -2.6836 -1.2577
H	-2.2158 -4.7454 -0.9872
H	3.0374 3.4474 1.5791
H	3.2818 -3.2093 1.5781
H	-3.2397 -3.2742 1.5075
H	-3.5081 2.9898 1.5045
H	0.8850 -1.6125 4.3590
H	0.7369 1.6864 4.3608
C	-0.0948 -0.0030 3.4564
H	-2.0376 -0.0919 4.2277

S3.5.2 X=CO

Ru	0.09387400	0.00014800	-0.00120900
N	0.13913700	-1.42270000	1.66505100
H	1.00938700	-1.43672900	2.19635100
H	-0.59129300	-1.23956200	2.35248000
N	0.13716600	-1.66560700	-1.42277800
H	0.05407100	-1.37706000	-2.39708500
H	0.98631300	-2.22882700	-1.38520100
N	0.09992100	1.43618200	-1.65430900
H	1.01193200	1.61304200	-2.07413800
H	-0.50385500	1.15811900	-2.42749900
N	0.14508700	1.66281500	1.42876700
H	0.43945500	1.38993500	2.36605200
H	0.76945200	2.42523900	1.16618800
N	2.35345100	0.00321900	-0.02259800
H	2.77837200	0.79273600	0.46330600
H	2.77504700	-0.81904300	0.40905100
H	-0.62925800	-2.32412300	-1.28652300
H	-0.25098800	2.35323500	-1.37967300
H	-0.76622300	2.10032200	1.55978600
H	2.75593700	0.03131300	-0.95940900
H	-0.01514000	-2.38985400	1.38172200
C	-1.78239300	-0.00853700	0.00532300
O	-2.92282900	-0.01267600	0.00961700

S3.5.3 X=NO_2^-

Ru	-0.33537500	0.00114700	0.00155100
N	1.65327000	-0.00226200	-0.00556700
O	2.27517100	1.08011400	-0.00764800
O	2.27154000	-1.08687300	-0.00675300
N	-0.16778800	1.57675600	1.49446500
H	-0.78128900	2.38401500	1.40655800
H	-0.23380100	1.28602500	2.46738300
N	-0.18144800	1.57929700	-1.49046100
H	-0.24845600	1.29039700	-2.46389600
H	-0.80247800	2.37995100	-1.39748600
N	-0.18634600	-1.57798700	-1.49046700
H	-0.80585200	-2.37935100	-1.39278900
H	-0.25590100	-1.29234100	-2.46476700
N	-0.17362200	-1.57689600	1.49276600
H	-0.24736300	-1.29174900	2.46687300
H	-0.78353100	-2.38584500	1.39520900
N	-2.59817400	0.00203100	0.00325600
H	-3.00076200	-0.68258200	0.63909800
H	-3.00689600	0.89403500	0.27244900
H	0.77300400	1.92528800	-1.35611000
H	0.76874800	-1.92288500	-1.35752900
H	0.78484000	-1.91247600	1.35949000
H	-2.98749100	-0.21123100	-0.91211400
H	0.78878500	1.91576600	1.35665900

S3.5.4 X=Cl^-

Ru	-0.22914900	0.00061300	0.00060800
N	-0.07091900	-1.73987100	1.30043100
H	-0.43667300	-1.65067000	2.24646500
H	-0.44442900	-2.61802900	0.94590800
N	-0.06181400	1.30016500	1.74039600
H	-0.43312700	2.24396400	1.65251000
H	-0.42841700	0.94526000	2.62130200
N	-0.06901500	1.74085100	-1.29913700
H	-0.44641300	1.65324200	-2.24054400
H	-0.43012300	2.62339500	-0.94218600
N	-0.07735300	-1.29962200	-1.73999100
H	-0.44920200	-2.24324500	-1.65031400
H	-0.44504700	-0.94389300	-2.62032300
N	-2.43521300	0.00325100	0.00337300
H	-2.83798500	-0.54757000	-0.75180000
H	-2.83569300	-0.37518200	0.85909000
H	0.94721900	1.39737000	1.86602200
H	0.93969600	1.86420300	-1.40224600
H	0.93106100	-1.39883100	-1.86881600
H	-2.83581700	0.93363400	-0.09564700
H	0.93768800	-1.87145900	1.39387500
Cl	2.19706000	-0.00426900	-0.00444300

S3.5.5 X=Pyridine

Ru	-0.93077900	-0.00066200	0.00056900
N	-0.91652700	-1.52140900	1.57759600
H	-1.56029800	-1.33866700	2.34658700
H	-1.14408000	-2.46768000	1.27427500
N	-0.92152800	1.51818600	1.58075600
H	-1.10630800	2.47235500	1.27320700
H	-1.60000300	1.35487700	2.32359400
N	-0.92262000	1.51991900	-1.57879600
H	-1.60296600	1.35640000	-2.32003100
H	-1.10415200	2.47499900	-1.27180900
N	-0.91752200	-1.51849900	-1.57937700
H	-1.14071800	-2.46704400	-1.27954600
H	-1.56407200	-1.33325100	-2.34552200
N	-3.14599200	0.00001400	-0.00101900
H	-3.55992400	-0.63607200	-0.68143900
H	-3.56328400	-0.27284600	0.88789800
H	-0.01764700	1.56022100	2.05068100
H	-0.01973500	1.55995100	-2.05076900
H	-0.00052700	-1.58704900	-2.01987100
H	-3.55495300	0.90990600	-0.20998300
H	0.00166600	-1.59403800	2.01494100
C	1.90806100	1.15298200	0.00037700
C	1.90924200	-1.15118100	-0.00045500
C	3.29486900	1.19600800	-0.00006400
H	1.33421100	2.07191000	0.00085100
C	3.29604300	-1.19313900	-0.00086800
H	1.33625800	-2.07073300	-0.00072200
C	4.01047500	0.00178100	-0.00068100
H	3.79954800	2.15475400	0.00012700
H	3.80149700	-2.15148300	-0.00129300
H	5.09419200	0.00229200	-0.00097500
N	1.19753500	0.00059000	0.00011100

S3.5.6 X=H_2O

Ru	-0.01842100	-0.01658500	-0.00827600
N	-1.19942600	-0.24443700	1.82517900
H	-2.19967000	-0.07747100	1.71752800
H	-1.13933500	-1.16124900	2.26755400
N	-1.32631300	1.64074400	-0.60818300
H	-0.89071200	2.30976900	-1.24268500
H	-2.17847100	1.35196800	-1.08803100
N	1.23857700	0.28753700	-1.76989700
H	1.61723500	-0.56259000	-2.18617900
H	0.80817100	0.78641800	-2.54803600
N	1.31992000	-1.64089100	0.60205200
H	1.19235100	-1.95873200	1.56249900
H	1.24547800	-2.48825300	0.03928800
N	-1.29030700	-1.40232400	-1.05217700
H	-0.98971800	-2.37463000	-0.98722600
H	-2.25448500	-1.41160600	-0.71966600
H	-1.65046700	2.20299000	0.17837600
H	2.05216000	0.84527700	-1.51068800
H	2.30441500	-1.38080000	0.54229400
H	-1.35611700	-1.21740600	-2.05292600
H	-0.89947200	0.41586700	2.54202100
O	1.34359700	1.42149800	1.01850500
H	1.28182900	2.38228700	0.96148500
H	1.92141100	1.21151300	1.76167600

S3.6 Complex S3

Rh	-0.06665100	-0.16893600	-0.03190800
Cl	-0.03608600	0.29037400	2.34203100
Cl	-0.44859400	-2.56473900	0.47527700
Cl	-0.14321300	-0.58416700	-2.42588300
P	2.24252600	-0.79448500	-0.04410100
P	-2.45809700	-0.03158800	0.02185200
C	0.15236300	1.71900400	-0.60209800
C	-3.20477400	-0.53896900	1.61570300
C	-3.27426200	-1.11166700	-1.21222900
C	-3.20485400	1.62535800	-0.29104200
C	2.61266000	-2.18084400	-1.18489400
C	2.85808200	-1.38456500	1.57828900
C	3.47723000	0.47864900	-0.55033700
H	2.79152800	-0.59040200	2.32118900
H	2.21828400	-2.20314700	1.90893800
H	3.89165400	-1.73105300	1.49395500
H	3.66097700	-2.47687100	-1.08882300
H	1.96273000	-3.01961400	-0.93827700
H	2.40206400	-1.87938200	-2.21011000
H	3.22823900	0.85152100	-1.54550800
H	3.47477700	1.31440600	0.15031300
H	4.48370900	0.05295200	-0.57797000
H	-2.92913500	1.97876800	-1.28669700
H	-4.29550900	1.58229100	-0.23030100
H	-2.84222000	2.33979700	0.45050500
H	-4.29484900	-0.55640400	1.53263700
H	-2.83466000	-1.53207100	1.86996900
H	-2.90138600	0.14598500	2.40596000
H	-2.99623300	-0.80404200	-2.21933500
H	-2.92077900	-2.13187400	-1.06297200
H	-4.36043200	-1.07160800	-1.09392600
H	-0.26901800	1.86919800	-1.59747100
N	0.67115600	2.83798800	-0.16068100
C	0.61651000	4.07389900	-0.95908900
C	1.35899100	3.01717100	1.12242100
H	0.11315900	3.88697100	-1.90475400
H	0.07727000	4.84674100	-0.40611800
H	1.63018400	4.43136500	-1.15523500
H	2.37201100	3.38384100	0.93587100
H	0.82573200	3.76314300	1.71644800
H	1.36917000	2.08360200	1.67147400

S4 Complex 3-H_2O

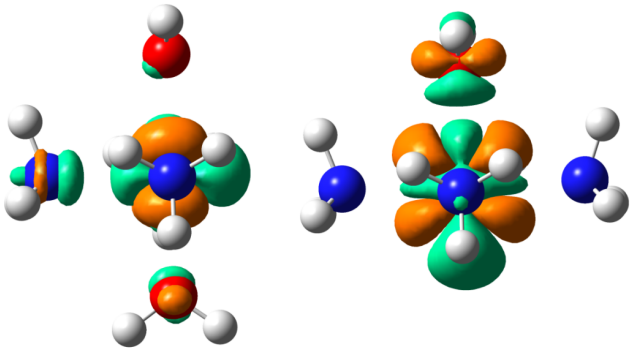

Figure S1: DD isosurfaces for the ML5 fragments deriving from **3-H_2O**, with a coordination vacancy *cis* (left) or *trans* (right) to the water molecule, with $-0.2 \leq \Delta s(\mathbf{r}) \leq 0.2$ a.u. Surfaces colours: orange, $\Delta s(\mathbf{r}) < 0$; green, $\Delta s(\mathbf{r}) > 0$. Colour scheme: red, O atoms; blue, N atoms; grey, C atoms; white, H atoms: clear blue, Rh atoms. The same orientation was chosen for the two molecular fragments (water molecules along the vertical axis).

Table S1: Integrated values of the electrophilic part of the DD for the *cis* and *trans* fragments built from **3-H_2O**. All values in atomic units.

	3-H_2O-cis	**3-H_2O-trans**
$\Delta s(D^+_{Rh})$	23.5	43.9
$V(D^+_{Rh})$	18.2	25.2
$\overline{\Delta s(D^+_{Rh})}$	1.29	1.74

S5 Complex 3-Cl

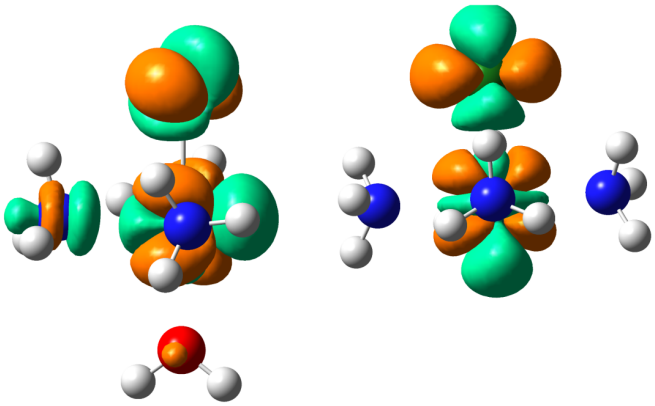

Figure S2: DD isosurfaces for the ML5 fragments deriving from **3-Cl**, with a coordination vacancy *trans* (left) or *cis* (right) to the chloride ligand. Same isovalues and colour scheme as figure S1.

Table S2: Integrated values of the electrophilic part of the DD for the *cis* and *trans* fragments built from **3-Cl**. All values in atomic units.

	3-Cl-cis	**3-Cl-trans**
$\Delta s(D^{+}_{Rh})$	43.7	21.9
$V(D^{+}_{Rh})$	26.2	19.2
$\Delta s(D^{+}_{Rh})$	1.67	1.14

S6 Complex S3: $[RhL(PMe_3)_2Cl_3]$, L=dimethylaminocarbene

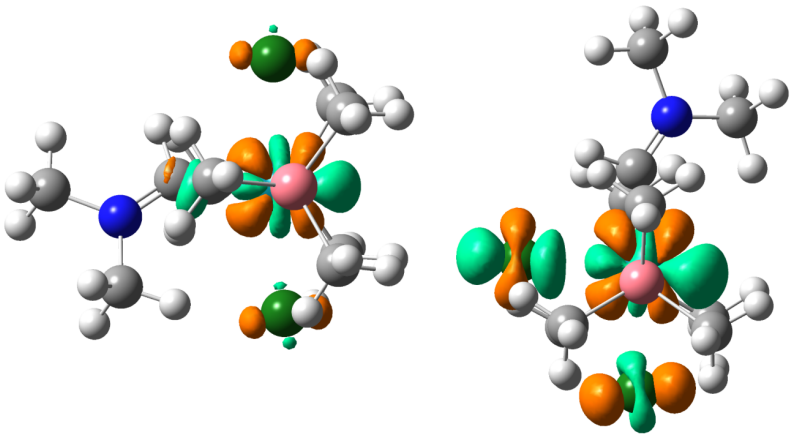

Figure S3: DD isosurfaces for the ML5 fragments deriving from **S3**, with a coordination vacancy *cis* (left) or *trans* (right) to the carbene ligand. Same isovalues and colour scheme as figure S1.

Table S3: Integrated values of the electrophilic part of the DD for the *cis* and *trans* fragments built from **S3**. All values in atomic units.

	S3-cis	**S3-trans**
$\Delta s(D^+_{Rh})$	47.3	19.8
$V(D^+_{Rh})$	30.7	20.3
$\Delta s(D^+_{Rh})$	1.54	0.97

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