Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting information for
Ultra-small rhenium clusters supported on graphene

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Energy profiles in high symmetry paths

The energy profiles for diffusion (energy vs. path coordinate), along with the total magnetization and distance from the surface vs. path coordinate, are shown in Figure S1. The two most important paths for diffusion are shown in Figure S1 (a) and (b).

For the hollow-bridge-hollow path, the plots are shown in Figure S1 (c). It can be seen, as noted in the manuscript, that the energy maximum is not located in the middle of the path. It can be observed that the energy maxima occur just before the change of spin. The change of spin is analyzed below, and it is caused for a change in the bonding state, being 1 μB and 5 μB tbe bonded and non-bonded magnetization, respectively. The change of spin is also correlated with a change in the distance from the surface, from 1.7 to 2.2 Å.

The hollow-top-bridge path, shown in Figure S1 (d), shows similar features than the previously analyzed path. The distance from the surface and magnetization vary in the same way, while the energy reaches a similar maximum value.

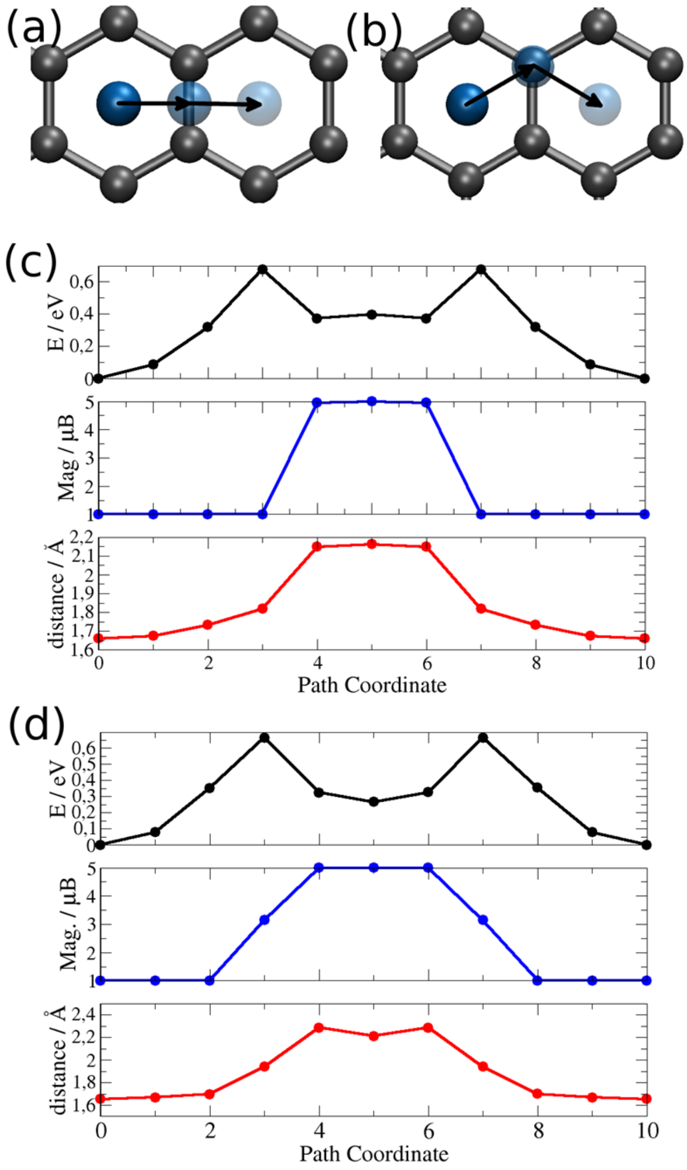

Figure S1. Hollow-bridge-hollow (a) and hollow-top-hollow (b) paths. Energy, magnetization and distance from the surface vs. path coordinate for the hollow-bridge-hollow path (c) and hollow-top-hollow path (d).

Analysis of density of states (DOS) and chemical bonding

The DOS of Re/graphene and isolated graphene, along with the projected density of states (PDOS) on the Re orbitals are shown in Figure S2, for both spin up and spin down states. It can be concluded from the difference between the graphene and the Re/graphene DOS that the bonding is predominantly covalent. There is evidence for hybridization between Re *s,p* and *d* orbitals with graphene states.

The *d* orbitals split into two peaks (plus a broad band), centered around approx. -1.0 and 0.0 eV in the spin up case, and -0.9 and +0.5 eV in the spin down case. This splitting is visualized in the charge density difference plots depicted in the paper (Figure 8), which evidence an accumulation of charge on the axial *d* orbitals (lower in energy) and depletion on the diagonal *d* orbitals (higher in energy, hence partially depleted). This splitting is the cause for the reduction of the magnetic moment (see next section).

From the Bader charge analysis, it was seen that a charge of +0.76 e was transferred to the graphene, which suggest that there is also partial ionic character. It is observed that the Dirac point of the graphene doesn't differ very much from the Fermi level in the spin up orbitals, but is shifted to lower energies by approx. 0.5 eV in the spin down states. This proves that spin down electrons are transferred from Re to graphene. The charge transfer implies an electrostatic contribution to the bonding energy.

For the spin up states, all of the Re valence states are partially occupied on the Fermi level, which suggests a metallic character. For the spin down case, however, the lower edge of the conduction band is close to the Fermi level, but there are not partially occupied states that could conduct electricity.

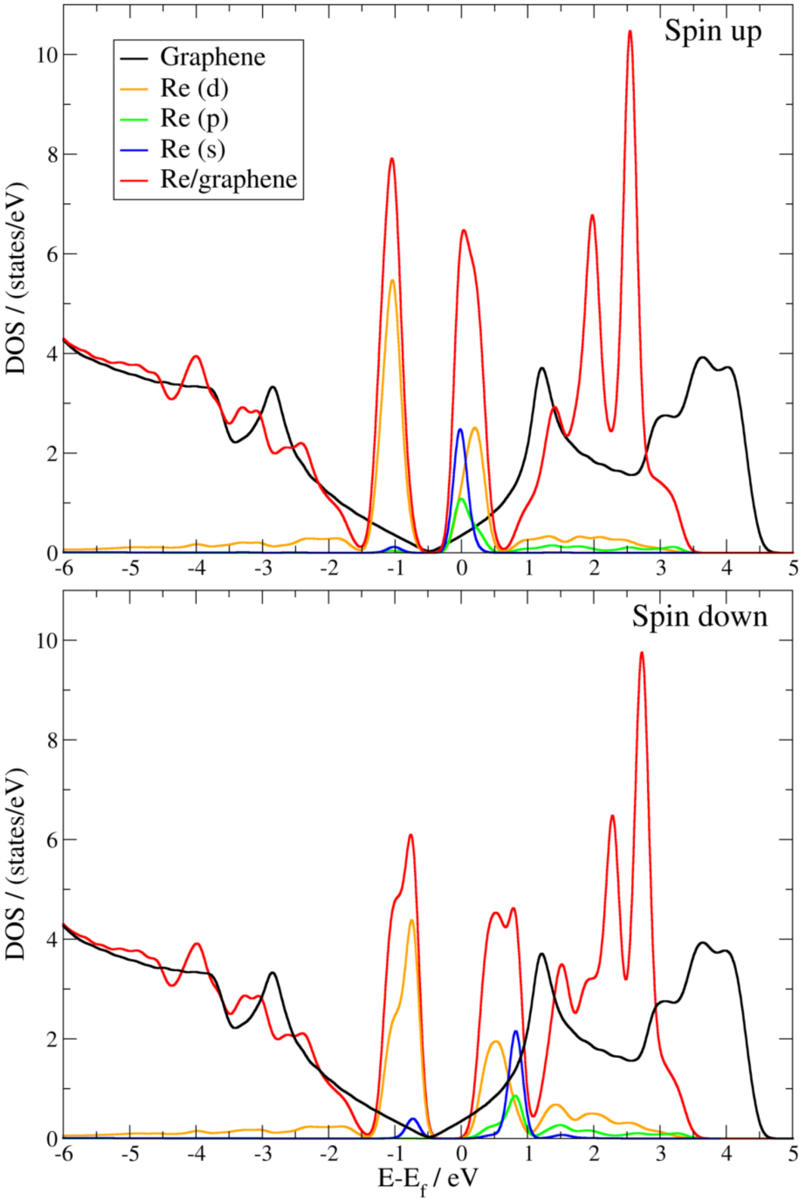

Figure S2. Re/graphene (DOS), Re (PDOS) and isolated graphene (DOS) plots for spin up (top) and spin down (bottom) states.

Analysis of magnetization and magnetic properties

As a result of the spin polarized calculations, the magnetic moment of the isolated Re clusters and the supported Re clusters could be found. This information is useful in the interpretation of the adsorption energies.

The change in magnetic moment of the Re atom is the most evident, since it has 5 unpaired d electrons in the vacuum (5 μB). When adsorbed, the d states split into two sets of states, those oriented to the x, y, z axis localized below the Fermi level. These states ($d_{x^2-y^2}$ and d_{z^2} perturbed by the graphene orbitals) fill with the 4*d* electrons, leaving 1 (unpaired) *d* electron occupying the more energetic (perturbed) *d* states, hence explaining the resulting magnetic moment (1 μB).

The analysis of the rest of the structures is more complicated, since the geometry is also a crucial factor. For example, among the octahedral structure in the three different orientations on the surface (3t, 3e, 3s), the 3s orientation shows zero net magnetic moment, which causes its absorption energy to become more negative (approx. 0.2 eV more stable than the other orientations).

The isolated 3e magnetic moment differs from the other orientations (which is not correct, since it is the same cluster in vacuum, and hence should have the same magnetic moment) because a different spreading for Brillouin zone integration had be used for the calculation to converge. The same is the case for the 5t and 5e orientations, although the difference between these is smaller. The relevance of the initial orientation is evident here, since both 5t and 5e structures relaxed approximately to the same geometry, but their magnetic moments differ.

Structure	**Magnetization of supported Re cluster (μ_B)**	**Magnetization of isolated Re cluster (μ_B)**
1	1.00	5.00
2	3.02	3.57
3t	1.20	1.68
3e	0.86	2.00
3s	0.00	1.67
4	0.01	1.99
5t	0.01	3.15
5e	0.73	2.97
6	0.54	0.97
7	1.01	1.93
8	0.00	0.00

Table S1. Magnetization of the structures 1-8, isolated (right) and supported on graphene (left).