Activation of the H–H bond by Ni_2-porphyrinate

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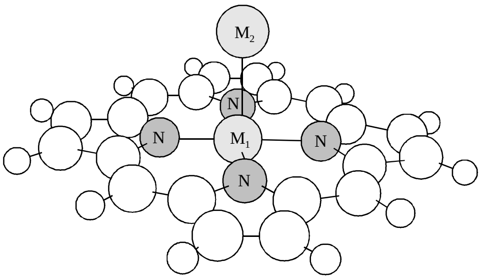
The H–H bond is activated without any barrier by Ni_2-porphyrinate, based on calculations in terms of the reaction-path Hamiltonian approximation.

The creation of catalytic cycles for selective alkane functionalization is one of the most important chemical problems. The reactions leading to H–H, C–H and C–C bond breaking (*i.e.*, H–H, C–H and C–C bond activation) are the key processes in such catalytic cycles.[1–4]

We have performed a theoretical study of H–H bond activation by bimetallic singlet coordinately unsaturated porphyrin complexes (Por–M_1–M_2, where $M_{1,2}$ = Ni).



Presently, there is no practical evidence that such a complex exists.

We studied the reaction in terms of the reaction-path Hamiltonian approximation.[5] The potential-energy surface (PES) was computed by the semiempirical CNDO/S^2 method that is aimed at an evaluation of the reaction PESs with participation of Pd and Ni atoms, Pd_2 and Ni_2 clusters, as well as their complexes.[6]

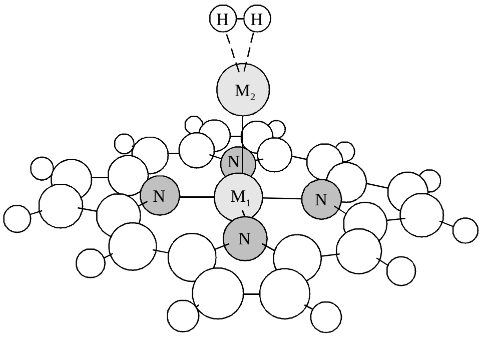
Three stationary points have been found on the PES of the activation. These are: precursor complex (PC), transition state (TS) and product (PR) (all the energies are given with respect to the separate reactants).

Data on the geometry structure (R, r, α) and the charges (q) on the atoms of the structures of the stationary points of the PESs are presented in Table 1.

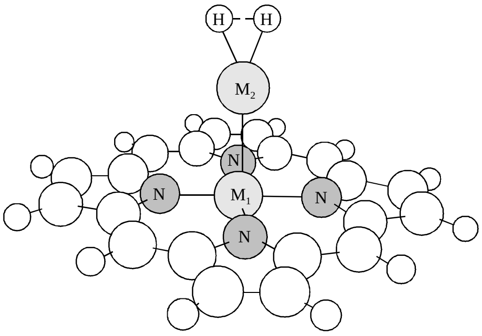
Analysis of the eigenvalues and eigenvectors of the Hessian matrices showed that in the TS–PR range displacements of the atoms corresponding to the vector directed along the reaction path (RP) were determined mainly by variation in the only internal coordinate, namely, α(H–Ni–H). We have obtained a similar result for oxidative dihydrogen addition to the Pd atom.[7]

Thus, the catalytic activity of a Por–M_1–M_2 system is determined by the M_2 atom lying above the plane of the porphyrin.

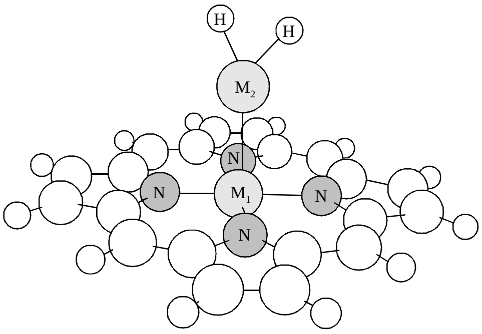
We have found only a PC minimum for the Por–Pd–Pd + H_2 reaction. The other stationary points are absent.



PC, E = –6.1 kcal mol^{-1}



TS, E = –0.4 kcal mol^{-1}



PR, E = –13.2 kcal mol^{-1}

In order to verify our results, we calculated the geometry structures of Por–Ni–Ni–H_2, Por–Pd–Pd–H_2 and Por–Ni–Pd–H_2 using the DFT program in ref. 8. These calculations confirmed our conclusions made earlier from the results of the CNDO/S^2 method, namely: the product Por–Ni–Ni–H_2 [r(Ni–H) = 1.45 Å, E = –15.9 kcal mol^{-1}] was found, while in the other two systems only molecular adsorption complexes were found to be formed [r(Pd–H) = 1.78 Å].

Table 1 Geometry data and atomic charges of the structures of the stationary points of the PES of H–H bond activation by Ni_2-porphyrinate. R, r are the distances between the Ni–Ni and Ni–H atoms, α is the H–Ni–H angle and q are nuclear charges.

Structure	R/Å	r/Å	α/°	q_{Ni_1}/e	q_{Ni_2}/e	q_H/e
PC	2.71	2.04	22	0.82	0.04	0.00
TS	2.98	1.50	39	0.82	0.02	–0.02
PR	2.92	1.45	92	0.80	0.45	–0.23

We think that complexes may exist in which the transition metal atoms would be as active as bare metal atoms (or, possibly, bare clusters), and such complexes would allow us to create real catalytic cycles.

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