A theoretical study of the hydrogen molecule activation by the Ni_2 cluster, nickel phthalocyanine and a complex formed by nickel phthalocyanine with the Ni_2 cluster

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A new system based on the addition of the Ni_2 cluster to a mononuclear phthalocyanine complex with an energy stability of about 26 kcal mol^{-1} was suggested for the barrierless activation of the H–H bond.

According to experimental data, mononuclear transition metal complexes in solutions[1–3] and metal surfaces[4,5] catalyse many reactions with the activation of H–H, C–H and C–C bonds.

Catalytic systems can also be developed in the absence of solutions on the basis of isolated mononuclear phthalocyanine complexes of transition metals (MPc). The complexes can be immobilised on solid surfaces, and they are the most active catalysts for oxidation by molecular oxygen.[6–8]

The reactions of H–H and C–H bond activation by mononuclear transition metal complexes take place with considerable activation barriers, and the energy of products may be higher than the energy of isolated reactants.[9–14]

Transition metal clusters are more effective than mononuclear transition metal complexes.[15,16]

We theoretically found[17(*a*)] that catalysts based on binuclear palladium complexes are best suited for ethylene hydrogenation.

In many cases, the processes of H–H bond activation by transition metal clusters in a gas phase are barrierless,[16,17(*b*),18] as distinct from the activation by mononuclear complexes. However, in contrast to metal complexes, clusters are unstable in a gas phase; they are produced by the action of powerful radiation on a metal surface before an activation process.[16]

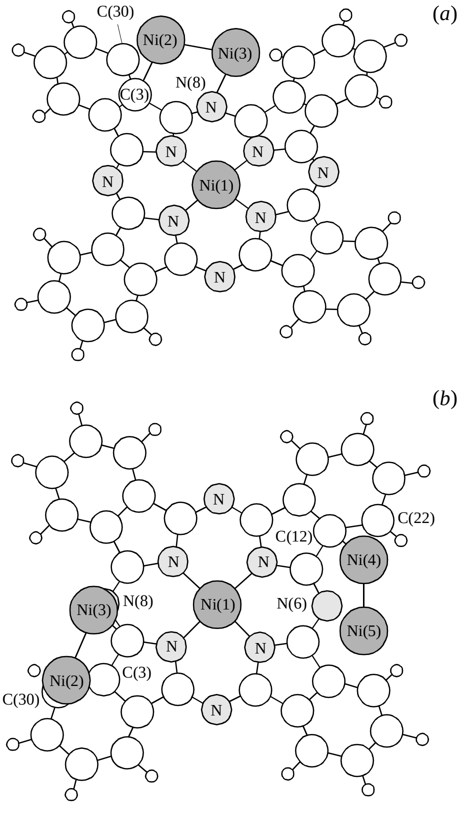

Figure 1 The numbering of atoms in the molecules (*a*) PR(I) and (*b*) PR(II) of the products of reactions (I) and (II).

Based on a theoretical study, we found that the Ni_2 clusters can be stabilised by the addition to the MPc=NiPc molecule with the formation of bonds with peripheral atoms of the macrocyclic ring:

$$\mathrm{Ni(1)Pc + (Ni\text{–}Ni) \rightarrow Ni(1)Pc(Ni\text{–}Ni)} \qquad \mathrm{(I)}$$

$$\mathrm{Ni(1)Pc(Ni\text{–}Ni) + (Ni\text{-}Ni) \rightarrow Ni(1)Pc[2(Ni\text{–}Ni)]} \qquad \mathrm{(II)}$$

We also found that Ni–Ni does not form a metal–metal bond with the Ni(1) atom of the Ni(1)Pc complex:

$$\mathrm{Ni(1)Pc + (Ni\text{–}Ni) \rightarrow [Ni\text{–}Ni(1)\text{–}Ni]Pc \rightarrow Ni(1)Pc(Ni\text{–}Ni)} \qquad \mathrm{(Ia)}$$

We examined the reactions of H–H bond activation by the NiPc molecule, the Ni–Ni cluster and the Ni(1)Pc(Ni–Ni) complex:

$$\mathrm{NiPc + H_2 \rightarrow (H\text{–}Ni\text{–}H)Pc} \qquad \mathrm{(III)}$$

$$\mathrm{(Ni\text{–}Ni) + H_2 \rightarrow H\text{–}(Ni\text{–}Ni)\text{–}H} \qquad \mathrm{(IV)}$$

$$\mathrm{Ni(1)Pc(Ni\text{–}Ni) + H_2 \rightarrow Ni(1)Pc[H\text{–}(Ni\text{–}Ni)\text{–}H]} \qquad \mathrm{(V)}$$

We found that reactions (IV) and (V) are barrierless.

The calculations were performed using the density functional theory (DFT), which was successfully applied to metal complexes such as metal porphyrins.[19–22] The published computer program[23] and the exchange correlation functional PBE[22] were used.

Large orbital basis sets of contracted Gaussian-type functions of the size (5s1p)/[3s1p] for H, (11s6p2d)/[6s3p2d] for C, N and (18s13p8d)/[12s9p4d] for Ni were used in conjunction with the density-fitting basis sets of uncontracted Gaussian-type functions of the size (5s1p) for H, (10s3p3d1f) for C, N and (18s6p6d5f 5g) for Ni. The basis set was optimised by D. N. Laikov.[23]

Based on the full optimisation of molecular systems, we examined the geometry of the products [PR(i), i = I, II], as well as the energy difference between PR and separated reactants (SR) $\Delta E(i) = E[\mathrm{PR}(i)] - E[\mathrm{SR}(i)]$, for reactions (I) and (II).

According to the molecular geometry of PR(I) = Ni(1)Pc(Ni–Ni), the Ni–Ni cluster occurs at a considerable distance from Ni(1), which is longer than 4.5 Å, and forms bonds with the peripheral atoms of Ni(1)Pc [see Figure 1(*a*) and Table 1]. The obtained value $\Delta E(\mathrm{I}) = -26.6$ kcal mol^{-1} is indicative of the stabilisation of the Ni–Ni cluster.

Qualitatively, the addition of the second cluster to Ni(1)–Pc(Ni–Ni) [reaction (II)] is analogous to reaction (I) [see Figure

Table 1 Atomic distances in the products of reactions (I) and (II)/Å.

Distance[a]	PR(I)	PR(II)
R[Ni(2)–Ni(3)]	2.45	2.40
R[Ni(2)–C(3)]	1.99	2.01
R[Ni(2)–C(30)]	2.01	1.93
R[Ni(3)–N(8)]	1.92	1.89
R[Ni(4)–Ni(5)]	0	2.44
R[Ni(4)–C(12)]	0	1.99
R[Ni(4)–C(22)]	0	2.01
R[Ni(5)–N(6)]	0	1.92

[a] The numbering of atoms is shown in Figure 1.

Table 2 Atomic distances in the product of reaction (V)/Å.

Distance	PR(V)
R[Ni(2)–Ni(3)]	2.35
R[Ni(2)–C(3)]	2.11
R[Ni(2)–C(30)]	2.08
R[Ni(3)–N(8)]	2.03
R[Ni(2)–H(17)]	1.62
R[Ni(2)–H(18)]	1.57
R[Ni(3)–H(17)]	1.64
R[Ni(3)–H(18)]	1.61
R[H(17)–H(18)]	1.81

1(*b*) and Table 1]. In this case, ΔE(II) = –25.5 kcal mol^{-1}, which is close to ΔE(I).

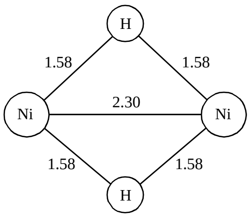

Figure 2 The structure of the product of reaction (IV) (bond lengths in angstrom units).

The [Ni–Ni(1)–Ni]Pc complex was examined because we assumed that the Ni–Ni cluster could be stabilised by the formation of metal–metal bonds with the Ni(1) atom of the Ni(1)Pc complex [reaction (Ia)].

The DFT optimisation of the Ni(1)Pc complex suggested that the Ni(1) atom has four bonds with four nitrogen atoms with the same lengths *R*[Ni(1)–N] = 1.91 Å. To form metal–metal bonds at the Ni(1) atom, the Ni–Ni cluster was oriented with the bond lengths *R*[Ni(1)–Ni] = 2.3 Å, which are close to *R*(Ni–Ni) in the Ni–Ni cluster (see Figure 2). In the [Ni–Ni(1)–Ni]Pc complex thus obtained the closest distances are *R*(Ni–N) ≈ 2.5 Å, which are much longer than *R*[Ni(1)–N] = 1.91 Å. The structure of the [Ni–Ni(1)–Ni]Pc complex changed after the optimisation. The internuclear distances Ni–Ni(1) increased from 2.3 to 2.5 and 2.7 Å. At the same time, the Ni–N bonds 1.9 Å long were formed. Thus, the [Ni–Ni(1)–Ni]Pc complex was converted into the PR(Ia) = Ni(1)Pc(Ni–Ni) complex. In the PR(Ia) complex, the Ni–Ni cluster is closer to Ni(1) than in the PR(I) complex. In this case, the energy difference ΔE(Ia) was –14.6 kcal mol^{-1}, which is 12 kcal mol^{-1} higher than ΔE(I). Thus, the Ni–Ni cluster on Ni(1)Pc becomes more stable by the formation of Ni–N and Ni–C bonds at the longest Ni–Ni distances from Ni(1).

To study the reaction of H–H bond activation by the NiPc complex [reaction (III)], we optimised (H–Ni–H)Pc with different fixed *R*(H–H). Figure 3 summarises the results. It can be seen that NiPc cannot activate the H–H bond of the hydrogen molecule. The optimisation of the (H–Ni–H)Pc complex with no fixed R(H–H) resulted in the separated reactants NiPc + H_2.

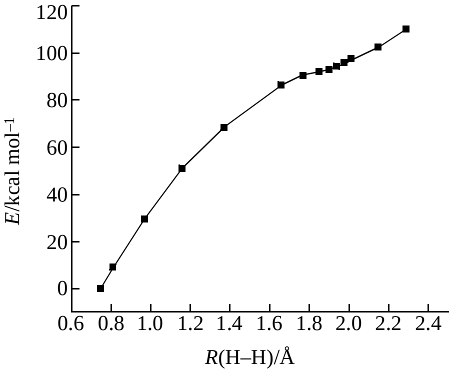

Figure 3 The energy profile constructed on the basis of the optimisation of (H–Ni–H)Pc with different fixed *R*(H–H): *E* is the energy difference *E*[(H–Ni–H)Pc] – *E*[SR(1a)].

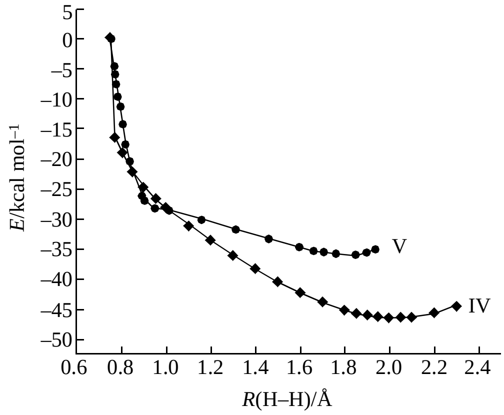

Figure 4 The reaction profiles for H–H bond activation in hydrogen molecules by (IV) the Ni–Ni cluster and (V) the Ni(1)Pc(Ni–Ni) complex: *R*(H–H) (Å) is the reaction coordinate.

To examine the reaction path (RC) of H–H bond activation in the hydrogen molecule by the Ni–Ni cluster [reaction (IV)], we optimised H–(Ni–Ni)–H with different fixed *R*(H–H). The rhombic orientation between H–H and Ni–Ni was retained over the entire path; this is consistent with the results of a study on the barrierless activation of the H–H bond by the Pd–Pd complex.[18] Figures 2 and 4 illustrate the results. Evidently, the H–H bond activation by the Ni–Ni cluster is barrierless and ΔE(III) = = –46.44 kcal mol^{-1} (with respect to the singlet state of Ni–Ni).

To examine the H–H bond activation in the hydrogen molecule by the Ni(1)Pc(Ni–Ni) complex [reaction (V)], we optimised the structure of Ni(1)Pc[Ni(H–H)Ni] with different fixed *R*(H–H). We found that the H_2 molecule can be activated by the Ni(1)Pc(Ni–Ni) complex (Figure 4), and this activation is barrierless, as well as the activation of H–H bonds by clusters in a gas phase.

In the activation of the H_2 molecule by the Ni(1)Pc(Ni–Ni) complex [PR(V)] the bond lengths *R*(Ni–N) and *R*(Ni–C) of the Ni–Ni cluster with NiPc atoms insignificantly increased by ~0.1 Å (Tables 1 and 2). The bond lengths *R*(H–Ni) of hydrogen atoms of the activated H_2 molecule with the Ni–Ni cluster atoms on the surface of NiPc are ~1.6 Å. They are insignificantly different from the corresponding bond lengths of the reaction product in the activation of the hydrogen molecule by isolated Ni–Ni clusters (Figure 2, Table 2).

The stabilisation energy is ΔE(V) = –35.5 kcal mol^{-1}; thus, the product of hydrogen molecule activation by the Ni(1)Pc(Ni–Ni) complex is more stable than that in the activation by mononuclear complexes.[9,12,14,24]

Thus, effective catalytic systems can be developed on the basis of isolated Ni(1)Pc molecules with transition metal clusters.

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