J. Am. Chem. Soc. **1998,** 120, 7770−7775

A DFT Investigation of Ethylene Dimerization Catalyzed by Ni(0) Complexes

Fernando Bernardi,* Andrea Bottoni,* and Ivan Rossi

Contribution from the Dipartimento di Chimica "G.Ciamician", Universita' di Bologna, via Selmi 2, 40126 Bologna, Italy

Received February 23, 1998. Revised Manuscript Received June 2, 1998

Abstract: In this paper we have studied the [2+2] cycloaddition of two olefins catalyzed by Ni(0) complexes using a hybrid DFT/B3LYP computational approach with the pseudopotential LANL2DZ basis set. Two model systems have been used to emulate the catalytic process: the ethylene−nickel complex $Ni(PH_3)_2C_2H_4$ and the bis(ethylene)−nickel complex $Ni(PH_3)_2(C_2H_4)_2$, both reacting with an ethylene molecule. For both these complexes we have investigated in detail the first steps of the catalytic process, corresponding to the formation of nickelacyclopentane, which has been experimentally demonstrated to produce the cyclobutane product by reductive elimination. We have found that the incoming ethylene molecule reacts with both complexes not at the metal center but at one ligand ethylene. This attack affords an *anti* 1,5-biradical intermediate that can lead to nickelacyclopentane and where the two unpaired electrons are mainly localized on the nickel atom and on the terminal methylene. While for the attack of the ethylene molecule on $Ni(PH_3)_2C_2H_4$ no catalytic effect is observed (the activation energy is almost identical to that found for the noncatalyzed process, i.e., about 40 kcal mol^{-1}), a catalytic effect, even if not very large, is found for the $Ni(PH_3)_2(C_2H_4)_2$ complex (the barrier decreases to 35.80 kcal mol^{-1}). A diabatic analysis has pointed out that the factors which are responsible for the catalytic effect of the $Ni(PH_3)_2(C_2H_4)_2$ complex are the energy gap between the singlet ground state and the first triplet state in the complex and the stability of the biradical intermediate.

1. Introduction

The [2+2] cycloadditions are an important class of reactions since they represent an effective synthetic approach to the formation of four-membered rings. Experimentally these cycloadditions, and in particular the nonpolar ones, take place at high temperatures (400−700 °C) owing to the large activation energies involved. However, when these reactions are catalyzed by transition metal complexes, they can proceed much faster and under milder conditions. A vast amount of experimental work on cycloaddition reactions catalyzed by transition metals has been carried out in the last two decades.[1] A typical example is the thermal isomerization of quadricyclane to norbornardiene. This reaction is known to proceed slowly ($t_{1/2}$ > 14 h at 140 °C if no catalyst is used) despite the extraordinary high strain energy (78.7 kcal mol^{-1}) that can be released through the isomerization. However Rh(I), Pd(II), Pt(II), and Ni(0) complexes catalyze this isomerization effectively even at low temperature: for instance the use of 2 mol % of di-μ-chloro-bis(norbornadiene)dirhodium accelerates this reaction by a factor of 10^{19}.[1a,f] Various transition metal compounds, notably of rhodium, are excellent catalysts for the isomerization of cubane and its derivatives to the corresponding syn-tricyclooctadienes.[1c] Complexes of zerovalent nickel have been shown to catalyze [2+2] cycloadditions of strained-ring olefins to give cyclobutane derivatives.[1g] Quite recently it has been demonstrated that [CpRuCl(cod)] (Cp = pentamethylcyclopentadienyl, cod = cyclooctadiene) is an excellent catalyst for the [2+2] cycloaddition of norbornene with various alkynes.[1j]

In addition to their synthetic importance, [2+2] catalyzed cycloadditions have also attracted much theoretical interest since transition metals apparently remove the symmetry constraints that make such reactions thermally forbidden in a concerted approach according to the Woodward−Hoffmann symmetry rules.[2] To explain this behavior two alternative mechanisms have been proposed. In the first mechanism the two new C−C bonds are formed simultaneously (concerted mechanism): in this case the function of the metal is to provide suitable d-orbitals which can combine with the olefin π orbitals making the reaction symmetry allowed. The second mechanism is nonconcerted and is schematically represented in Scheme 1. This mechanism involves the formation of 1:1 and 1:2 metal−olefin complexes (steps a and b) followed by the formation (step c) of a metal−carbon σ-bonded intermediate (metallacyclopentane) that can lead (step d) to the cyclobutane product by reductive elimination.

The fact that metallacyclopentanes have been trapped from metal-catalyzed cycloaddition reactions and also prepared as stable compounds[3] provides evidence for this nonconcerted

---

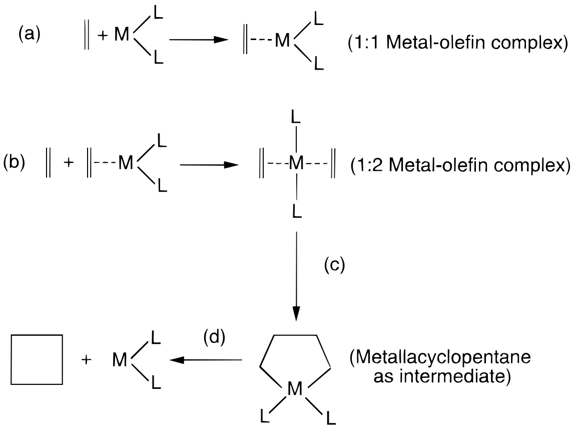
[1] (a) Hogeveen, H.; Volger, H. C. *J. Am. Chem. Soc.* **1967**, *89*, 2486. (b) Katz, T. J.; Cerefice, S. A. *J. Am. Chem. Soc.* **1969**, *91*, 6519. (c) Cassar, L.; Eaton, P. E.; Halpern, J. *J. Am. Chem. Soc.* **1970**, *92*, 3515. (d) Noyory, R.; Kumagai, Y.; Takaya, H. *J. Am. Chem. Soc.* **1974**, *96*, 634. (e) Binger, P.; Schroth, G.; McMeeking, J. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 465. (f) Noyory, R.; Umeda, I.; Kawauchi, H.; Takaya, H. *Angew. Chem., Int. Ed. Engl.* **1975**, *97*, 812. (g) Doyle, M. J.; McMeeking, J.; Binger, P. *J. Chem. Soc., Chem. Commun.* **1976**, 376. (h) Mitsudo, T.; Kokuryo, K.; Shinsugi, T.; Nakagawa, Y.; Watanabe, Y.; Takegami, Y. *J. Org. Chem.* **1979**, *44*, 4492. (i) Mitsudo, T.; Hory, Y.; Watanabe, Y. *J. Organomet. Chem.* **1987**, *334*, 157. (j) Mitsudo, T.; Naruse, H.; Kondo, T.; Ozaki, Y.; Watanabe, Y. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 580.

[2] (a) Woodward, R. B.; Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 781 and references therein. (b) Mango, F. D.; Schachtsschneider, J. H. *J. Am. Chem. Soc.* **1967**, *89*, 2484.

[3] (a) Fraser, A. R.; Bird, P. H.; Bezman, S. A.; Shapley, J. R.; White, R.; Osborn, J. A. *J. Am. Chem. Soc.* **1973**, *95*, 597. (b) Grubbs, R. H.; Miyashita, A.; Liu, M-I. M.; Burk, P. L. *J. Am. Chem. Soc.* **1977**, *99*, 3863. (c) Grubbs, R. H.; Miyashita, A. *J. Am. Chem. Soc.* **1978**, *100*, 1300.

S0002-7863(98)00604-0 CCC: $15.00

Scheme 1



mechanism. For example, in the symmetry-forbidden dimerization of norbornadiene catalyzed by the [Ir(1,5-cyclooctadiene)Cl] complex, a metallacyclopentane compound has been isolated where two norbornadiene molecules form a metallacyclopentane by insertion of the Ir atom into the four-membered ring of an incipient norbornadiene dimer molecule.[3a] Further, a series of phosphinenickelacyclopentanes has been shown to undergo β-carbon−carbon bond cleavage (the reverse of the first step of the [2+2] cycloaddition reaction) and reductive elimination (the required second step of the [2+2] cycloaddition reaction).[3b] There is also evidence that these compounds decompose by reversible carbon−carbon bond cleavage to produce 1:2 metal−olefin complexes,[3b] like those postulated in Scheme 1.

In this paper we present the results of a theoretical study, carried out at the density functional theory (DFT)[4] level, of the catalyzed [2+2] cycloaddition of two ethylenes which, to our knowledge, has never been investigated with theoretical methods. It is our goal to apply the DFT theory to shed light on the mechanistic details (energetics and kinetics) of this important transition metal-catalyzed reaction. In particular we focus our attention on the first steps of the reaction which lead to the formation of the metallacyclopentane complex. The model system that we have considered is formed by a $Ni(PH_3)_2$ fragment that can bond either one or two ethylene molecules to form the $Ni(PH_3)_2C_2H_4$ or $Ni(PH_3)_2(C_2H_4)_2$ complexes that we assume to represent two possible active forms of the catalyst. For both complexes we investigate the reaction with an additional ethylene molecule. To check the reliability of the DFT computational approach used throughout the paper we also reexamine at this computational level the noncatalyzed [2+2] cycloaddition of two ethylenes. These results are presented in the next section and compared with the results previously obtained for the same reaction at the CASSCF-MP2 level.[5]

2. Choice of the Method

In a previous paper[5] we have demonstrated that the CASSCF-MP2 computational approach for the noncatalyzed thermal dimerization of ethylene provides results which are in good agreement with the experiment. However, this method cannot be used to study the catalyzed reaction, since, even for the simple model system studied here, it requires such a large active-orbital space that makes computations too demanding to be used effectively. Recently it has been reported in the literature that the DFT method based on the hybrid B3LYP functional[6] can be used to study cycloaddition processes: in particular it has been shown that B3LYP reliably describes both the concerted and the biradical pathways for some [4+2] cycloadditions.[7] Furthermore, in a very recent study on the $Ni(C_2H_4)_2$ complexes,[8] we have demonstrated that the DFT approach, using several different functionals and either the all-electron DZVP basis[9] or the LANL2DZ pseudopotential basis,[10] satisfactorily reproduces the results obtained with the CASPT2 method and an extended basis set.

To further test the method we have investigated at the unrestricted B3LYP level with the 6-31G* basis[11] (B3LYP/6-31G* level) the first step of the noncatalyzed [2+2] dimerization of ethylene, i.e., the formation of the intermediate tetramethylene biradical. We have considered in this study only the *anti* approach of two ethylenes since previous studies have shown that it corresponds to the lowest-energy reaction path.[5]

All the DFT computations reported here have been performed with the Gaussian 94[12] series of programs. In all cases the geometries of the various critical points have been fully optimized with the gradient method. The nature of each critical point has been characterized by computing the harmonic vibrational frequencies.

Along the *anti* reaction path we have identified an *anti* transition state (TS), corresponding to the formation of a new C−C bond, and an *anti* biradical intermediate (M) whose structures are schematically represented in Figure 1. In this figure we have reported the values of the most relevant geometrical parameters obtained either at the B3LYP/6-31G* level in this work or at the CASSCF/6-31G* level in our previous work[5] (values in parentheses) and also the values of the energies relative to reactants represented by two noninteracting ethylene molecules (the energy values reported in parentheses had been obtained by means of single-point multireference MP2 computations on the CASSCF optimized geometries: CASSCF-MP2 computations). The optimum values for the new forming C−C bond in the transition state and in the biradical intermediate are 1.796 and 1.612 Å, respectively, and compare quite well with the CASSCF values (1.801 and 1.640 Å, respectively). Also the energetics determined with the two computational approaches are in satisfactory agreement: the B3LYP method provides an activation energy for the formation of the biradical intermediate of 40.34 kcal mol^{-1} and a fragmentation barrier of 1.35 kcal mol^{-1}. These values agree very well with the values computed at the CASSCF-MP2 level (42.20 and 1.33 kcal mol^{-1}, respectively) and also with the experimental estimate of the activation energy (43.8 kcal

---

[4] Parr, R. G.; Yang, W. *Density-Functional Theory of Atoms and Molecules*; Oxford University Press: New York, 1989.

[5] Bernardi, F.; Bottoni, A.; Celani, P.; Olivucci, M.; Robb, M. A.; Venturini, A. *Chem. Phys. Lett.* **1992**, *192*, 229.

[6] (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 1372, 5648. (b) Stephens, P. J.; Devlin, F. J.; Chabalowsky, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623.

[7] (a) Li, Yi; Houk, K. N. *J. Am. Chem. Soc.* **1993**, *115*, 7478. (b) Goldstein, E.; Beno, B.; Houk, K. N. *J. Am. Chem. Soc.* **1996**, *118*, 6036. (c) Barone, V.; Arnaud, R. *J. Chem. Phys.* **1997**, *106*, 8727.

[8] Bernardi, F.; Bottoni, A.; Calcinari, M.; Rossi, I.; Robb, M. A. *J. Phys. Chem.* **1997**, *101*, 6310.

[9] Godbout, N.; Salahub, D. R.; Andzelm, J.; Wimmer, E. *Can. J. Chem.* **1992**, *70*, 560.

[10] Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270. Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 284. Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299.

[11] Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

[12] *Gaussian 94, Revision B.2*; Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; J. A. Pople Gaussian, Inc.: Pittsburgh, PA, 1995.

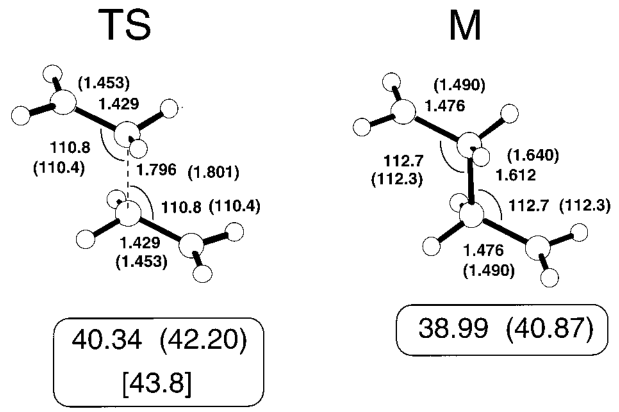


Figure 1. Schematic structures of the *anti* biradical transition state TS and the *anti* biradical tetramethylene intermediate M for the noncatalyzed ethylene dimerization obtained at the B3LYP/6-31G* level. The values obtained at the CASSCF/6-31G* level (geometries) and CASSCF-MP2/6-31G* level (energies) are reported (ref 5) in parentheses. Bond lengths are in angstroms and angles in degrees. The energy values (kcal mol^{-1}) are reported in the two frames and are relative to reactants (the reactant energy at the B3LYP/6-31G* level is −157.15641 hartrees). The value reported in square brackets for TS corresponds to the experimental activation energy taken from ref 13.

mol^{-1}).[13] Thus these computational evidences indicate that an unrestricted B3LYP approach can be used with confidence to study the model system of the catalyzed ethylene dimerization. All the B3LYP computations for the catalyzed reaction have been carried out with the LANL2DZ pseudopotential basis which, as previously pointed out, is capable of providing a reliable description of ethylene and bis(ethylene)−nickel complexes.[8]

3. Results and Discussion

In this section we discuss in detail the following steps of the catalyzed reaction: (i) the formation of the ethylene−nickel and bis(ethylene)−nickel complexes ($Ni(PH_3)_2C_2H_4$ and $Ni(PH_3)_2(C_2H_4)_2$) which should correspond to the active forms of the catalyst; (ii) the attack of a free ethylene to the active catalysts resulting in the formation of biradical intermediates; and (iii) the intramolecular coupling of the biradicals leading to the formation of nickelacyclopentane. The geometries corresponding to the various critical points located on the surface are schematically represented in Figures 2−5. For each structure we have reported the values of the most significant geometrical parameters and the corresponding energy values.

(a) The Ethylene−Nickel and Bis(ethylene)−Nickel Complexes. In the study of the first steps of the catalytic process we have identified two complexes, both arising from the interaction between the $Ni(PH_3)_2$ fragment with ethylene molecules. The two complexes are denoted as M_1 and M_2 and are schematically represented in Figure 2. M_1 is a planar tricoordinated complex with only one ethylene molecule bonded to Ni while M_2 is a tetracoordinated complex characterized by a tetrahedral geometry that forms from M_1 after coordination of an additional ethylene molecule to the metal atom. A comparison between the two structures shows that the addition of one ethylene molecule on passing from M_1 to M_2 is responsible for a lengthening of the Ni−C and Ni−P bonds: the two Ni−C bonds are 1.986 Å in M_1 and become 2.068 and 2.107 Å in M_2 while the Ni−P bonds change from 2.268 to 2.358 Å. As a consequence of the lengthening of the Ni−C bonds the C−C bond in ethylene is shorter in M_2 than in M_1.

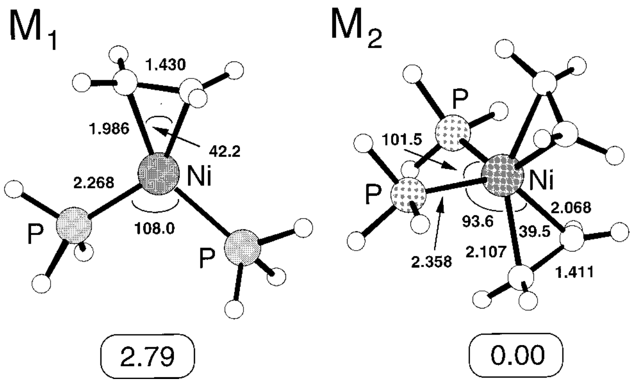


Figure 2. Schematic structures of the ethylene−nickel and bis(ethylene)−nickel complexes M_1 and M_2 obtained at the B3LYP/LANL2DZ level. Bond lengths are in angstroms and angles in degrees. The energy values (kcal mol^{-1}) are reported in the two frames and are relative to the M_2 complex (−343.05139 hartrees).

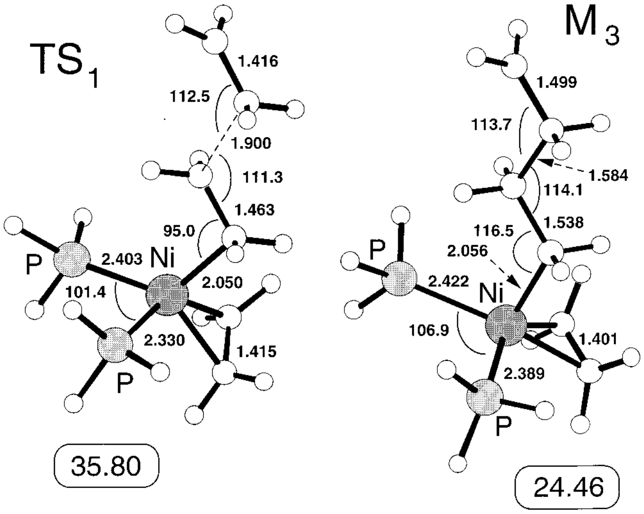


Figure 3. Schematic structures, obtained at the B3LYP/LANL2DZ level, of the *anti* biradical transition state TS_1 and of the *anti* biradical intermediate M_3 associated with the attack of an ethylene molecule on the M_2 complex. Bond lengths are in angstroms and angles in degrees. The energy values (kcal mol^{-1}) are reported in the two frames and are relative to the system formed by the M_2 complex and a noninteracting ethylene molecule (−421.62959 hartrees).

The energies reported in Figure 2 are relative to the M_2 complex. These values indicate that M_2 is more stable by 2.79 kcal mol^{-1} than M_1 and a noninteracting ethylene molecule. Furthermore, the computations have shown that both M_1 and M_2 form without any barrier from the corresponding noninteracting fragments ($Ni(PH_3)_2$ and ethylene in the former case and M_1 and ethylene in the latter).

(b) Attack of a Free Ethylene on the Active Catalyst and Formation of Nickelacyclopentane. In this section we discuss the reaction path corresponding to the attack of an additional ethylene molecule on the M_2 complex. The most remarkable feature is that the ethylene molecule attacks the complex not at the metal center but at one of the two ligand ethylenes and leads to the formation of biradical species similar to those already found for the noncatalyzed reaction. In analogy with the noncatalyzed ethylene dimerization also in this case we have limited our investigation to the *anti* attack of the approaching ethylene molecule on one of the metal bonded ethylenes. Along this reaction channel we have located an *anti* transition state (TS_1) corresponding to the formation of a new C−C bond

---

(13) Quick, L.; Knecht, D.; Back, M. *Int. J. Chem. Kinet.* **1972**, *4*, 61.

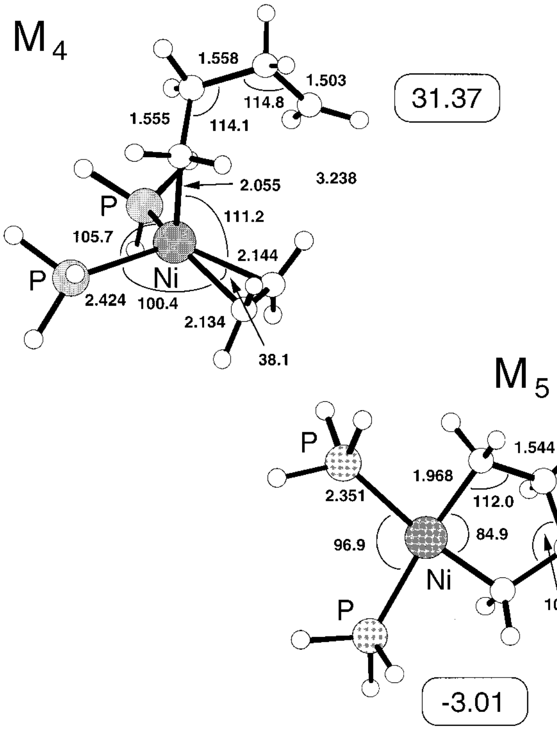


Figure 4. Schematic structures of the *syn* biradical intermediate M_4 and of the nickelacyclopentane complex M_5 obtained at the B3LYP/LANL2DZ level (bond lengths are in angstroms and angles in degrees). The energy values (kcal mol^{-1}) are reported in the two frames and are relative to the system formed by the M_2 complex and a noninteracting ethylene molecule (−421.62959 hartrees).

between the attacking ethylene and a ligand ethylene and an *anti* intermediate (M_3). Both these species, schematically represented in Figure 3, are biradical in nature with one of the unpaired electrons mainly localized on the nickel atom and the other on the terminal methylene. The energy values reported in Figure 3 are relative to the system formed by the M_2 complex and a noninteracting ethylene molecule (asymptotic limit). Thus the energy of TS_1 approximately represents the activation energy (35.80 kcal mol^{-1}) for the formation of the biradical species M_3. This biradical species is 24.46 kcal mol^{-1} higher in energy than the asymptotic limit, and it is characterized by a fragmentation barrier of 11.34 kcal mol^{-1}. A further investigation of the reaction surface has shown that a rotation around the new C−C bond leads from the *anti* intermediate to a *syn* intermediate M_4 (see Figure 4), which is 6.91 kcal mol^{-1} higher in energy than M_3. Also the *syn* intermediate is biradical in nature with the two unpaired electrons mainly localized on the nickel atom and the terminal methylene. In this situation the two electrons easily couple to form with a negligible barrier the nickelacyclopentane complex M_5 (see Figure 4), which is 34.38 kcal mol^{-1} lower in energy than M_4 (3.01 kcal mol^{-1} under the asymptotic limit). Additional computations have demonstrated that the ring closure to form the new Ni−C bond of nickelacyclopentane leads to the elimination of the ligand ethylene molecule not involved in the reaction.

We have also investigated the possibility that an intramolecular attack occurs in M_2 between the two ligand ethylenes to form directly the nickelacyclopentane (path c in Scheme 1). However, despite extensive search, we have not located any transition state leading to the cycle formation. We have found that the region of the potential surface corresponding to the motion of one ligand ethylene toward the second ligand ethylene to form the new C−C bond in the cycle is very high in energy with respect to the TS_1 transition state.

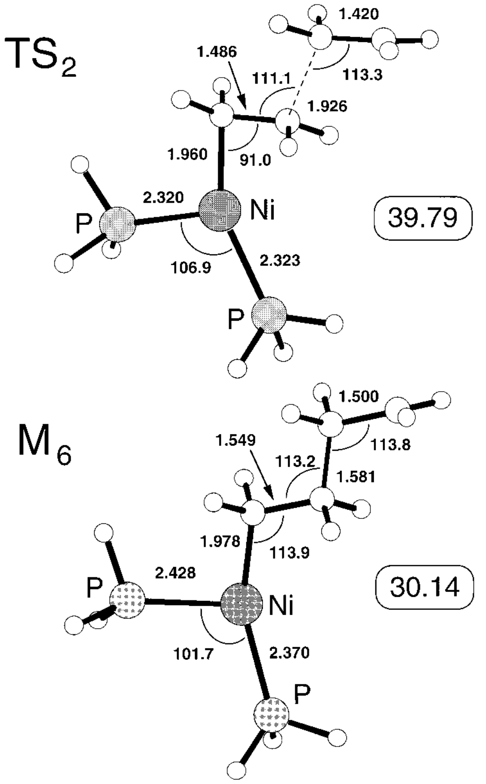


Figure 5. Schematic structures, obtained at the B3LYP/LANL2DZ level, of the *anti* biradical transition state TS_2 and of the *anti* biradical intermediate M_6 associated with the attack of an ethylene molecule on the M_1 complex. Bond lengths are in angstroms and angles in degrees. The energy values (kcal mol^{-1}) are reported in the two frames and are relative to the system formed by the M_1 complex and a noninteracting ethylene molecule (−343.04694 hartrees).

In analogy with the *anti* attack on M_2 we have also considered an *anti* attack of one ethylene molecule on the M_1 complex. We have found that also in this case an *anti* transition state and an *anti* intermediate exist (TS_2 and M_6 in Figure 5). TS_2 and M_6 are 39.79 and 30.14 kcal mol^{-1} higher in energy than M_1, respectively. The fragmentation barrier for M_6 is 9.65 kcal mol^{-1}.

The energy profiles associated with the *anti* attack of an ethylene molecule on both M_1 and M_2 are shown in Figure 6. The most interesting quantities which must be considered in this diagram are the activation energies for the formation of the two biradical intermediates M_3 and M_6 which are associated with the *anti* attack of ethylene on the M_2 and M_1 complexes, respectively. A comparison of these energies with the corresponding value found for noncatalyzed reaction (40.34 kcal mol^{-1}) indicates that, while a catalytic effect, even if not very large, exists in the case of the bis(ethylene)−nickel complex M_2, where the barrier is 35.80 kcal mol^{-1}, this effect is lacking in the case of the *anti* attack on M_1 where the barrier remains almost identical to that found for the noncatalyzed reaction. The small catalytic effect observed for the attack on M_2 could be a consequence of the fact that our model is too simple to emulate satisfactorily the real system where, for example, each PH_3 ligand is a triphenilphosphine group.[3b,c] However, this study seems to provide interesting information about the nature of the reaction path followed by the catalyzed reaction and the factors responsible for the catalytic effect.

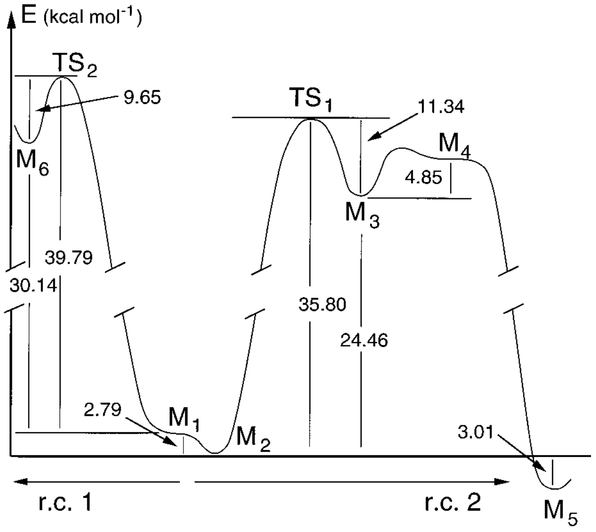


Figure 6. Energy profile describing the attack of an ethylene molecule on the M_1 and M_2 complexes; r.c. 1 and r.c. 2 indicate the two reaction coordinates leading to the formation of the M_6 and M_3 biradical complexes, respectively.

4. Diabatic Analysis

The mechanistic scheme suggested by the computational results can be easily rationalized by means of a simple diabatic analysis[14] based upon spin recoupling in VB theory. In this type of analysis, at any point along the reaction coordinate, the total wave function can be represented to a good approximation (see eq 1) as a linear combination of two configurations Φ_R and Φ_P which describe the electron coupling of reactants and products, respectively.

$$\Psi = a\Phi_R + b\Phi_P \tag{1}$$

At the beginning of the reaction Φ_R is much lower in energy than Φ_P and represents the dominant contribution ($a \gg b$). On going from reactants to products the importance of Φ_R decreases (its energy increases) and that of Φ_P increases (its energy decreases). In the transition state region the two configurations are almost degenerate and the corresponding contributions are approximately equivalent. After the transition state region, on the product-side along the reaction coordinate, Φ_P becomes lower in energy than Φ_R and consequently dominates ($b \gg a$). Thus the variation of the relative importance of Φ_R and Φ_P describes the change from the reactant electron coupling to the product electron coupling that occurs in most organic reactions when we break covalent bonds in reactants and form new bonds in the products.

This process can be conveniently represented in a diagram where we report the energy of the reacting system versus the reaction coordinate and where the total energy profile is decomposed into two component curves: one, denoted as *reactant diabatic*, describes the energy behavior of the reactant configuration Φ_R (reactant spin coupling) along the reaction coordinate; the other, denoted as *product diabatic*, describes the energy trend of the product configuration Φ_P (product spin coupling). The reactant diabatic, on passing from reactants to products, is repulsive while the product diabatic is attractive. The crossing between the two diabatics determines the position of the transition state and the magnitude of the activation energy.

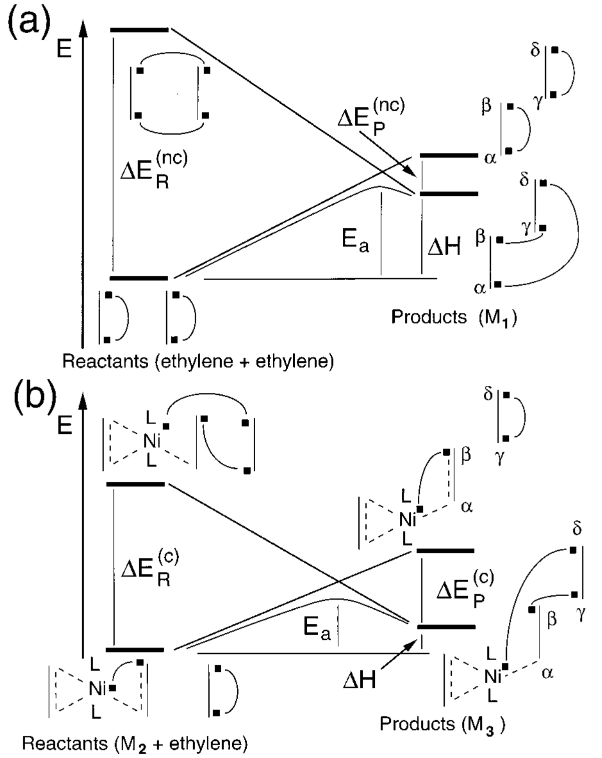


Figure 7. Correlation diagrams for the noncatalyzed (a) and catalyzed (b) ethylene dimerization.

This type of analysis has recently been applied to a variety of reactivity problems, either at a qualitative or quantitative level.[14]

Here we focus our attention upon the first step of the noncatalyzed (ethylene + ethylene) and catalyzed (ethylene + M_2) reactions that connects the reactants to the *anti* biradical intermediate. The qualitative behavior of the two diabatics for the two processes is shown in the two diagrams of Figure 7. For the noncatalyzed reaction (Figure 7a) the reactant diabatic corresponds to a situation where the 2pπ electrons on each ethylene are singlet spin-coupled to form the two π bonds, while in the product diabatic the two ethylenes are in a triplet state coupled to an overall singlet (each π electron of one ethylene molecule is coupled to a singlet with one π electron of the other ethylene molecule). For the catalyzed reaction the reactant diabatic describes a singlet coupling of the two π electrons in the free ethylene and of the two π electrons involved in the bonding between the ligand ethylene, which undergoes the reaction, and the metal atom (M_2 complex). In the product diabatic the free ethylene and the M_2 complex are in a triplet state and each π electron of the M_2 complex is singlet spin-coupled with one π electron of the free ethylene. A schematic representation of the reactant and product coupling schemes is given in Figure 7, diagrams a and b.

In this type of diagram the position of the crossing, and consequently the size of the barrier, is determined by three factors: (i) the energy difference between the product diabatic at the product geometry and the reactant diabatic at the reactant geometry (ΔH), (ii) the energy difference between the reactant and product diabatic at the reactant geometry (ΔE_R on the left side of the diagram), and (iii) the energy difference between the reactant and product diabatic at the product geometry (ΔE_P on the right side of the diagram).

ΔH can be computed on the basis of the quantomechanical energy values of reactants and products and approximately corresponds to the reaction enthalpy: from the energy values discussed in the previous section it is evident that this term is

---

[14] (a) Pross, A.; Schaik, S. S. *Acc. Chem. Res.* **1983**, *16*, 363. (b) Bernardi, F.; Olivucci, M.; McDouall, J. J. W.; Robb, M. A. *J. Chem. Phys.* **1988**, *89*, 6365. (c) Bernardi, F.; Bottoni, A. *J. Phys. Chem.* **1997**, *101*, 1912.

larger for the noncatalyzed (38.99 kcal mol^{-1}) than for the catalyzed reaction (24.46 kcal mol^{-1}). The evaluation of ΔE_R and ΔE_P is less obvious. ΔE_R represents the energy required for decoupling the two electron pairs associated with the π bonds in two free ethylene molecules (noncatalyzed reaction) or in a free ethylene molecule and in a metal-bonded ethylene (M_2 complex in the catalyzed reaction). In the former case this quantity can be evaluated to a good approximation from the energy needed for exciting both ethylenes from the singlet ground state to the first triplet state. In the latter case we can estimate ΔE_R from the singlet−triplet energy gap in a free ethylene molecule and the singlet−triplet energy gap in the M_2 complex. Since the triplet excitation energy is significantly smaller for the M_2 complex than in a free ethylene, ΔE_R decreases on going from the noncatalyzed to the catalyzed process, i.e., $\Delta E_R^{(nc)} > \Delta E_R^{(c)}$.

In a similar way we can try to evaluate qualitatively the variation of ΔE_P on going from the noncatalyzed ($\Delta E_P^{(nc)}$) to the catalyzed process ($\Delta E_P^{(c)}$). In the former case ΔE_P is approximately given by the algebraic sum of the energy required to break the new formed $C_\beta - C_\gamma$ single bond (positive destabilizing contribution) and the energy obtained from the coupling of the two electron pairs associated with the two ethylene moieties (negative stabilizing contribution associated with the $C_\alpha - C_\beta$ and $C_\gamma - C_\delta$ bonds). In the latter case the coupling on one ethylene moiety ($C_\alpha - C_\beta$ ethylene) must be replaced by the coupling of two electrons which are mainly localized on the β carbon and the metal atom. Since these two electrons are far away the stabilizing contribution of this coupling is smaller than in the other ethylene moiety ($C_\gamma - C_\delta$ free ethylene) and consequently $\Delta E_P^{(c)}$ is larger than $\Delta E_P^{(nc)}$.

While the effect of the change of ΔE_P on going from the noncatalyzed to the catalyzed reaction is that of increasing the activation barrier for the formation of the *anti* biradical intermediate, that of ΔH and ΔE_R is opposite and dominant: the final overall effect of the simultaneous variation of ΔH, ΔE_R, and ΔE_P is a catalytic effect (decrease of the activation energy E_a) associated with the nickel atom. This analysis also provides useful suggestions for obtaining a stronger catalytic effect and thus a more effective catalyst. Since the two key factors responsible for the decrease of the barrier E_a are ΔH and ΔE_R, to obtain a stronger catalytic effect a metal complex characterized by a small singlet−triplet energy gap and a higher stability of the resulting biradical intermediate should be chosen. In M_2, in addition to the two PH_3 ligands, there is the additional ethylene ligand not involved in the reaction that can further delocalize the metal unpaired electron. This augmented capacity of M_2 with respect to M_1 of delocalizing the unpaired electron is the likely cause for both the reduced singlet−triplet energy gap in M_2 and the reduced endothermicity of the biradical formation process (however, we must point out that, if a more realistic ligand such as PMe_3, which is a better π acceptor than PH_3, were used, the degree of delocalization would probably increase also in M_1). An indirect confirmation of the previous statement can be found in the following computational evidence: (i) for M_1, where only the two PH_3 ligands can behave as π acceptors, the activation energy is almost identical to that found for the noncatalyzed process and (ii) the endothermicity of the reaction $M_1 \rightarrow M_6$ is 30.14 kcal mol^{-1} while that of the reaction $M_2 \rightarrow M_3$ is 24.46 kcal mol^{-1}.

5. Conclusions

In this paper we have investigated the [2+2] cycloaddition of two olefins catalyzed by Ni(0) complexes using a DFT computational approach based on the hybrid B3LYP functional and the pseudopotential LANL2DZ basis set. Two model systems have been considered: one is formed by an ethylene−nickel complex ($Ni(PH_3)_2C_2H_4$) and the other by a bis(ethylene)−nickel complex ($Ni(PH_3)_2(C_2H_4)_2$). We have assumed that these two species represent two possible active forms of the catalyst and for both we have considered the reaction with a free ethylene molecule. In particular we have investigated in detail the first steps of the process corresponding to the formation of nickelacyclopentane, which has been experimentally demonstrated to produce the cyclobutane product by reductive elimination. We have found that the incoming ethylene molecule reacts with both complexes not at the metal center but at one ligand ethylene. This attack leads to an *anti* 1,5-biradical intermediate where the two unpaired electrons are mainly localized on the nickel atom and on the terminal methylene. This intermediate is very similar to the biradical tetramethylene found in the noncatalyzed dimerization of ethylene. However, while for the attack of the ethylene molecule on $Ni(PH_3)_2C_2H_4$ the activation energy is almost identical to that found for the noncatalyzed process (about 40 kcal mol^{-1}), for the $Ni(PH_3)_2(C_2H_4)_2$ complex the barrier decreases (35.80 kcal mol^{-1}). This computational finding indicates that a catalytic effect exists only for the 1:2 ethylene−nickel complex and not for the 1:1 ethylene-nickel complex. A further investigation of the reaction surface has shown that a rotation around the new formed C−C bond leads from the *anti* biradical intermediate to a *syn* biradical intermediate where the unpaired electrons can easily couple to form a nickelacyclopentane complex without any barrier. The above results provide a further indication that these processes, such as olefin dimerization, proceed through a nonconcerted mechanism and enforce the hypothesis, based on experimental evidence,[3c] that the equilibrium between bis(olefin)−metal complexes and metallacyclopentanes is a key step in metal-catalyzed olefin cycloadditions.

Our computational results (catalytic effect found only for the 1:2 ethylene−nickel complex and comparison with the noncatalyzed ethylene dimerization) have been rationalized by means of a diabatic analysis. This analysis has detected two factors which are responsible for the decrease of the activation barrier found for the $Ni(PH_3)_2(C_2H_4)_2$ complex: the energy difference between the singlet ground state and the first triplet state in the metal complex M_2 and the stability of the resulting biradical intermediate. Thus a small singlet/triplet energy gap and a highly stable intermediate should be the basic requirements for obtaining an effective catalyst. These requirements seem to be associated with the presence of ligands capable of effectively delocalizing the unpaired electron on the metal atom.

JA980604R