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Reactions of $C_5H_5M^+$ (M = Fe, Ni) with substituted thiophenes

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Abstract

The ion molecule reactions between $C_5H_5M^+$ (M = Fe, Ni) with some substituted thiophenes have been studied in an ion trap mass spectrometer. The reactions of halogen substituted thiophenes lead to the formation of a new C–C bond between the cyclopentadiene ring and the thiophene with the loss of a neutral HX. The reaction mechanism has been investigated by means of DFT calculations and it was found that the insertion of the metal atom in the C–X bond is the key step in the process.
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1. Introduction

Reactions of $C_5H_5M^+$ ions, where M is a transition metal, with different ligands have been studied since 1973 [1] but only recently a new interest in these reactions has aroused. After the explosion [2,3] of investigations in the ion–molecule reactions between free metal ions and organic molecules chiefly aimed to explore the possibility of C–C and C–H bonds activation, studies of coordinated metals ions indicated several interesting reactivity differences [2]. In spite of the fact that the Cp(η^5-C_5H_5) ligand is very common in the organometallic chemistry and its complexes are widely employed in several reaction of industrial relevance [4] the reaction of cyclopentadienylic transition metals complexes are not studied very extensively.

A brief review on these reactions has been published [5]. In a series of papers [6–9] Bohme et al. demonstrated that $C_5H_5Fe^+$ ions react with faster rates compared to that of the naked Fe^+ ion and that the reactions with NO or CO lead to the sequential addition of two and three molecules. The efficiency of the reactions of several $C_5H_5M^+$ ions have been studied [10] and it was indicated that a positive activa-

tion entropy could be responsible of the low efficiency found in several cases.

In the above cases the cyclopentadienyl ring is not directly involved in the reaction but recently [11] we found that in the gas phase reactions between the ion $C_5H_5Fe^+$ and some substituted pyridines two different reactions were observed: a simple addition process, found in almost all the cases, and a reaction with loss of HX found with the halogen substituted pyridines; in this last reaction the formation of a new C–C bond between the cyclopentadienyl ring and the pyridine was postulated. Now we extend this study to the reactions of some substituted thiophenes with $C_5H_5M^+$ (M = Fe, Ni) not only to exploit the possibility of this reaction with other ligands but also for the still current interest in the coordination mode of the thiophenes [12–15]; the study of the different coordination chemistry of thiophenes is important for understand the mechanism of the catalytic hydrodesulfurization, the process by which sulphur is removed from petroleum feedstock.

1.1. Experimental

Measurements have been done with a Finnigan ion trap mass spectrometer (ITMS) whose ion source was kept at 150 °C. The metallocenes are introduced in the ion trap

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via the direct insertion probe, while helium and the thiophenes are introduced in the mass spectrometer via two different standard gas inlet devices. The metallocene pressure was usually around 8×10^{-5} Pa, the He pressure was kept at 3.5×10^{-2} Pa. The ion $C_5H_5M^+$ is formed by electron ionization with an ionization time of 10 ms while the radio-frequency applied to the ion trap is such that ions with m/z lower than 100 are in the instability region so that they are ejected from the ion source. The ion is then cooled for 50 ms (this high cooling time was necessary to assure the thermalization of the reacting ions) and then isolated in two successive steps in order to eject the lower and the higher m/z mass ions; after the isolation spectra are acquired at different reaction times.

2. Computational procedure

All computations reported here have been performed with the Gaussian 03 series of programs [16]. DFT methods are widely used for the prediction of geometries and molecular properties of metallocenes [14,17–20] and in this work we used the hybrid Becke three parameter exchange functional [21] (B3LYP) was used along with the DZVP basis set [22] which is a local spin density optimized basis set of double-ζ quality in the valence shell plus polarization functions. This basis set seems appropriate to describe the structure involved in the reaction mechanisms here investigated, however to obtain more accurate energy values calculations have been also performed with a more extended basis set: the 6-311G* for all atoms except nickel; the metal was described by the pseudopotential basis set by Preuss [23]. The structure optimized with the DZVP basis set were optimized again with the more extended basis set; for each critical point the vibrational frequencies have been calculated to determine their nature and the geometries and energies reported in the following have been obtained with this second basis set; the intrinsic reaction coordinate approach [24] was used to ascertain that the transition states found connect the stationary states. The energies of all the critical structures have been corrected for the zero point energy.

3. Results and discussion

3.1. The reactions

The reactions of the ions $C_5H_5M^+$ in the ITMS in the presence of thiophenes derivatives RC_4H_3S (R = 2Cl-, 2Br-, 3Cl-, 3Br-, 2Me-, H-thiophene) lead to a variety of products; formation of $(C_5H_5)_2M^+$ and of $(C_5H_5)_3M_2^+$ is always observed as a result of the reaction with neutral metallocene; these reactions are minimized at low metallocene pressure so that only the reactions involving the thiophenes are prominent; in this condition we observe different reaction products according to the following scheme:

Product [1] is the addition ion; [2] is a product which results from the loss of HR from the addition; [3] is formed by the addition of a second thiophene molecule and loss of another HR molecule. The addition ion [1] is observed with the unsubstituted thiophene and in the reaction of 2-methyl thiophene with $C_5H_5Fe^+$ and $C_5H_5Ni^+$, this ion does not give rise to further reaction; in the reactions of the halogen substituted thiophenes we do not observe any addition product but only products [2] and [3] are present, loss of HR was found also in the reaction of the ion $C_5H_5Ni^+$ with 2-methyl thiophene.

In Fig. 1, the variation of the relative intensity for the reactant and product ions is shown for the reaction of $NiC_5H_5^+$ with 2-chloro thiophene as function of the reaction time up to 500 ms; the behaviour is typical of a consecutive reaction; in addition after the isolation of the ion [2] it can react again with 2-chloro thiophene to form the end product [3]; this is the only reaction observed for the ions [2] which do not show any decomposition reaction when subject to a tickle frequency to increase the energy of collisions with the buffer gas.

The use of perdeuteroferrocene to form the ion $C_5D_5Fe^+$ establishes that the hydrogen atom of the HX comes from the cyclopentadienylic ring; in this case indeed we observe only the loss of DX and a second DX molecule is lost in the second step. As a consequence in the reactions with loss of HX the

Fig. 1. Relative intensities of the ions in the reaction of $C_5H_5Ni^+$ with 2Cl-thiophene.

formation of a new C–C bond between the thiophene ring and the cyclopentadienylic ring is highly probable.

The absence of any successive reaction after the simple addition reaction indicates that the centre for the ligand attack is no more available in the addition ion while it is again available after the loss of HX; it seems therefore that, after the loss of HX, the metal atom is again free to start a new reactive step.
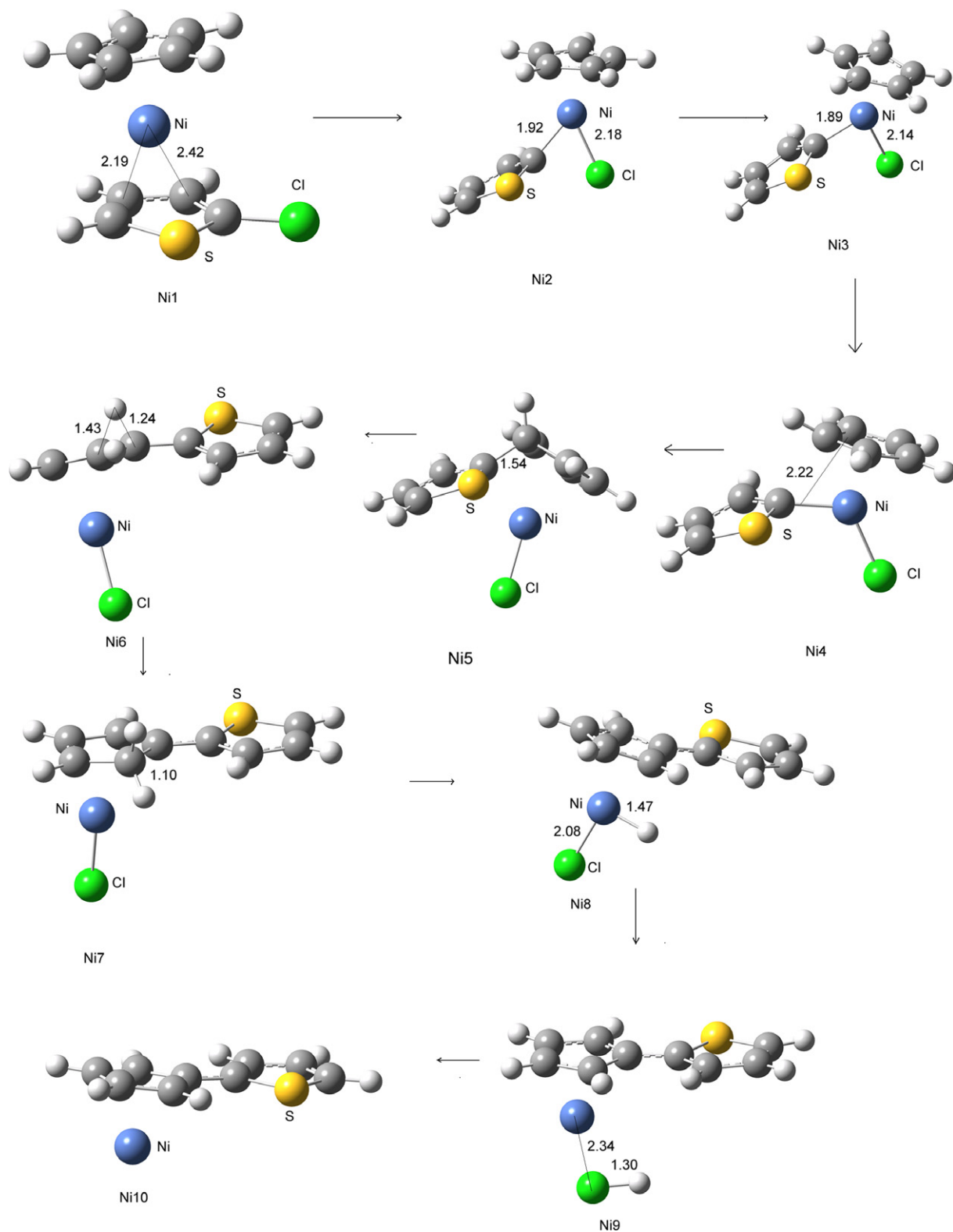

Fig. 2. Structures of critical points in the reaction mechanism of $NiC_5H_5^+$ with 2Cl-thiophene.

4. Computational study

Computational study has been made for the reaction of $C_5H_5Ni^+$ with 2Br- and 2Cl-thiophene and 2Me-thiophene.

The ground state of the reactant ion $C_5H_5Ni^+$ is found to be the triplet state which is more stable than the singlet

Table 1
Relative energies (kJ/mol) for the reaction of $C_5H_5Ni^+$ with 2Cl- and 2Br-thiophene

Structure	2Cl-thiophene	2Br-thiophene
Reactants	0	0
Ni1	−168.1	−170.2
Ni2	−84.7	−44.3
Ni3	−99.5	−120.5
Ni4	−46.3	−60.7
Ni5	−192.0	−208.2
Ni6	−99.2	−117.7
Ni7	−227.8	−245.4
Ni8	−93.5	−114.5
Ni9	−178.4	−188.6
Ni10	−85.9	−98.4

state by 88.7 kJ/mol; in this ion the Ni atom is symmetrically bonded to the ring with a bond distance Ni–C equal to 2.14 Å; the structure of the singlet state is less symmetric with the distances Ni–C ranging from 2.04 to 2.24 Å and the five carbon atoms of the ring do not lie in the same plane. A lower energy for states with higher multiplicity has been already reported for the ion $C_5H_5Fe^+$ [25,10] and is also found for $C_5H_5Co^+$ [26].

For all the reactions the singlet surface was also explored; in all the structures the energies of the stationary states were higher than the corresponding triplet structure (energy differences range from 33 to 84 kJ/mol) so that the reaction path is likely to occur on the triplet surface.

The geometries of the stationary points found in the minimum energy reaction path are shown in the Fig. 2 for the reaction of 2Cl-thiophene; the relative energies for the reactions of the two halogen substituted thiophenes are reported in Table 1 and the energetic profile for the two reactions is drawn in Fig. 3. The lowest energy structure (Ni1) for the adduct ions is a sandwich one with a preferential bond between the nickel atom and the two carbon
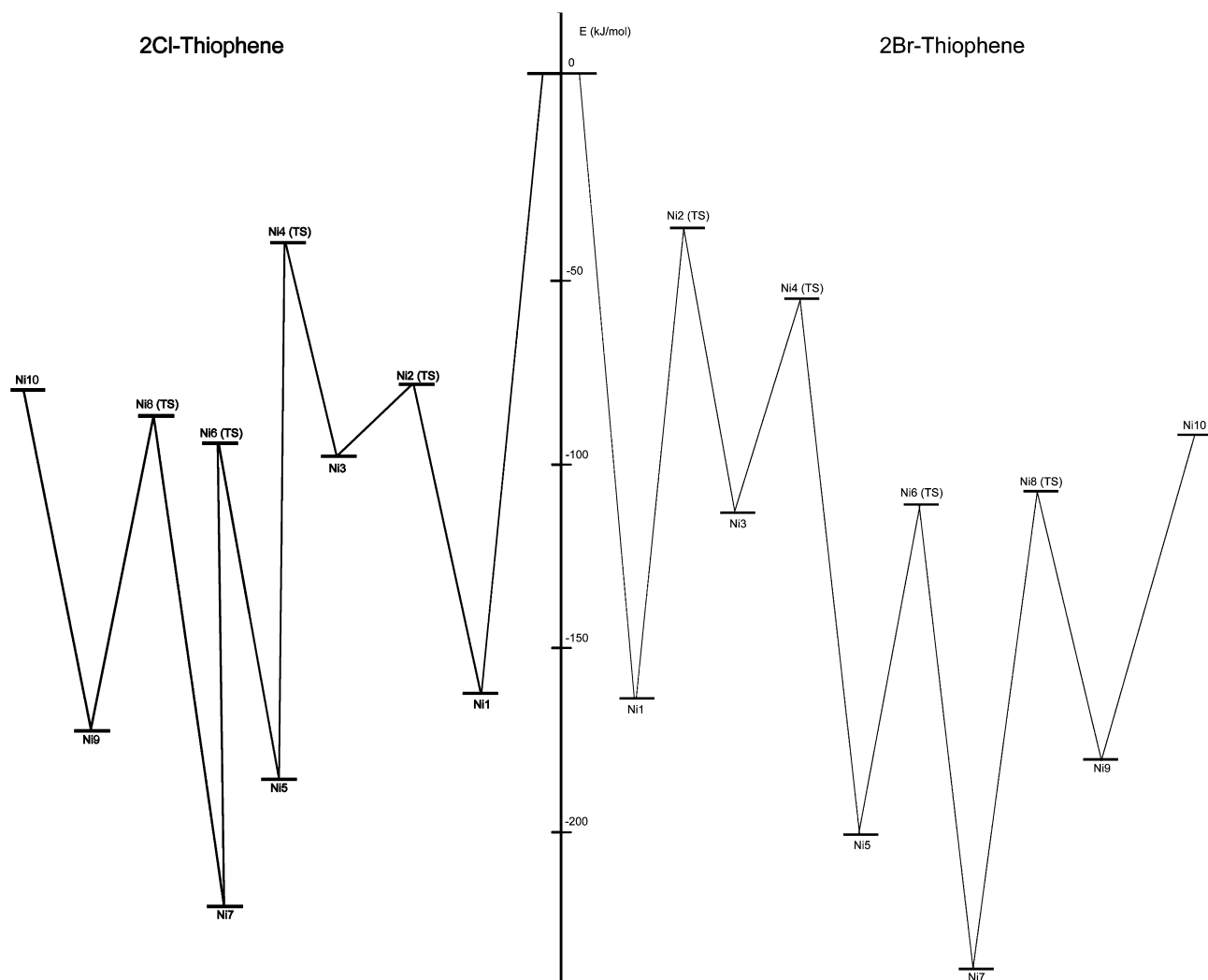
Fig. 3. Energy profile for the reaction of $NiC_5H_5^+$ with 2Cl- and 2Br-thiophene. The numbering refers to the structures of Fig. 2.

atoms opposite to the sulphur atom. No stationary state with a direct bond between S and Ni was found while this kind of structure has been reported in the reaction of Ni^{+} with pyridine [27] and Fe^{+} [28]. In this gas phase structure therefore the mode of coordination of thiophene is an η^5 one which is also the more common coordination mode of this ligand [12,13]. This result is in agreement with the well known low coordinating capacity of the sulphur atom of the thiophenes. Even if the interaction of an H^{+} with a sulphur atom is more complicated than the interaction of the $C_5H_5Ni^+$ with S, this can be related to the fact that the sulphur atom in the thiophene ring has a significant lower proton affinity than the nitrogen atom of a pyridine ring; the proton affinity of thiophene is indeed 815 kJ/mol while the proton affinity of pyridine is 930 kJ/mol [29]. Electron delocalization of the sulphur lone pairs through conjugation with the π system of the ring has been invoked [12] to explain the low Lewis basicity of the sulphur atom.

The reaction path proceeds through the transition state Ni2 which leads to the formation of another local minimum (Ni3), where the Ni atom is inserted in the C–Cl bond; from this structure, via the transition state Ni4, a structure (Ni5) with a new C–C bond between the two rings is formed and then there are two hydrogen transfer steps (Ni6, Ni7, Ni8) which form Ni9, where the hydrogen atom has migrated to the chlorine atom; the calculated H–Cl bond length (1.30 Å) in this last structure is very near to that of the free HCl. This last structure loses HCl without transition state leading to the final structure Ni10; the reaction of the 2-bromo thiophene proceed with similar structures. In both cases all the structures lie well under the energy of the separate reactants so allowing very fast reactions which rapidly consume the addition product [1] in a time scale which does not allow its observation in the ITMS ion source.

A different situation holds for the reaction of the 2-methyl thiophene; in this case (Fig. 4) the adduct ion is stable for 197.1 kJ/mol with respect to the reagents but the insertion product is higher in energy by 29.5 kJ/mol and the relative transition state is more high in energy by 0.1 kJ/mol; this unfavourable energetic situation slows down this first reaction so that the loss of methane now is
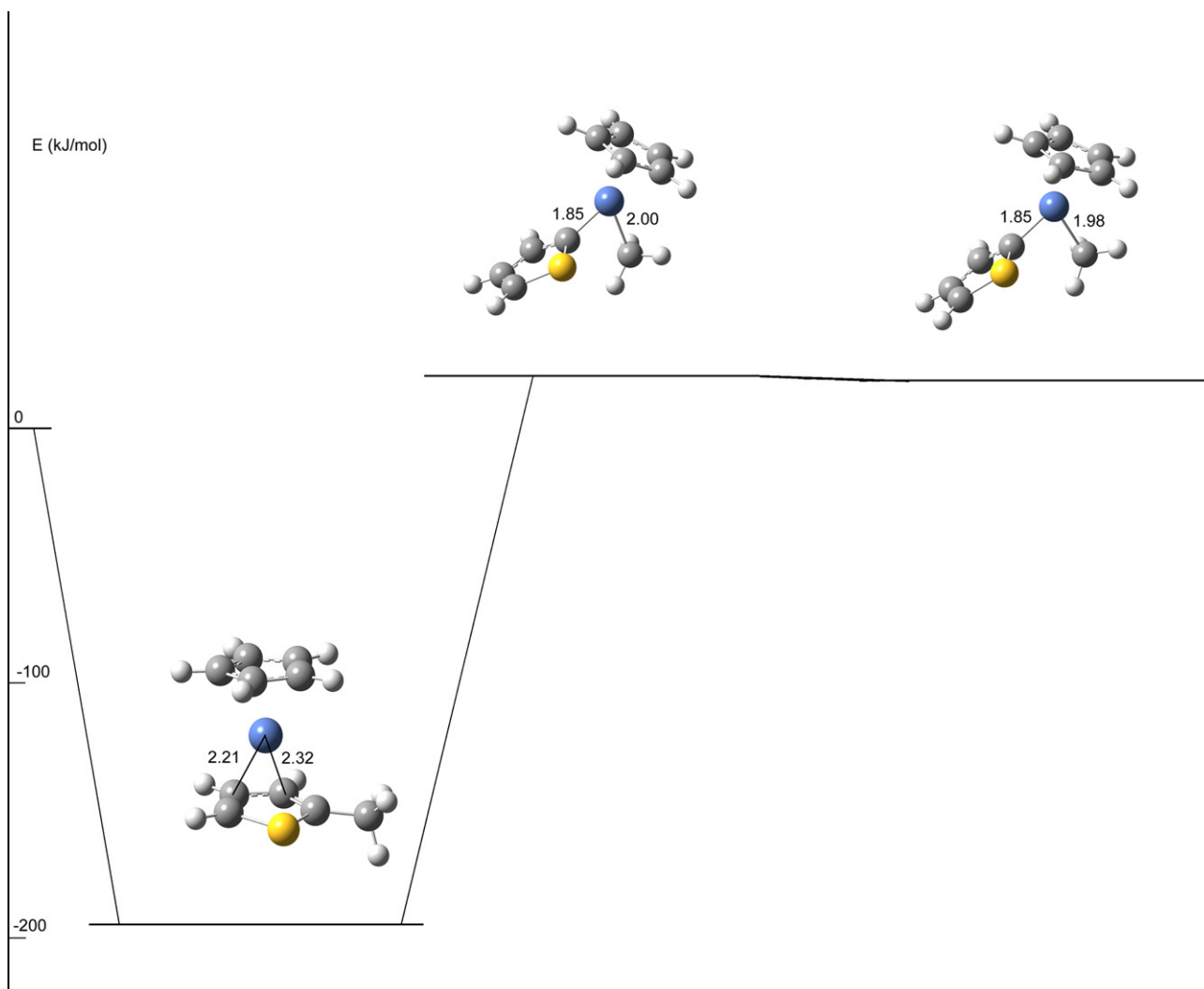

Fig. 4. Structures and relative energies for the first steps of the reaction of $NiC_5H_5^+$ with 2Me-thiophene.

not the predominant reaction and both the two reaction products are observed. The reaction mechanism for the 2Me-thiophene was not further explored since we were interested only in explain the low yield of reaction 2 in this case. The energy necessary to overcome the barrier to the insertion product can derive from a contribution of the radio frequency field to the ion energy [30–32]. The quite high energy of the insertion product can be ascribed to the involved bond energies. A rough estimate of the relevant bond energies have been made by means of unrelaxed scans of the involved bond length both in the free ligands and in the insertion products; it is found that the breaking of the C–methyl bond in 2-methyl thiophene requires about 502 kJ/mol while the breaking of C–Cl bond requires 398 kJ/mol so that the insertion of the Ni atom is favoured in the chlorine derivative; in addition the new bonds formed in the insertion products favour again the chlorine derivative since in the formation of the Ni–Cl bond about 243 kJ/mol are gained while in the formation of the Ni–methyl bond the energy gain is about 192 kJ/mol. It can be concluded that the possibility of an insertion of the metal atom in a bond of the ligand is a necessary condition for the formation of the new bond between the cyclopentadienylic ring and the entering ligand. Thus, the key intermediate for the observed reaction is the insertion ion (Ni3) which is the result of an oxidative addition to the nickel atom. Structure of this kind have been already found or suggested as intermediate in several condensed phase reactions of nickelocene with a variety of molecules [33–37] and the mechanism that we propose for the formation of the new C–C bond in the cyclopentadienylic ring is another example of the reactivity analogies which exist between gaseous and condensed phases.

Acknowledgement

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