

# Propane activation by $MC_5H_5^+$ ( $M = Ni$ and $Co$ ): An experimental and theoretical work

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## Abstract

The reactions of  $MC_5H_5^+$  ( $M = Ni$  and  $Co$ ) with propane in gaseous phase have been studied with an ion trap mass spectrometer; the  $MC_5H_5^+$  ions are able to activate the propane molecule which undergoes a dehydrogenation reaction. At variance with the reactions of the bare metal ions no loss of methane is observed; the reaction mechanism has been explored by means of DFT calculations and a possible explanation is offered for the different reactivity of these ligated ions.

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*Keywords:* Ion–molecule reaction; DFT; Sigma bond activation

## 1. Introduction

The activation of  $\sigma$  bonds in alkanes has been the subject of many investigations [1]; there are practical as well theoretical reasons for this interest: the alkanes are important raw materials for the chemical industry but they are relatively unreactive compounds so that the knowledge of the possible means for the C–H and C–C bonds activation is very valuable; in addition the activation of these bonds involves the breaking and the forming of  $\sigma$  bonds and these processes are of fundamental interest for chemistry.

Reactions of bare transition metal ions with hydrocarbons received much attention [2–18] and several aspects of their reactivity have been clarified, even with the aid of accurate theoretical calculations [19–21]. Much less extensive is our knowledge about the reactivity of ligated metal ions, although it is well known that the presence of a ligand influences the reactivity of a metal ion [22]. For example, the atomic metal ion  $Fe^+$  does not react with ethane, but  $FeL^+$  ( $L = CH_2, C_5H_6, O$ ) does to give a series of products [23,24].

In spite of the fact that the Cp ( $\eta^5-C_5H_5$ ) ligand is very common in the organometallic chemistry and its complexes are widely employed in several reaction of industrial relevance [25] the reaction of cyclopentadienylic transition metals complexes with small alkanes have been studied much less extensively. In an earlier work Jacobson and Freiser [26] reported that  $C_5H_5Co^+$  does not react with methane, but readily dehydrogenates ethane to probably form an (ethene)(cyclopentadienyl)  $Co^+$  complex; more recently [27,28] it was found that also with methane a dehydrogenation reaction is possible. Propane [26] reacts with  $C_5H_5Co^+$  with hydrogen elimination but the loss of methane, very common in the reactions of bare metal transition ions, is not observed. The dehydrogenation is the exclusive or dominant reaction also for higher alkanes [26]. The reactions of  $C_5H_5M^+$  ( $M = Fe, Co$  and  $Ni$ ) with ethane have been studied in a Fourier transform (FT)-ICR cell at low pressure [29]. It was confirmed that dehydrogenation occurs for  $M = Co$  and  $Ni$ , but  $FeC_5H_5^+$  reacts in a different way to give the product ion  $FeC_3H_5^+$ , which was suggested to originate from one or more excited states of  $FeC_5H_5^+$ . The lack of reactivity of the last ion in its ground state was attributed to its electronic structure albeit obtained by use of low level calculations. Also medium chain-length  $n$ -alkanes react with  $C_5H_5Co^+$  by the loss of

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two hydrogen molecules as the dominant reaction channel and with a reaction efficiency becoming larger with increasing chain length [30]. The presence of the cyclopentadienyl ring therefore seems to have two important effects on the reactivity of the metal ions: a higher reactivity towards ethane and a better selectivity in the reactions with higher alkanes.

To obtain information regarding the difference in the reactivity between the ligated and bare metal ions, we report an experimental and theoretical study of the reaction of  $MC_5H_5^+$  ( $M = Co, Ni$ ) with propane.

## 2. Experimental

Measurements have been performed with a Finnigan ion trap mass spectrometry (ITMS). The theory, instrumentation and methodology of this instrument was described by March and Hughes [31].

The general procedure to obtain kinetic data are as follows. The metallocene is introduced in the ion trap via the direct insertion probe while helium and propane are introduced via two different standard gas inlet devices; the metallocene pressure was usually around  $1 \times 10^{-5}$  Pa, the He pressure was kept at  $3.5 \times 10^{-2}$  Pa and the propane pressure changed between  $7 \times 10^{-6}$  and  $3 \times 10^{-4}$  Pa. In a single experiment, at fixed metallocene, propane and helium pressure, the ITMS software managed the experiment loading the scan function and changing the reaction time. The scan function, reported in Fig. 1, operates as follows: the ion  $C_5H_5M^+$  was formed by electron ionization of the corresponding metallocene (70 eV) with an ionization time of 10 ms with the radio frequency set to a starting  $m/z = 100$  (period A in Fig. 1); in this way ions of lower mass are ejected from the ion source. The ion is then cooled for 50 ms (period B) and isolated (period C); the isolation is accomplished applying a radio frequency (RF) pulse in such a way to shift the position of the ion in the stability diagram [31] of the trap at  $q_z = 0.78$  and applying a negative DC voltage to the ring electrode. The reaction time (period D) was changed and two spec-

tra were collected at each reaction time in a time range sufficient (typically between 0 and 100 ms) to reduce the relative intensity of the parent ion from 100% to about 10–5%. Then (period E) the ions present in the ion source are ejected and recorded; at the end of each scan the RF voltage is lowered to clean the trap from all ions (period F). The high cooling time (period B) was necessary to assure the thermalization of the reacting ions by means of collisions with the He buffer gas. Lower cooling time gave rise to first order kinetic plots with a marked upward curvature which is attributable to a non-homogeneous distribution in energy of the ions formed by electron ionization; this suggests that ions with a high energy content form initial adduct which cannot efficiently dissipate the internal energy before redissociation. Increasing the helium pressure above the adopted value has no influence on the kinetic data indicating that the saturation limit for the collision stabilization process is reached.

To get the kinetic data, the relative intensity of the  $C_5H_5M^+$  signal was calculated with respect to the total ion intensities. In the adopted experimental conditions the propane pressure, in a single kinetic run, is constant so that the disappearance of the ion  $C_5H_5M^+$  must follow a pseudo-first-order kinetics. From the plots of the ln of its relative intensity vs reaction time, the pseudo-first-order rate constants is obtained. From these constants the second order rate constants have been obtained by plotting their values vs the propane pressure. The kinetic data have been checked for homogeneity by using the *F*-test; the test was applied to at least three independent runs; the reported uncertainties are the standard errors [32]; those last values indicate the reproducibility of the measurements while the precision of the kinetic constant values strongly depends upon the pressure measurements and an uncertainty of about 25% is reasonable for the kinetic constants.

## 3. Computational procedure

All computations reported here have been performed with the GAUSSIAN-03 series of programs [33].

The hybrid Becke three parameter exchange functional [34] (B3LYP) was used along with the 6-311G\* basis set for all atoms except the metal ions which were described by the pseudo-potential basis set by Preuss and co-workers [35]. The use of density functional theory (DFT) combined with effective core potentials is widely employed in calculations involving big atoms [36] and in particular the use of pseudo-potentials not only reduces the computational effort but also allow for an effective treatment of relativistic effects still maintaining a good degree of accuracy [37]. For each critical point the vibrational frequencies have been calculated to determine their nature; the intrinsic reaction coordinate approach [38] 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.

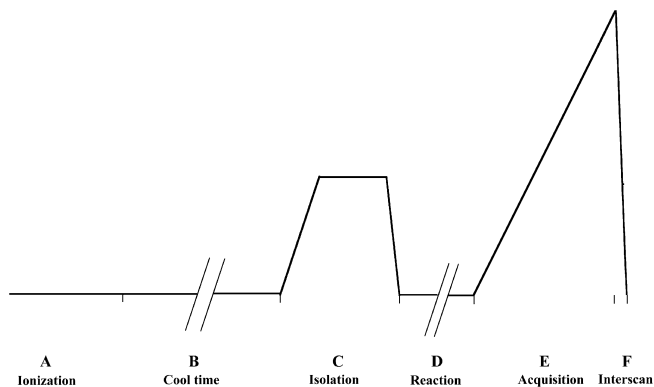


Fig. 1. Radio frequency voltage scan function for isolation and reaction of selected ions.

## 4. Results and discussion

### 4.1. The reactions

The reaction of  $\text{NiC}_5\text{H}_5^+$  with propane in the ITMS ion source give rise to an unique ion due to the loss of  $\text{H}_2$  from the adduct ion so that in the mass spectra only the precursor ion  $\text{MCp}^+$  and the reaction product appear. The variation of the relative intensities of these two ions with the reaction is reported in Fig. 2 for a typical case. By using 2,2D<sub>2</sub>-propane we observe loss of  $\text{H}_2$  and HD in the ratio 2/1. No loss of methane was observed while this process is prominent in the reactions of the  $\text{Ni}^+$  [5] and observed also in the reaction of  $\text{Co}^+$  [4]. A similar situation is found for the reactions of  $\text{CoC}_5\text{H}_5^+$ : the only ion observed in its reaction with propane is due to the loss of  $\text{H}_2$  from the adduct ion but in the reaction with 2,2D<sub>2</sub>-propane the ratio between the loss of  $\text{H}_2$  and HD is 1/5. It is evident that a striking difference exists non-only in the reaction mechanism of the ligated and bare metal ions but also between that of the two ligated ions. Jacobson and Freiser already reported [26] that in the reaction of  $\text{CoC}_5\text{H}_5^+$  with propane only the loss of  $\text{H}_2$  is present and on the grounds of a collisional activation experiment on the ion  $\text{CoCp}(\text{C}_3\text{H}_6)^+$  suggested the formation of a propene(cyclopentadienyl)cobalt species. In the reactions of the bare metal ions the process with methane elimination has a more favourable  $\Delta H$  with respect to the hydrogen elimination both for nickel [15] and cobalt [13] so that it can be assumed that also in these ligated ions the methane loss should be thermodynamically favoured as confirmed by the energies of the final states reported in Tables 2 and 3 for the nickel system.

The kinetic data here obtained are reported in Table 1 along with the reaction efficiency calculated as the ratio of the reaction rate constant and the collision rate evaluated according to Su and Chesnavich [39]. Few kinetic data

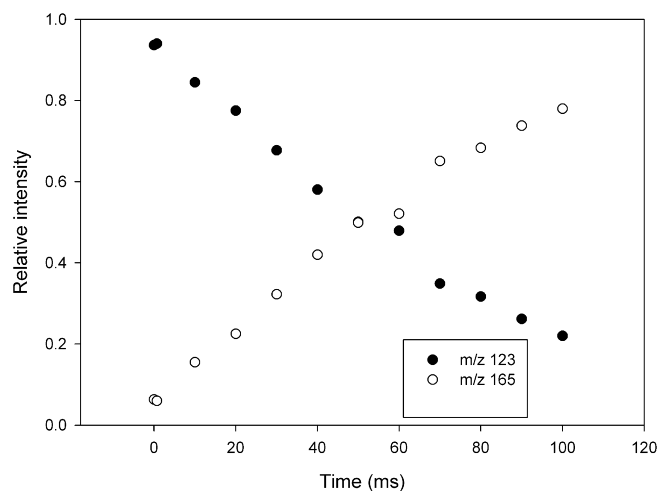


Fig. 2. Relative intensities of the ions observed in the mass spectra obtained in the reaction of  $\text{NiCp}^+$  with propane.  $m/z$  123 is the initial adduct ion and  $m/z$  165 is the reaction product.

Table 1

Kinetic data for the  $\text{H}_2$  elimination reactions in the reaction of  $\text{MCp}^+$  with propane

Ion	Rate constant	Efficiency
$\text{C}_5\text{H}_5\text{Ni}^+$	$5.21 \times 10^{-10} \pm 0.6 \times 10^{-10}$	0.51
$\text{C}_5\text{H}_5\text{Co}^+$	$9.75 \times 10^{-10} \pm 0.9 \times 10^{-10}$	0.84

are available for the reactions of bare metal ions and propane; van Koppen et al. [14] reported a value of  $1.7 \times 10^{-11} \text{ cm}^3/\text{s}$  for the overall reaction rate of  $\text{Co}^+$  with propane, a rather low value compared to the Langevin rate constant evaluated as  $1.17 \times 10^{-9} \text{ cm}^3/\text{s}$  and this low value was attributed to the formation of a tight transition state from the  $\text{Co}(\text{C}_3\text{H}_8)^+$  initial adduct. Higher reaction rate and efficiency are now found for the reactions of the  $\text{CoCp}^+$  ion; also the ion  $\text{NiCp}^+$  reacts with a similar rate constant. As already reported [28–30] the presence of the cyclopentadienyl ring enhances the reactivity of the metal ion as a consequence of the increased number of oscillators provided by the ring.

To explore the causes of the different reactivity of the bare and ligated ions, we studied theoretically the mechanism of the two reactions.

### 4.2. The $\text{NiCp}^+$ propane system

Extensive experimental investigations [11,13–15] demonstrated that both the hydrogen and methane elimination reactions in the reaction of  $\text{Ni}^+$  with propane proceed via the insertion of the metal atom in the C–H and in the C–C bond, respectively; these experimental results were confirmed in an accurate theoretical work by Weisshaar et al. [19]; in this work it was found that the first step for the loss of  $\text{H}_2$  is a process implying a secondary C–H insertion which is followed by a transfer of hydrogen atom to form the complex  $\text{Ni}(\text{C}_3\text{H}_6)(\text{H}_2)^+$ , while for the methane loss a C–C bond insertion is the first step of the mechanism leading to the complex  $\text{Ni}(\text{C}_2\text{H}_4)(\text{CH}_4)^+$  which is the exit channel of the reaction. In a successive work Weisshaar et al. [21] confirmed the same mechanism for the reaction of  $\text{Co}^+$  with propane.

According to the previously described level of theory the lowest energy state of  $\text{Ni}(\text{C}_5\text{H}_5)^+$  is the triplet state, which is 21.4 kJ/mol lower than the singlet state. It was pointed out that [28,40] the calculation method here used tends to favour high spin states in transition metal complexes and that the OPTX [41] exchange functional performs better for the spin-state splittings for iron complexes as well as for a series of metallocenes; we used also this functional with no significant change in the relative energy of the singlet and triplet state which remains the ground state for  $\text{Ni}(\text{C}_5\text{H}_5)^+$ . However, no stable insertion structure was found for the triplet state nor a possible low energy reaction path for the elimination reactions was found in the triplet surface even if some stable structures for the adduct ions were found. The absence of any insertion stable struc-

ture can be explained by an inspection of the electronic occupancy of the molecular orbitals. Referring to the general molecular orbital diagram for a  $\text{MCp}^+$  ion [30], our calculations indicate that in the singlet structure both the HOMO and LUMO are the two essentially non-bonding e1 orbitals with a predominant metal d character while in the triplet state both these two orbitals are occupied and in this case the LUMO is the weakly antibonding a1 orbital with a predominant metal s character. The empty e1 non-bonding orbital can accept electron density from the bond being broken of the propane giving rise to the insertion process in the singlet surface while in the triplet state the presence of the electron in this orbital gives rise to a repulsive interaction which hinders the reaction. On the grounds of these results we explored the singlet surface and the relevant structures involved in the minimum energy reaction path for the loss of  $\text{H}_2$  are represented in Fig. 3; the energies of these structures are reported in Table 2 and a schematic potential energy diagram is reported in Fig. 4 along with the reaction profile of the reaction for the loss of methane. The two lower energy structures found for the addition product of propane to the  $\text{C}_3\text{H}_5\text{Ni}^+$  ion are indicated in Fig. 3 as Ni1 and Ni3; in the first structure, which

Table 2

Energetic data for the  $\text{H}_2$  elimination in the reaction of  $\text{NiCp}^+$  with propane

Structure	Energy (kJ/mol)
Ni1	-115.6
Ni2	-91.85
Ni3	-114.28
Ni4	-54.42
Ni5	-64.69
Ni6	-30.1
Ni7	-105.8

is analogous to that found [19] for the reaction of  $\text{Ni}^+$  with propane, the Ni atom is symmetrically bound to the two primary carbon atoms while the propane structure is not affected by this coordination mode; in the second structure the nickel atom is coordinated with two adjacent carbon atoms. These two structures, which are connected by the transition state represented by the structure Ni2, are at almost the same energy and the low energy barrier of the transition state should assure a rapid interconversion between the two forms. From the structure Ni3, a migration of an hydrogen atom from the secondary carbon atom

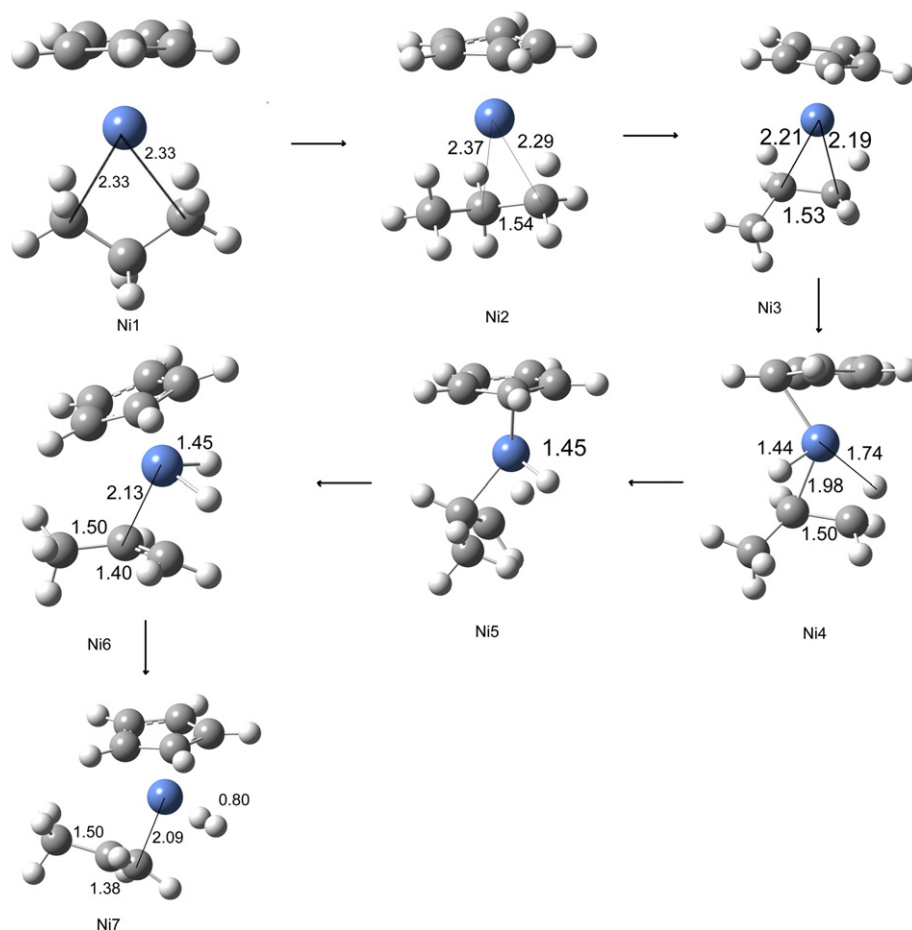


Fig. 3. Critical structures in the reaction path of  $\text{NiC}_3\text{H}_5^+$  with propane: loss of  $\text{H}_2$ .

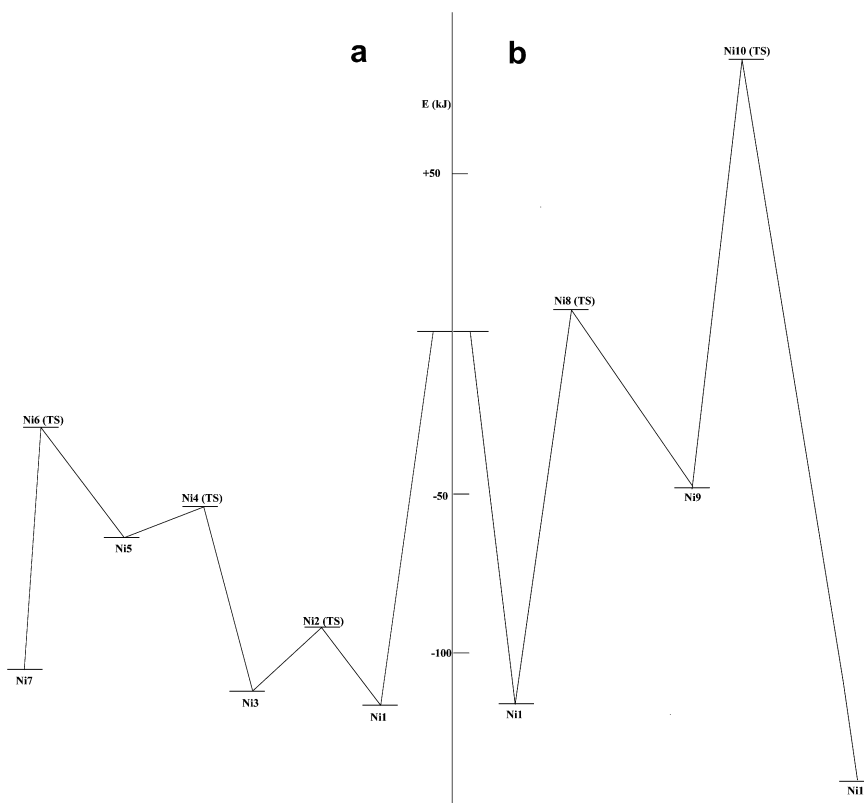


Fig. 4. Critical structures in the reaction path of  $\text{NiC}_5\text{H}_5^+$  with propane: loss of  $\text{CH}_4$ .

to the nickel atom give rise to Ni5 via the transition state Ni4; in Ni5 the C–C bond is shortened to 1.49 Å. A second hydrogen transfer from the terminal carbon atom to the nickel atom occurs via the transition state Ni6 giving rise to the structure Ni7 where an hydrogen molecule is clearly formed and the nickel atom is now bonded to the double C–C bond of a propene molecule in agreement with hypothesis previously advanced [19] for the reaction of the bare  $\text{Ni}^+$ . The transition state Ni6, which is the highest energy structure in the reaction path, is responsible for the observed ratio in the  $\text{H}_2$  and HD loss in the experiment with deuterated propane; this transition state allows the transfer of a deuterium atom to the terminal carbon atom so that the three terminal hydrogen atom and one deuterium atom become equivalent justifying the observed ratio. The proposed mechanism is very similar to that reported for the reaction of the  $\text{Ni}^+$  with propane [19]; common features are the insertion of the nickel atom in the C–H secondary bond and the nature of the rate determining step which is the transfer of an hydrogen atom from a primary carbon atom to the nickel atom; there are, however, significant differences in the relative energies and in the geometries of the structure involved. The energy of Ni1 is 115.6 kJ/mol lower than the reactants while the formation of  $\text{Ni}(\text{C}_3\text{H}_8)^+$  releases 148.8 kJ/mol; the substantial lower energy for this last ion could be due to the difference in the net charge of the nickel atom in the two cases. The presence of the cyclopentadienyl ring adds negative charge to the metal atom whose Mulliken charge is now +0.4 causing

a substantial reduction of the interaction energy of the two moieties. This effect is also present in the final reaction product Ni7. Another important difference is found in

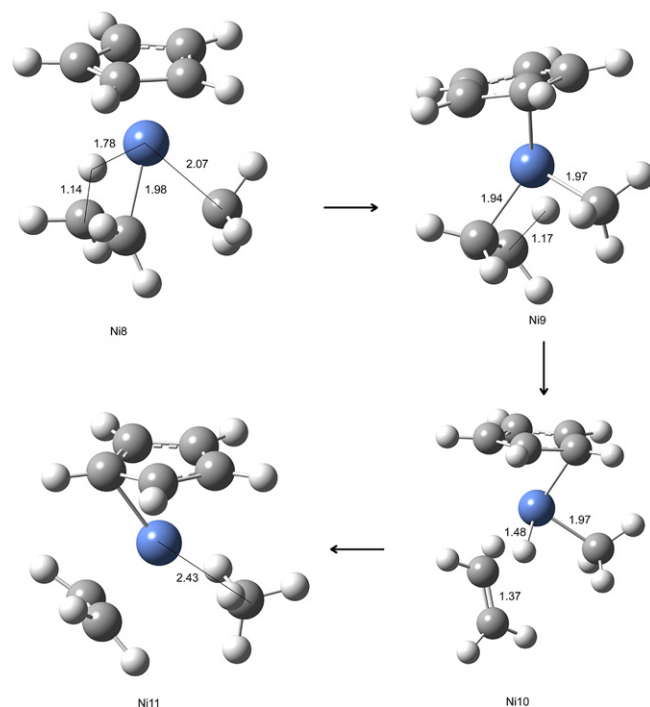


Fig. 5. Energy profile for the reactions of  $\text{NiC}_5\text{H}_5^+$  with propane.

Table 3  
Energetic data for the CH<sub>4</sub> elimination in the reaction of NiCp<sup>+</sup> with propane

Structure	Energy (kJ/mol)
Ni8	8.12
Ni9	-47.44
Ni10	84.48
Ni11	-139.26

the geometry and relative energy of the rate limiting step Ni6; the energy of this structure is now lower than the energy of the reactants by 30.1 kJ/mol while the multicenter transition state found in the reaction of Ni<sup>+</sup> was found higher than the energy of the reactants or slightly lower in the adjusted model used by Weisshaar.

A reaction path for the methane elimination was found and the structures are shown in Fig. 5 while their energies are reported in Table 3. Starting from the Ni1 a transition state (Ni8) is found for the formation of the insertion product Ni9 which is stable by 47.44 kJ/mol with respect to the reactants. From this structure the loss of methane goes through the transition state Ni10 to Ni11 where the methane molecule is formed. The energy of the transition state (Fig. 4) is much higher than the energy of the reactants explaining the absence of methane loss in this reaction. It seems that the bulky cyclopentadienyl

ring does not allow the formation of a multicenter transition state at lower energy as found in the reaction of the bare Ni<sup>+</sup> atom.

#### 4.3. The CoCp<sup>+</sup> propane system

For the same reasons already explained in the case of the reaction of the nickel system, the study of the reaction of CoCp<sup>+</sup> with propane has been restricted to the doublet state. The structures found for the minimum energy path are presented in Fig. 6 and their relative energies are reported in Table 4. The first three structure (Co1, Co2 and Co3) are very similar to those discussed for the nickel; the structure Co4 is again similar to Ni4 since the distances between the metal atom and the propane carbon atoms, as well as the distances in the propane moiety, are almost equal. However, there is a significant difference in the metal–hydrogen bond and in the angle HMC which is 62.5° in Ni4 and 75.9° in Co4; as a consequence of this increase the hydrogen atom is much near to the cyclopentadienyl ring: the distance to the nearest carbon atom is 2.48 Å in Ni4 while is 1.67 Å in Co4. These two transition states give rise to two different structures, Ni5 with the hydrogen atom bonded to the Ni atom, and Co5 where the hydrogen atom jumps into the cyclopentadienyl ring. From Co5, via the transition state Co6, a terminal hydrogen transfer on the cobalt atom give rise to Co7 and then

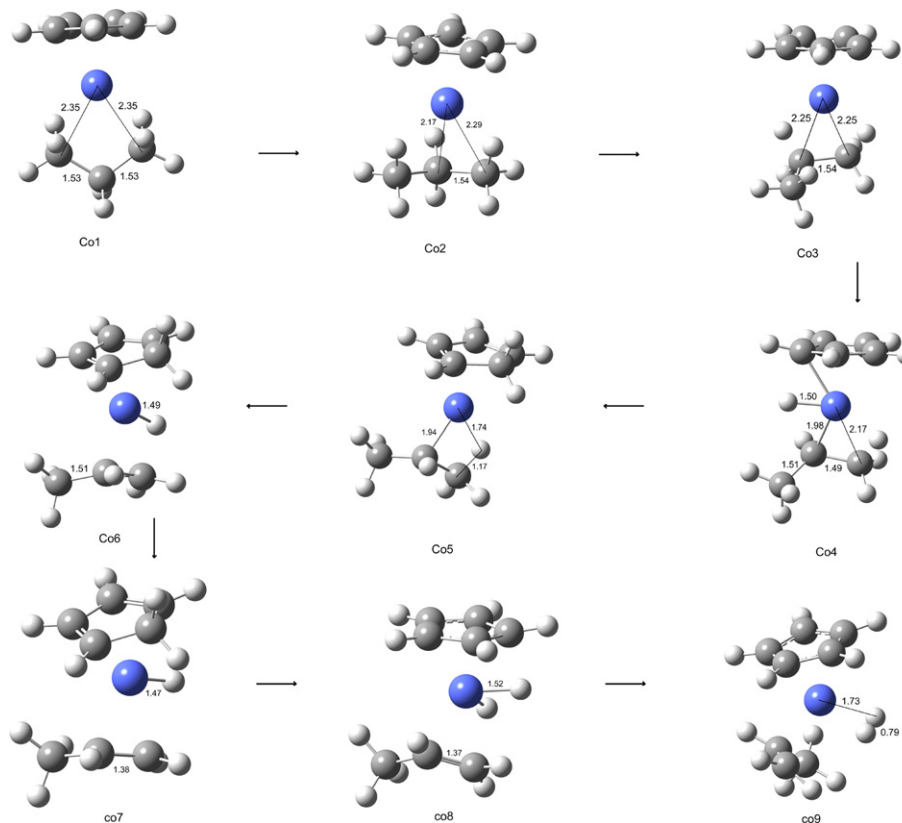


Fig. 6. Critical structures in the reaction path of CoC<sub>3</sub>H<sub>5</sub><sup>+</sup> with propane: loss of H<sub>2</sub>.

Table 4  
Energetic data for the H<sub>2</sub> elimination in the reaction of CoCp<sup>+</sup> with propane

Structure	Energy (kJ/mol)
Co1	-117.6
Co2	-108.7
Co3	-113.1
Co4	-15.9
Co5	-86.9
Co6	-60.1
Co7	-61.3
Co8	+13.7
Co9	-77.5

the transition state Co8 leads to the structure Co9 where the hydrogen molecule is formed.

While the highest energy structure is the transition state Co8, the key step in the mechanism is the formation of Co5 which differentiates the reaction path respect to the nickel reaction and that requires a direct intervention of the cyclopentadienyl ring in the mechanism in a way resembling that reported for the reaction of CoC<sub>5</sub>H<sub>5</sub><sup>+</sup> with methane [28]. The different structure of the intermediate Co5 and of the transition state Co8 account also for the ratio of HD and H<sub>2</sub> loss observed in the cobalt system.

A mechanism for the methane loss involving the cyclopentadienyl ring was not found but the loss of methane is possible through a transition state similar to that found for the nickel system (structure Ni10) but also in this case the energy of this transition state is well above (133.3 kJ) the energy of the reactants so that this reaction is suppressed in favour of the hydrogen loss.

## 5. Conclusion

The different reactivity of the bare and ligated ions can be justified by kinetic considerations; the presence of the bulky cyclopentadienyl ring does not allow the formation of the multicenter transition states reported for the reactions of the bare ions. The transition states calculated in this work indicate a much higher activation energy for the C–C activation process so that only the hydrogen loss is observed.

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