

Reactivity of a cationic alkyl amino-functionalized cyclopentadienyl aluminum compound with olefins: NMR observation and computational investigation of the single propene insertion product into an Al-C bond.

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8 **with olefins: NMR observation and computational investigation of the single propene**
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10 **insertion product into an Al-C bond.**
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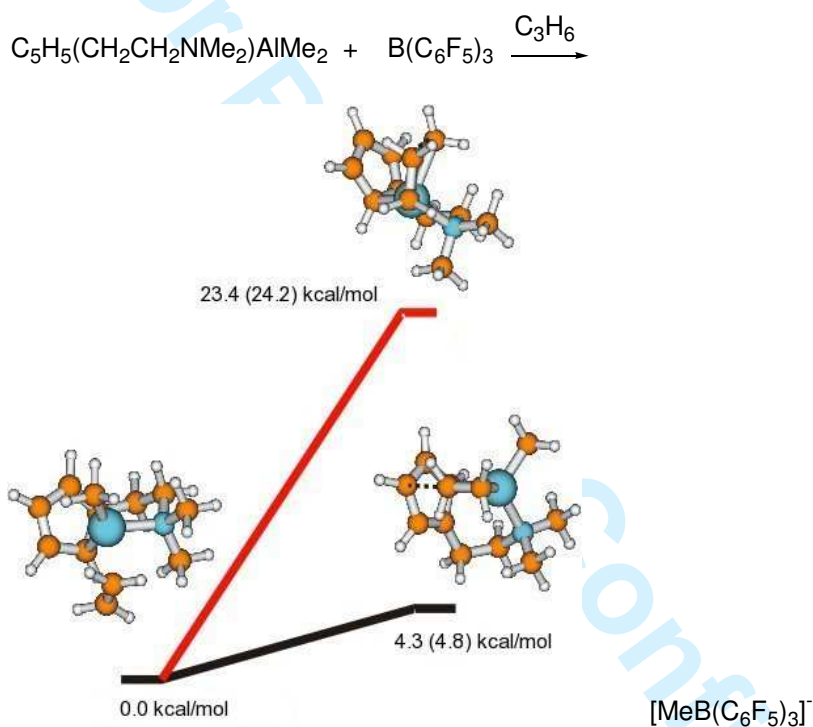
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The reaction of dimethyl [2-(*N,N*-dimethylethylen)cyclopentadienyl]Al(III) with a ionizing agent provided a stable cationic species, which selectively insert one propene molecule into an Al-C bond of the Al-Cp moiety rather than into the Al-Methyl bond. Density functional and *ab initio* calculations were used to characterize the energy landscape of the insertion into the Al-Cp bond for ethylene and propene. The computational results suggest this reaction to be more facile than the insertion into the Al-Me bond.

Abstract

In this study the reactivity of the compound dimethyl [2-(*N,N*-dimethylethylen)cyclopentadienyl]Al(III) toward ionizing species and the subsequent reactivity toward ethylene and propene have been explored. Reactions were studied *via* NMR tube experiments. Upon methyl abstraction by the Lewis acid B(C₆F₅)₃, the amine donor on the ligand side arm coordinates to aluminum, stabilizing the resulting cationic species *versus* secondary reactions. The obtained cationic species was able to polymerize ethylene, albeit with low activity. Reaction with propene resulted in the selective 1,2-insertion of one propene molecule into an Al-C bond of the Al-Cp moiety. Density functional and *ab initio* calculations were used to characterize the energy landscape of the insertion into the Al-Cp bond for both ethylene and propene. The computational results suggest this reaction to be more facile than the insertion into the Al-Me bond.

Introduction

Oligomerization and polymerization of ethylene and olefins are among the most important homogeneous catalytic processes. Since the discovery by Ziegler of the aufbau reaction, aluminum alkyls have long been known as ethylene oligomerization catalysts,¹ and widely used as “cocatalysts” or “scavenger” in Ziegler-Natta olefins polymerization catalysis.² On the contrary, olefin polymerization by means of transition metal-free aluminum based catalytic specie is a quite recent achievement. In 1992 Martin demonstrated that the simple bis(dichloroaluminum)ethane and trialkylaluminum are able to produce polyethylene of high molecular weight in considerably smooth condition.³ In the last decade several examples have been described in the literature concerning olefin polymerization at aluminum, although with low activity. Following the reports of Jordan on mono- and bis(amidinate) complexes of aluminum,⁴ a few related dialkyl aluminum derivatives carrying chelating monoanionic ligands, such as aminotroponimine,⁵ bis(imino)pyridine,⁶ salicylaldimine,⁷ 2-anilinetropone⁸ and, more recently, a bis(iminophosphorano)methandiide aluminum complex, based on a spirocyclic carbon centre subtended by two AlMe₂ units,⁹ have been

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3 also shown to polymerise ethylene. Activation of these compounds was usually achieved by the
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5 ionising agents traditionally used in homogeneous Ziegler-Natta catalysis (i.e. $B(C_6F_5)_3$ or
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7 $[(C_6H_5)_3C][B(C_6F_5)_4]$). Very interestingly, Sen *et al.* reported that simple aluminum alkyls, after
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9 reaction with ionizing agents, catalyse the polymerization not only of ethylene but also of
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11 propene,¹⁰ while recently simple aluminum alkyls in the presence of chloro activators were shown
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13 to promote ethylene polymerization in mild conditions with higher activity.¹¹
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17 The nature of the active species involved in the ethylene polymerization with aluminum based
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19 systems has been investigated; although cationic alkyl complexes have been isolated and
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21 characterized, it is still unclear if they are directly responsible for the catalytic activity. Monitoring
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23 the reaction of perdeuterio-ethylene with aminotroponimate aluminum complex, Jordan excluded
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25 that intact cationic species are the active ethylene polymerisation catalysts, while the main reaction
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27 is a β -H transfer to generate the corresponding cationic aluminum hydride.^{5a} According to a
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29 theoretical study on ethylene polymerisation at aluminum centres, mononuclear aluminum species
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31 are implausible to produce polymers, because chain transfer is much faster than propagation.¹²
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33 Therefore, the observed polymerization activity could be due to minor unidentified species
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35 produced *in situ*, and probably more complex structures have to be considered.
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44 We noted that there has been little investigation into the reactivity with olefins of
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46 aluminum(III) compounds bearing cyclopentadienyl ligand,¹³ which instead were widely used for
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48 olefin polymerization catalysts.² Moreover, although cationic species represent potential candidates
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50 for catalysis due to the increased Lewis acidity,¹⁴ cationic aluminum species are quite unstable, and
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52 very often they undergo ligand scrambling reactions with the anion.¹⁵ The stability of the cationic
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54 species could be strongly improved by the presence of a Lewis base in the solvent medium,¹⁶ or,
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56 even better, in the ligand himself.^{7a,b} Cyclopentadienyl ligands with tethered donor units have been
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58 largely used in the preparation of several compounds of s-, p-, d-, and f-block elements.¹⁷ In
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60 particular, cyclopentadienyl compounds with dialkylaminoalkyl side chain have been also

employed in transition metal olefin polymerization catalytic systems.^{17a, 18} In this study we have explored the reactivity of dimethyl [2-(*N,N*-dimethylethylen)cyclopentadienyl]Al(III)¹⁹ toward ionizing species and the subsequent reactivity toward ethylene and propene. Monitoring the reaction of the obtained cationic species with propene allowed the observation of an unprecedented propene insertion product into an Al-C bond. The energy landscape of this reaction channel was also investigated by means of electronic structure calculations in the gas phase and shown to proceed through a low-lying transition state.

Results and discussion

Experimental results

Dimethyl [2-(*N,N*-dimethylethylen)cyclopentadienyl]Al(III) (**1**), synthesized according to the literature,¹⁹ was allowed to react with 1 eq of B(C₆F₅)₃²⁰ to give the cationic species [C₅H₅(CH₂CH₂NMe₂)AlMe]⁺ [MeB(C₆F₅)₃]⁻ (**2**). The reaction was studied *via* NMR in C₆D₅Cl solution at 25 °C (Figure 1a). Diagnostic resonances in the ¹H NMR spectrum of **2** are a singlet at -1.07 ppm attributable to the AlMe (3 H), and a singlet at +1.07 ppm (3 H) attributable to the “free” anion MeB(C₆F₅)₃⁻.²⁰ Consistently, in the ¹³C NMR spectrum, a signal at -16.3 ppm attributable to AlMe, and a signal at 10.1 ppm attributable to MeB(C₆F₅)₃⁻ appears. In addition, the ligand resonances are shifted at higher field in comparison with those of the neutral starting compound. Concerning the cyclopentadienyl ligand, the presence of two singlets (6.15 ppm and 5.79 ppm, 2 H each) in the ¹H NMR spectrum, and of three signals (129.2, 121.3 and 96.5 ppm) in the ¹³C NMR spectrum is compatible with a “windscreen-wiper” fast haptotropic rearrangement process, already observed in analogous neutral compound (*Scheme 1*).²⁰ Lower temperature ¹H NMR experiments performed in CD₂Cl₂ resulted in more complex spectra, with new signals in the Cp regions and two broad singlet at -1.09 and -1.78 ppm attributable to AlMe hydrogen atoms; the ¹³C NMR spectrum, registered at -60 °C, displayed five signals (130.1, 128.0, 124.7, 116.1, 111.6 ppm). These data indicates that at lower temperature the “windscreen-wiper” fluxional behaviour is frozen out. It is

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3 worth noting that such a cationic species is stable for days in C_6D_5Cl solution at room temperature.
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5 On the contrary, the analogous reaction of $CpAlMe_2$ and $B(C_6F_5)_3$ did not result in stable or
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7 observable cationic species. Probably in our case the extra donor $-NMe_2$ unit could stabilize the
8
9 cation against side reactions such as ligand redistribution.¹⁵
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12 The reactivity of the cationic species **2** toward olefins was explored: compound **1**, when activated
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14 with 1 equiv. of $B(C_6F_5)_3$, polymerised ethylene (1 atm) to solid polyethylene albeit with low
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16 activity ($80 \text{ g (PE) mol}^{-1} \text{ h}^{-1} \text{ atm}^{-1}$), while, in the same conditions, it resulted inactive in the propene
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18 polymerization.
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22 Interesting results derived from the study of the reactivity of the cationic species **2** toward olefins by
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24 NMR tube reactions. To a solution of compound **2** in C_6D_5Cl was added propylene, and the reaction
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26 was monitored via 1H NMR (Figure I b, c). New resonances appeared just after a few minutes from
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28 the injection of propylene. After two hours their intensities were in 1:2 ratio with respect to the
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30 original cationic aluminum species **2**. These resonances were attributed to a new organometallic
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32 cationic aluminum species (**3**), arising from the insertion of propylene into an Al- C bond of **2**
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34 (*Scheme 2*). Unexpectedly, the propylene does not insert into the Al-*Me* bond, but into the Al-Cp
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36 moiety of **2**. Density functional and *ab initio* calculations (*vide ultra*) were used to characterize the
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38 energy landscape of the reaction for both ethylene and propene, and predicted a barrier of at least
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40 23.4 Kcal/mol for the insertion of the ethylene into Al-*Me* bond, while the insertion into Al-Cp
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42 bond presented very low barriers (4.3-4.8 Kcal/mol). The structure of **3** was completely elucidated
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44 by the use of 1H and ^{13}C , mono- and bi-dimensional NMR experiments, including DEPT, COSY,
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46 direct and long-range $^1H - ^{13}C$ correlation (Tables 1, 2 and 3), disclosing interesting features. First,
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48 the anion $MeB(C_6F_5)_3^-$ is not involved in the reaction, neither interacts with the new cationic
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50 species; in the 1H NMR spectrum the intensities of the singlet at + 1.07 ppm (3 H, $MeB(C_6F_5)_3^-$)
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52 remains constant. Coherently, the ^{19}F NMR data are as expected for symmetric methyl-borate
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54 anions, showing no evidence of methyl or fluorine interactions with the cationic centre.
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3 In the ^1H NMR spectrum characteristic resonance of the new species (**3**) is the singlet at -0.81 ppm
4 (3 H), accounting for the Al-Me protons. In the ^{13}C NMR spectrum the corresponding carbon
5 displays a resonance at -11.4 ppm. In the ^1H NMR spectrum diagnostic resonances for the propene
6 insertion are the two doublet of doublet at -0.25 and -0.55 ppm, relative to the diastereotopic
7 geminal hydrogen atoms (H_a and H_b) bound to the carbon in α position respect to Al. H-H COSY
8 analysis confirms that both hydrogen atoms H_a and H_b correlates with the same CH hydrogen (H_c ,
9 2.18 ppm); likewise, this H_c hydrogen is coupled with a methyl group, appearing as a doublet at
10 1.01 ppm (Figure 2). HMBC (heteronuclear multiple bond correlation) ^1H - ^{13}C 2D NMR experiment
11 established unambiguously the structure, through observation of the C-H correlation between the β
12 carbon atom of the propene inserted unit (Al-CH₂-CHMe, 35.6 ppm) and the hydrogen bound to the
13 sp^3 hybridized C5-ring carbon atom (H_d , 2.90 ppm). In addition, in the ^1H NMR spectrum a long
14 range coupling constant ($^4J = 1.5$ Hz) between H_a and the hydrogen atom bound to the sp^3 carbon
15 atom of the C5 ring (H_d) was observed, consistent with a stereorigid "W" conformation of the four
16 bonds between these two hydrogen atoms.
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36 The insertion of propylene therefore resulted highly regiospecific, affording exclusively the
37 1,2-insertion product. The structure of the product was identified by careful consideration of the
38 coupling constants to H_a in the ^1H NMR spectrum. In fact, the signal at -0.55 ppm appears as a
39 doublet of doublet, with further fine structure due to the long-range coupling. The geminal ($^2J(\text{H}_a$ -
40 $\text{H}_b) = 15.0$ Hz) and the vicinal ($^3J(\text{H}_a$ - $\text{H}_c) = 6.8$ Hz) coupling constants reveal significantly different
41 values depending on the small H_a -C-C- H_c dihedral angle. The molecule seems to be locked in a
42 *pseudo*-metallacycle, where the methyl group originated from propene insertion occupy
43 preferentially an equatorial position. The nitrogen atom should be strongly coordinated to the Al, as
44 evidenced by the appearance of two singlets for the $\text{NM}e_2$ groups both in the ^1H (1.92 and 1.97
45 ppm) and ^{13}C (44.4 and 44.7 ppm) NMR spectra. Concerning the C5 ring, in the ^{13}C NMR spectrum
46 five distinct resonances are observed (68.0, 129.6, 138.0, 149.0, 157.0), clearly indicating a locked
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3 position of the two C-C double bonds. The low field ^1H NMR spectrum pattern, in fact, is the one
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5 expected for a 1,3 di-substitute cyclopentadiene ring.
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8 Coherently, density functional and *ab initio* calculations (*vide ultra*) also indicated a better
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10 stability and a lower transition state energy barrier for the regioisomers deriving from the 1,2
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12 insertion, which could be also explained in terms of Mulliken population of the olefin sp^2 carbon
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14 atoms. Moreover, as a further support to the whole structure, the calculated proton chemical shifts
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16 (*vide ultra*) are in good agreement with the experimental results.
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20 In order to force the reaction to completion, the solution was warmed up at higher temperature (i.e.
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22 $50\text{ }^\circ\text{C}$), but as a result only decomposition products were obtained. Removal of propene did not
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24 cause any de-insertion reaction. Coherently with this result, the computed barrier to the de-insertion
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26 reaction resulted high (*see* Table 4). On the contrary, when more propene was added to replace the
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28 consumed one, the reaction was forced to completion; at room temperature in a 30 hours reaction
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30 period the **3** became the prevalent species (in 1.5 : 1 molar ratio respect to **2**). Attempts to isolate
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32 the species **3** as analytically pure material, performed on larger scale reaction, were unsuccessful:
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34 the reactions gave no clean products, probably due to the extreme air sensitivity of the cationic
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36 aluminium species.
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40 The reactivity of compound **2** toward ethylene was studied in analogous experiments.
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43 Monitoring the reaction of compound **2** with ethylene (3 equiv) in $\text{C}_6\text{D}_5\text{Cl}$ solution at $23\text{ }^\circ\text{C}$ showed
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45 that the amount of **2** and ethylene gradually decreased in 1:1 molar ratio. After 6 h, the
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47 concentrations of (**2**) and of ethylene were respectively 55 % and 80 % of the initial ones.
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50 Conversely new resonances, attributable to the Al-Cp ethylene insertion product (**4**), analogous to **3**,
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52 appeared. Characteristic resonances were the singlet at -0.85 ppm , attributable to the AlMe^+ of the
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54 new cationic aluminum species, and two doublets of doublets at -0.26 and -0.46 ppm attributable to
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56 the diastereotopic geminal hydrogen atoms (H_a and H_b) bound to the carbon in α position respect to
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58 Al.
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3 Consistently with the above structure, compound **3** does not further react with propene; formation
4 of polypropene was not detected even on a prolonged reaction time (24 hours). Following a
5 reviewer suggestion, in another experiment, **3** was preformed in situ, and then some ethylene was
6 further added. The reaction was monitored by ^1H NMR. Interestingly, after a four hours period, the
7 concentration of **3** remained unchanged. On the contrary, the concentration of **2** decreased, as well
8 as the concentration of ethylene, and as already observed above formation of **4** was detected. In
9 conclusion while at the moment the identification of the real catalytic species responsible of the
10 ethylene polymerization is still elusive, the performed NMR experiments clearly indicates a
11 preference for olefin insertion into the Al-Cp bond.
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27 **Computational results**

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29 The final structure of the stationary points on the B3LYP/6-311+G(d,p) potential energy surface for
30 the ethylene insertions (i.e. the cation (**2**), its complex with ethylene (**CE**), the transition state (TS)
31 describing the insertion of ethylene into the Al-Cp bond (**TS-E1**), the TS for the insertion of
32 ethylene into the Al-Me bond (**TS-E2**) and the end product (**PE1**) of the insertion into the Al-Cp
33 bond) is shown in Figure III. Figure IV shows the equivalent structures for the propene insertion
34 into the Al-Cp bond. Table 4 provides the relative energetics of **TS-E1**, **TS-E2**, **PE1** with respect to
35 the ethylene-cation (**CE**) complex, and of the transition states (**TS-P1-4**) and products (**PP1-4**) with
36 respect to the related complexes (**CP1-4**) for the propene insertion.
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48 From Figure III, we notice that the geometry of **CE**, **TS-E1** and **PE1** present a relatively short Al-
49 Cp distance suggesting the presence of an interaction between Al and the Cp ring during all reaction
50 stages. The structures of **CE** and **TS-E1** seems to suggest Al to feature a η^1 coordination with the
51 Cp ring, whereas the proximity of Al to the ring in **PE1** is likely due to the polarization of the Cp
52 ring by the positively charged metal ion. One also notices that the gas phase equilibrium structure of
53 **2** has Al located over the electron rich Cp ring, thus suggesting a η^5 coordination with the latter.
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The low temperature ^{13}C NMR spectrum for this species indicates an asymmetric chemical

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3 environment for the ring carbons. Theoretical ^{13}C NMR chemical shifts for **2** (129.7 ppm for C1,
4 101.4 ppm for C2, 125.4 ppm for C3, 123.2 ppm for C4, and 108.1 ppm for C5, as computed at the
5 B3LYP/6-311+G(2d,2p) level) show, accordingly, a non-symmetric pattern in agreement with the
6 experimental data. A similar lack of symmetry is found also in the distances between Al and the
7 carbon atoms in the Cp ring (2.165, 2.180, 2.314, 2.322, and 2.192 Å) and in the Al-C bond orders
8 (0.2779, 0.3175, 0.2308, 0.2259 and 0.3095) computed using the Natural Bond Order (NBO)
9 approach. The difference in Al-C distances appears to be due to a weak strain in the structure
10 induced by the specific conformation of the $\text{CH}_2\text{CH}_2\text{NMe}_2$ ligand obtained during geometry
11 optimization, which should disappear upon increasing the system temperature thanks to a more
12 fluxional behaviour of the $\text{CH}_2\text{CH}_2\text{NMe}_2$ group. As for the Al-C bond orders, we notice that our
13 data indicate the presence of a fractional bonding of Al with *all* the ring carbons, although a weak
14 preference is present toward the substituted carbon in the ring and its two neighbours. In our view,
15 this suggests Al to have either a η^3 or η^5 coordination with the Cp ring in **2**.

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Despite the aforementioned similarity between experimental and theoretical ^{13}C NMR shift patterns
and the fact that ring coordinated cationic complexes between Al and dicarbollylamine ligands
similar to **2** were previously characterized by X-ray crystallography, NMR spectroscopy and DFT
calculations, we feel however that it would be a hazard to draw a definitive conclusion about the
possible changes induced by temperature in the structure of **2**.²¹ This uncertainty is mostly due to
the absence of explicit solvent molecules in our calculations, which may induce further distortions
in the structure of **2** following coordination with the Al cation as found in the case of **CE**.

As for the energetics of the ethylene insertions, Table 4 indicates already at first glance a good
agreement between the energy profile for the insertion into both the Al-Cp and Al-Me bonds
provided by the two levels of theory. Overall, our theoretical results indicate the insertion into the
Al-Cp bond to be more facile than the one into the Al-Me bond by roughly 19 kcal/mol, in good
agreement with the experimental results that indicate the preferential formation of **3**.

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3 In an attempt of interpreting the driving force and mechanism (electrophilic attack of the activated
4 olefin on the Cp ring or *vice versa*) for the latter reaction, Mulliken atomic charges were computed
5 for **CE**. Unfortunately, this method failed to provide a clear-cut suggestion, with the C atoms
6 involved in the reaction in both ethylene and the Cp ring bearing negative partial charges. In fact, if
7 one excludes the C atoms in position 1 (+0.08) and 2 (-0.36) with respect to the ring substituent and
8 in close proximity of the positive Al atom in **CE**, the remaining carbons in the Cp ring bear smaller
9 negative charges (-0.20 on C3, -0.11 on C4 and -0.16 on C5) than the olefin ones (-0.36 on the
10 carbon closer to the ring and -0.30 on the other). An inspection of the DFT molecular orbitals on
11 **TS-E1** highlighted, however, the presence of an overlap between the unoccupied ethylene π^* and
12 an occupied orbital of the Cp ring (TS/HOMO, Fig. Va). The latter interaction appears to be
13 stabilizing the HOMO orbital (-10.4 kcal/mol at the B3LYP/6-311+G(d,p) level) at the TS
14 geometry with respect to the HOMO in the complex, which is highly localized on the ring. Roughly
15 speaking, this finding may be interpreted as indicating that the electron donation from the occupied
16 Cp HOMO to the unoccupied ethylene π^* may be identified as largely responsible for lowering the
17 barrier. In fact, the other highly lying valence orbitals (HOMO-1-HOMO-3) describing the π
18 systems on both Cp and ethylene increase in energy at the TS geometry. In other words, the
19 mechanism of the transformation appears to be mostly driven by the nucleophilic attack of the Cp
20 ring onto ethylene despite the smaller Mulliken charges borne by the ring carbon atoms (also, *vide*
21 *infra* for propene).

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51 A similar conclusion is reached studying the regio-selectivity of the propene insertion into the Cp-
52 Al bond, on which we decided to focus given the substantially lower energy barrier found in the
53 study with ethylene. Similarly to the latter case, the barriers separating the complexes from the
54 insertion products are predicted to be low by both theoretical methods, with MP2 suggesting
55 slightly lower barriers than DFT. From these results, however, it also appears that the formation of
56 products having the methyl group of the propene closer to the ring (**PP1** and **PP2**) is more facile
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(roughly 4-6 kcal/mol depending on the theoretical method) than for the other two regio-isomers (**PP3** and **PP4**). This finding is clearly in optimal agreement with the NMR characterization of the product suggesting the formation of species with only a hydrogen close to the Cp ring. This result can be easily understood on the basis of our mechanistic suggestion surveying the coordination and Mulliken population of the olefin sp^2 carbon atoms in the complexes as shown for two representative complexes (**CP1** and **CP4**) in Fig. Vb. Due to their geometry, both **CP1** and **CP2** present the almost neutral secondary carbon atom in the coordinated propene ($CH_2=CHMe$, +0.02) geometrically available for the nucleophilic attack by the Cp ring thanks to a preferential η^1 coordination between Al and the unsubstituted CH_2 carbon atom. Conversely, the formation of **PP3** and **PP4** from **CP3** and **CP4** requires the olefin to shift closer to the Cp ring in order to facilitate the nucleophilic attack onto the negatively charged carbon (-0.51) in CH_2 , a displacement that should be expected to somewhat contributing to the increase in the energy barrier for the process. The larger negative charge and the structural requirement to form **PP3-4** also help in explaining the higher barrier that needs to be surmounted in forming **PP3** and **PP4** than in the case of **PE1**. As a final comment, it is also useful to mention that the reaction energy, computed as difference between complex and product energies (Tab. 4), indicates a somewhat better stability for **PP1** and **PP2** than for **PP3** and **PP4** with respect to their parent complexes, thus suggesting that **PP1** and **PP2** should be preferentially found even in case of an equilibrium process.

An additional support for the preferential formation of **3**, either in the **PP1** or **PP2** form, is provided by the computed chemical shifts⁽²²⁾ of H_a , H_b and H_c (Scheme 2) reported in Table 5 for the four possible regioisomers. As discussed in the experimental section, the signals of these three protons play a key role in elucidating the structure of **3**. Similarly, the theoretical results indicate a distinctively different pattern for the **PP1-2** and **PP3-4** pairs: whereas the former presents a single proton resonating around 3 ppm (lower field) and two protons absorbing around 0 ppm (higher field), the latter has two protons shifted at lower field and one at slightly higher field. Comparing

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3 with the chemical shifts reported in Table 1, it appears evident that only the chemical shifts of the
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5 **PP1-2** pair match the experimentally observed pattern of signals. As for the absolute accuracy of
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7 the computed NMR shifts, we point out that an offset of roughly 0.5 ppm between the experimental
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9 and theoretical data is a quite acceptable result⁽²³⁾ considering that possible effects due to solvation
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11 have not been taken into account in our model calculations. Due to this, a definitive discrimination
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13 between **PP1** and **PP2** based on a finer matching of chemical shifts would be inappropriate.
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17 18 19 20 **Conclusions**

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22 In this study, we have explored the reactivity of dimethyl [2-(*N,N*-
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24 dimethylethylen)cyclopentadienyl]Al(III) toward ionizing species and the subsequent reactivity
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26 toward ethylene and propene. After abstraction of the methyl group by the ionizing agent B(C₆F₅)₃,
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28 the amine function on the side arm coordinates to aluminum, stabilizing the resulting cationic
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30 species versus secondary reactions. The cyclopentadienyl ligand having a tethered amine unit offers
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32 a good balance of stability and reactivity. The obtained cationic species was able to polymerize
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34 ethylene, albeit with low activity. Quite surprisingly, conversely, reaction with propene resulted in
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36 the selective insertion of one propene molecule into an Al-C bond of the Al-Cp moiety. The energy
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38 landscape of both processes was explored by means of electronic structure methods, with results for
39
40 the transition state barrier heights and proton chemical shifts strongly supporting the interpretation
41
42 of the experimental results.
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48 The carbalumination, i.e. the insertion of olefins into an Al-C bond, is a well known reaction;²⁴ it is
49
50 enough to mention that the insertion of ethene into Al-ethyl bonds is the basis of the original
51
52 Aufbau reaction for the preparation of mixture of α -alkene or alcohols (C₄-C₃₀).¹ Nevertheless, to
53
54 our knowledge, direct observation of the reaction product deriving from the single insertion of
55
56 propene into an Al-C bond has never been reported. Single olefin insertion products have been
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58 instead observed with some early transition metal, and constituted model of intermediates for the
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60 insertion mechanism in Ziegler-Natta polymerization.²⁵ The observation that propene undergoes

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2
3 insertion reaction into the Al-Cp moiety of the species **2** showed that this bond is more reactive than
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5 the Al-Me bond, which acts instead as a spectator ligand. It is worth nothing that this behaviour is
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7 the opposite of the one observed with the classical homogeneous transition metal based catalytic
8
9 systems for olefin polymerization, for which the Metal-Alkyl bond is the reactive one, while the
10
11 cyclopentadiene acts as “ancillary” ligand.² Actually, the present case has much in common with an
12
13 earlier report by Jordan on the reversible cycloaddition reactions of ethylene and alkynes to cationic
14
15 β -diketiminato aluminum complexes.²⁶ Density functional theory²⁷ was used to study the factors
16
17 that influence these reactions and predicted barriers for the cycloaddition reactions significantly
18
19 lower than those previous calculated for ethylene insertion in the Al-alkyl bonds of cationic
20
21 aluminum alkyl complexes.¹²
22
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27 Such results nicely agree with our present conclusions, and further confirm the experimental
28
29 observation that the cationic species **2** selectively inserts one propene molecule into an Al-C bond
30
31 of the Al-Cp moiety rather than into the Al-Methyl bond.
32
33

34 35 36 **Experimental**

37
38 **General.** Manipulations of sensitive materials were carried out under a dry nitrogen atmosphere
39
40 using Schlenk or glove-box techniques. $\text{C}_6\text{H}_5\text{Cl}$ and $\text{C}_6\text{D}_5\text{Cl}$ were dried over CaH_2 and distilled
41
42 prior to use. Polymerization grade ethylene and propene (SON) were used without purification. The
43
44 compounds dimethyl [2-(*N,N*-dimethylethylen)cyclopentadienyl]Al(III)¹⁸ and $\text{B}(\text{C}_6\text{F}_5)_3$ ¹⁹ were
45
46 synthesized according to literature procedures. NMR spectra were recorded on a Bruker Advance
47
48 400 MHz spectrometer (¹H, 400 MHz; ¹³C, 100 MHz; ¹⁹F 376MHz); chemical shifts were
49
50 referenced to the residual protio impurity of the deuterated solvent.
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56
57 **Ethylene Polymerization Tests:** A typical polymerization test was carried out in a 100-mL glass
58
59 flask charged under nitrogen with 12 mL of dry $\text{C}_6\text{H}_5\text{Cl}$ and thermostated at 23 °C. The inert gas
60
was replaced by ethylene at 1 atm, then 0.05 mmol of dimethyl [2-(*N,N*-

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2
3 dimethylethylen)cyclopentadienyl]Al(III) and 0.05 mmol of B(C₆F₅)₃ (each dissolved in 1.0 mL of
4 ClC₆H₅) were injected into the flask. The flask was fed with constant monomer pressure, and after
5
6
7
8 1h the reaction was stopped by injecting methanol. The mixture was poured into acidified methanol,
9
10 and the polymer was recovered by filtration, washed with fresh methanol, dried under vacuum, and
11
12 analyzed by DSC and NMR (m.p.: 137 °C; ¹³C NMR in C₂D₂Cl₄; 120 °C, δ in ppm from TMS:
13
14 30.00).
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19

20 **Generation of [C₅H₅(CH₂CH₂NMe₂)AlMe]⁺ [MeB(C₆F₅)₃]⁻ (2).** In a glove-box dimethyl [2-(N,N-
21 dimethylethylen)cyclopentadienyl]Al(III) (13 mg, 0.065 mmol) was allowed to react with B(C₆F₅)₃
22 (33 mg, 0.065 mmol) in 0.5 ml of C₆D₅Cl at 20 °C. The solution was analysed by NMR
23
24 spectroscopy at room temperature. ¹H NMR (ClC₆D₅, 293 K): δ= -1.07 (s, 3H, Al-CH₃), 1.07 (s,
25
26 3H, B-CH₃), 1.69 (s, 6H, N-(CH₃)₂), 2.11 (t, 2H, Cp-CH₂), 2.35 (t, 2H, NCH₂), 5.79 (s, 2H, Cp-H),
27
28 6.15 (s, 2H, Cp-H). ¹³C NMR (ClC₆D₅, 293 K): δ= -16.35 (Al-CH₃), 10.12 (B-CH₃), 25.25 (Cp-
29
30 CH₂), 44.17 (N-(CH₃)₂), 59.30 (NCH₂), 96.55 (Cp-C_{2,5}), 116.94 (Cp-C_{3,4}), 129.22 (Cp-C₁). ¹⁹F
31
32 NMR (ClC₆D₅, 293 K): δ= -132.2 (d, ³J = 22 Hz), -164.9 (t, ³J = 21 Hz), -167.3 (t, ³J = 21 Hz).
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39 **Reaction of [C₅H₅(CH₂CH₂NMe₂)AlMe]⁺ [MeB(C₆F₅)₃]⁻ (2) with ethylene.** In a J-Young NMR
40 tube, dimethyl [2-(N,N-dimethylethylen)cyclopentadienyl]Al(III) (0.001 mmol) and B(C₆F₅)₃
41 (0.001 mmol) were dissolved in 0.7 ml of C₆D₅Cl containing C₆H₆ (0,04 M) as internal standard
42 and previously saturated with ethylene (3 equiv, measured by ¹H NMR) at 23 °C. The reaction was
43
44 monitored via NMR spectroscopy at 23 °C. The NMR spectra showed that the amount of **2** and
45
46 ethylene gradually decreased in 1:1 molar ratio. After 3 h, the concentrations of (**2**) and of ethylene
47
48 were respectively the 70 % and the 89 % of the initial ones, and, after 6 hours the 55 % and the 80
49
50 % of the initial ones. Conversely new resonances, attributable to the Al-Cp ethylene insertion
51
52 product (**4**), appeared. After 6 hours the molar ratio **4** : **2** was almost 1 : 1. ¹H NMR for compound
53
54 **4**, selected resonances (ClC₆D₅, 293 K): δ= -0.85 (s, 3H, Al-CH₃), 1.07 (s, 3H, B-CH₃), -0.46 (dd,
55
56 1H, Al-CH_aH_b-), -0.26 Al-CH_aH_b- (dd, 1 H, Al-CH_aH_b-), 1.84 (s, 3H, NMeMe'), 1.89 (s, 3H, N-
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MeMe'), 2.95 (m, 1H, Hd), 5.94 (d, 1H, H Cp), 6.26 (d, 1H, H Cp), 6.47 (s *br*, 1H, H Cp). ^{19}F NMR (C_6D_5 , 293 K): $\delta = -132.2$ (d, $^3J = 22$ Hz), -164.9 (t, $^3J = 21$ Hz), -167.3 (t, $^3J = 21$ Hz).

Reaction of $[\text{C}_5\text{H}_5(\text{CH}_2\text{CH}_2\text{NMe}_2)\text{AlMe}]^+ [\text{MeB}(\text{C}_6\text{F}_5)_3]^-$ (2) with propene. In a glove-box dimethyl [2-(N,N-dimethylethylen)cyclopentadienyl]Al(III) (13 mg, 0.065 mmol) was allowed to react with $\text{B}(\text{C}_6\text{F}_5)_3$ (33 mg, 0.065 mmol) in 0.5 ml of $\text{C}_6\text{D}_5\text{Cl}$ containing C_6H_6 as internal standard (0,08 M) at 23 °C. Propylene was injected by syringe (3 equiv, measured by ^1H NMR). The reaction was monitored via NMR spectroscopy at room temperature, giving the reaction product **3**. After 2 hours since the addition of propene the amount of species **3** resulted in 1:2 ratio with respect to the species **2**. The species **3** was characterized by ^1H , ^{13}C , DEPT, homonuclear and heteronuclear COSY, direct and long-range $^1\text{H} - ^{13}\text{C}$ correlation NMR experiments. The NMR data are reported in Table 1, 2 and 3. ^{19}F NMR (C_6D_5 , 293 K): $\delta = -132.2$ (d, $^3J = 22$ Hz), -164.9 (t, $^3J = 21$ Hz), -167.3 (t, $^3J = 21$ Hz).

A second experiment was performed as above but, after a two hours period reaction time, some of the propene was removed by three freeze pump thaw cycle, becoming one third of the species **2**. The tube was maintained at 23 °C, and the reaction was monitored by ^1H NMR. The NMR spectra, registered every 15 minutes in a 12 hours period, showed that the molar ratio between the species **2**, **3** and propene was unchanged.

In another experiment, performed as above, after the two hours period reaction time, more propene was added by syringe, replacing the consumed one. The tube was kept at 23 °C, and the reaction was monitored by ^1H NMR. The NMR spectra showed that the species **2** was gradually converted in the species **3**; in a 30 hours reaction period the species **3** became the prevalent one (in 1.5 : 1 molar ratio respect to species **2**).

In a further experiment, performed as above, after two hours reaction since the addition of propene, ethylene was added by syringe and the reaction was monitored by ^1H NMR. After four hours the concentration of the species **3** remained unchanged. On the contrary, the concentration of the

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3 species **2** decreased, as well as the concentration of ethylene, and resonances attributable to species
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5 **4** were detected.
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8 9 **Computational details.**

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11 Gas phase electronic structure calculations were carried out using the ADF²⁸ and Gaussian03²⁹
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13 suites of codes, employing both Density Functional Theory (DFT) and post Hartree-Fock *ab initio*
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15 methods, the latter at the second order Møller-Plesset (MP2) level of theory. The DFT calculations
16
17 employing the ADF program were carried out using the local exchange-correlation potential by
18
19 Vosko et al.³⁰, augmented in a self-consistent manner with Becke's exchange-gradient correction³¹
20
21 and Perdew's correlation gradient correction³², and mostly used to obtain initial geometries for
22
23 further refinement. Double-zeta Slater type orbitals (STO) were used for carbon (2s,2p) and
24
25 hydrogen (1s), augmented with single 3d, and 2p functions (respectively). Aluminium was
26
27 described using a triple-zeta STO quality basis set augmented with a 4d polarization function.
28
29 Calculations carried out with the Gaussian suite employed the 6-311+G(d,p) basis set in
30
31 conjunction with DFT-B3LYP and MP2 models. Mulliken population analysis was carried out
32
33 using the 6-31G(d) basis set. Geometries for all species (i.e. cation, olefin complexes, transition
34
35 states, TS's, and final products) were fully optimized using B3LYP/6-311+G(d,p) and the stationary
36
37 points found were characterized by means of frequency calculations. Structural optimizations of the
38
39 putative catalytic cationic species (**2**) suggested in Scheme 1 were carried out using two different
40
41 DFT functionals starting from sensible initial geometries with the aluminium coordinated to the
42
43 amine group and the Cp ring. Structures for the complex between the cation and ethylene (**CE**)
44
45 were subsequently optimized adding the olefins in positions favouring the interaction between the
46
47 vacant coordinative site of Al and the olefin π bond to the lowest energy structure of the cationic
48
49 species.
50
51 The search for a transition state (TS) describing the insertion of ethylene into the Al-Cp bond (**TS-**
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53 **E1**) was conducted by means of constrained scans along the distance between an ethylene carbon
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3 atom and one of carbon atoms in position 3 from the dimethylaminoalkyl group on the Cp ring;
4
5 putative TS structures were successively refined with a normal TS optimization carried out with the
6
7
8 Berny algorithm in conjunction with analytical second derivatives. Geometries for the end product
9
10 (PE1) were obtained relaxing structures having surmounted the energy barrier for the reaction.
11
12 Similarly, the TS search for the insertion of ethylene into the Al-Me bond (TS-E2) was performed
13
14 by means of a two-step procedure. First, an energy minimization was carried out with the system
15
16 being constrained to have the distance between the C atom of the Me-Al group and a sp² carbon of
17
18 the olefin at 2.1 Å. The TS geometry was successively refined as indicate above for the insertion
19
20 into the Al-Cp bond. A similar strategy was used for locating the stationary points on the potential
21
22 energy surface of the reaction between propene and (2).
23
24
25

26
27 Single point MP2 calculations using the 6-311+G(d,p) basis set were carried out on the B3LYP/6-
28
29 311+G(d,p) optimized structures. NMR chemical shifts for carbon and hydrogen were computed at
30
31 the B3LYP/6-311+G(2d,2p)//B3LYP/6-311+G(d,p) level of theory in the gas phase with the Gauge
32
33 Independent Atomic Orbitals (GIAO)²² using analytical derivatives.
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Supporting Information Available: Additional NMR spectra and Cartesian coordinates for the optimized species are available free of charge via Internet XXX.

Captions

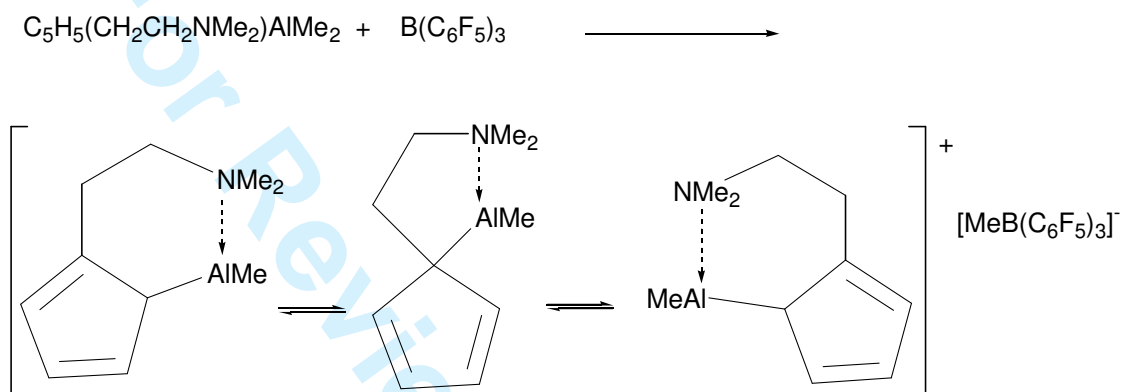
Figure I. (a) ^1H NMR spectrum ($\text{C}_6\text{D}_5\text{Cl}$, 25°C) of $[\text{C}_5\text{H}_5(\text{CH}_2\text{CH}_2\text{NMe}_2)\text{AlMe}]^+ [\text{MeB}(\text{C}_6\text{F}_5)_3]^-$ (2). (b, c) ^1H NMR spectra ($\text{C}_6\text{D}_5\text{Cl}$, 25°C) monitoring the reaction of (2) respectively after 5 minutes and 2 hours since the addition of propene.

Figure II. Aliphatic region H-H COSY NMR spectrum ($\text{C}_6\text{D}_5\text{Cl}$, 25°C) of the reaction of $[\text{C}_5\text{H}_5(\text{CH}_2\text{CH}_2\text{NMe}_2)\text{AlMe}]^+ [\text{MeB}(\text{C}_6\text{F}_5)_3]^-$ (2) with propene.

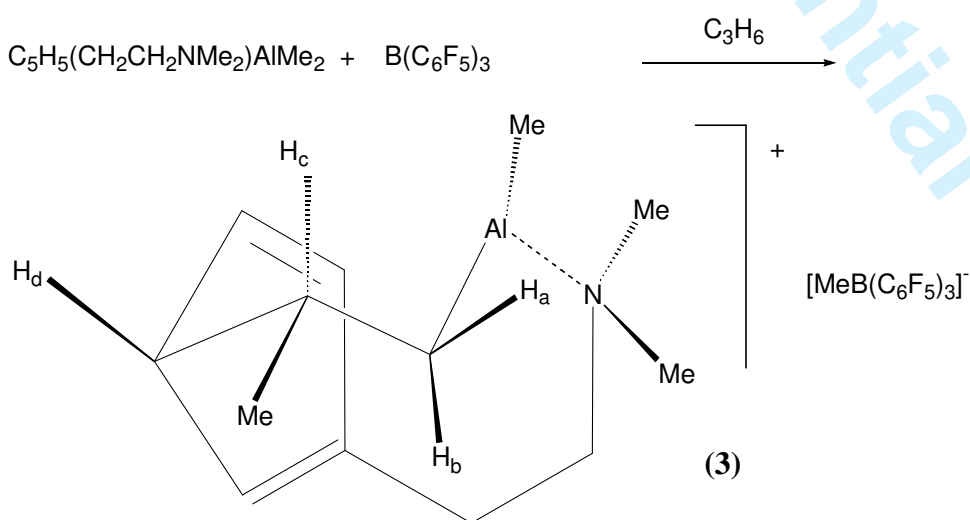
Figure III. Optimized structures of the cationic species (2), its complex with ethylene (CE), the transition state for the ethylene insertion into the Al-Cp (TS-E1) and Al-Me (TS-E2) bonds, the product of the ethylene insertion into the Al-Cp bond (PE1).

Figure IV. Optimized structure for the complexes between the cationic species (2) and propene (CP1-4), the transition states (TS-P1-4) and products (PP1-4) for the propene insertion into the Al-Cp bond.

Figure V. a) Transition state HOMO molecular orbital at the B3LYP/6-311+(d,p) level (energies in hartree). b) Mulliken charge population for complexes CP1 and CP4 at the B3LYP/6-31(d) level.



Scheme 1



Scheme 2

Table 1. ^1H NMR ($\text{C}_6\text{D}_5\text{Cl}$, 25°C) data for the species (**3**)^a

δ (^1H)	assgnt
-0.81 (3 H, s)	AlMe
-0.55 (1 H, dd, $^2J = 15.0$, $^3J = 6.8$, $^4J = 1.5$)	Al-CHaHb-
-0.25 (1 H, dd, $^2J = 15.0$, $^3J = 1$)	Al-CHaHb-
1.01 (3 H, d, $^3J = 6.6$)	CHaHb-CHcMe
1.07 (3 H, s)	$[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$
1.92 (3 H, s)	$\text{CH}_2\text{CH}_2\text{NMeMe}'$
1.97 (3 H, s)	$\text{CH}_2\text{CH}_2\text{NMeMe}'$
2.18 (2 H, m)	$\text{CH}_2\text{CH}_2\text{NMeMe}'$
2.30 (2 H, m)	$\text{CH}_2\text{CH}_2\text{NMeMe}'$
2.42 (1 H, m)	CHaHb-CHcMe
2.90 (1 H, m)	Hd (C_5 ring)
6.05 (1 H, d, $^3J = 5.6$)	H (C_5 ring)
6.47 (1 H, s, <i>br</i>)	H (C_5 ring)
6.50 (1 H, d, $^3J = 5.6$)	H (C_5 ring)

^aAll chemical shifts are in ppm and J values in Hz.

Table 2. ^{13}C NMR ($\text{C}_6\text{D}_5\text{Cl}$, 25°C) data for the species (**3**)^a

δ (^{13}C)	assgnt
-11.4	AlMe
7.9	$\text{Al-CH}_2\text{-CHMe}$
11.2	BMe
25.0	$\text{Al-CH}_2\text{-CHMe}$
25.5	$(\text{C}_5\text{H}_4)\text{CH}_2\text{CH}_2\text{NMeMe}'$
35.6	$\text{Al-CH}_2\text{-CHMe}$
44.4	$(\text{C}_5\text{H}_4)\text{CH}_2\text{CH}_2\text{NMeMe}'$
44.7	$(\text{C}_5\text{H}_4)\text{CH}_2\text{CH}_2\text{NMeMe}'$
58.9	$(\text{C}_5\text{H}_4)\text{CH}_2\text{CH}_2\text{NMeMe}'$
68.0	CHd (C_5 ring)
129.6	CH (C_5 ring)
138.0	CH (C_5 ring)
149.5	CH (C_5 ring)
157.0	C (quaternary; C_5 ring)

^aAll chemical shifts are in ppm.

Table 3. A summary of the long-range correlations observed in the HMBC spectrum (C_6D_5Cl , 25°C) for the species (**3**) ($\Delta = 100 \mu s$).^a

δ (1H)	assgnt	δ (^{13}C)	assgnt
-0.55 (1 H, dd, $^2J = 15.0$, $^3J = 6.8$, $^4J = 1.5$)	Al-CHaHb-CHcMe	35.6	Al-CH ₂ -CHcMe
		25.0	Al-CH ₂ -CHcMe
-0.25 (1 H, dd, $^2J = 15.0$, $^3J = 11$)	Al-CHaHb-CHcMe	35.6	Al-CH ₂ -CHcMe
1.01 (3 H, d, $^3J = 6.6$)	Al-CHaHb-CHcMe	68.0	CHd <i>C</i> ₅ ring
		35.6	Al-CH ₂ -CHcMe
1.92 (3 H, s)	(C ₅ H ₄)CH ₂ CH ₂ NMeMe'	58.9	(C ₅ H ₄)CH ₂ CH ₂ NMeMe'
		44.4	(C ₅ H ₄)CH ₂ CH ₂ NMeMe'
1.97 (3 H, s)	(C ₅ H ₄)CH ₂ CH ₂ NMeMe'	58.9	(C ₅ H ₄)CH ₂ CH ₂ NMeMe'
		44.7	(C ₅ H ₄)CH ₂ CH ₂ NMeMe'
2.18 (2 H, m)	(C ₅ H ₄)CH ₂ CH ₂ NMeMe'	129.6	<i>C</i> ₅ ring
		58.9	(C ₅ H ₄)CH ₂ CH ₂ NMeMe'
		44.7	(C ₅ H ₄)CH ₂ CH ₂ NMeMe'
2.30 (2 H, m)	(C ₅ H ₄)CH ₂ CH ₂ NMeMe'	157.0	<i>C</i> ₅ ring
		58.9	(C ₅ H ₄)CH ₂ CH ₂ NMeMe'
2.42 (1 H, m)	Al-CHaHb-CHcMe	157.0	<i>C</i> ₅ ring
		138.0	<i>C</i> ₅ ring
		68.0	CHd <i>C</i> ₅ ring
2.90 (1 H, m)	<i>Hd C</i> ₅ ring	157.0	<i>C</i> ₅ ring
		138.0(w)	<i>C</i> ₅ ring
		129.6	<i>C</i> ₅ ring
		35.6	Al-CH ₂ -CHcMe
6.05 (1 H, d, $^3J = 5.6$)	<i>H C</i> ₅ ring	138.0	<i>C</i> ₅ ring
6.47 (1 H, s)	<i>H C</i> ₅ ring	157.0	<i>C</i> ₅ ring
		68.0	CHd <i>C</i> ₅ ring
6.50 (1 H, d, $^3J = 5.6$)	<i>H C</i> ₅ ring	129.6	<i>C</i> ₅ ring

^aAll chemical shifts are in ppm and *J* values in Hz. Weaker correlations, corresponding to smaller coupling constants, are identified with “w”.

Table 4: Energetics of ethylene and propene insertion processes into the Al-Cp and Al-Me bonds.

Relative energy ^a	B3LYP/6- 311+G(d,p)	MP2/6- 311+G(d,p)
Ethylene		
TS-E1 Al-Cp bond insertion	4.3	4.8
TS-E2 Al-Me bond insertion	23.4	24.2
Product (PE1) Al-Cp bond insertion	-14.1	-18.3
TS-E1 Al-Cp bond de-insertion	18.3	23.1
Propene		
TS-PP1 Al-Cp bond insertion	7.6	4.6
TS-PP2 Al-Cp bond insertion	7.4	4.7
TS-PP3 Al-Cp bond insertion	16.5	9.4
TS-PP4 Al-Cp bond insertion	13.7	9.4
Product (PP1) Al-Cp bond insertion	-6.4	-14.1
Product (PP2) Al-Cp bond insertion	-8.0	-15.9
Product (PP3) Al-Cp bond insertion	-3.3	-14.4
Product (PP4) Al-Cp bond insertion	-4.1	-11.6
TS-PP1 Al-Cp bond de-insertion	13.9	18.6
TS-PP2 Al-Cp bond de-insertion	15.4	20.6
TS-PP3 Al-Cp bond de-insertion	19.8	23.8
TS-PP4 Al-Cp bond de-insertion	17.8	21.1

^aEnergies (kcal/mol) computed using the complex between the cationic species and each olefin as reference.

1
2
3 **Table 5:** ^1H chemical shifts characterizing the four possible products of the propene insertion into
4
5 the Al-Cp bond computed at the B3LYP/6-311+G(2d,2p) level.
6
7

Species	^1H δ (ppm)
	Ha, Hb, Hc
PP1	3.1098, 0.2855, -0.1894
PP2	2.9345, 0.3317, -0.4666
PP3	2.1623, 2.896, 0.4032
PP4	3.2951, 1.9425, 0.6886

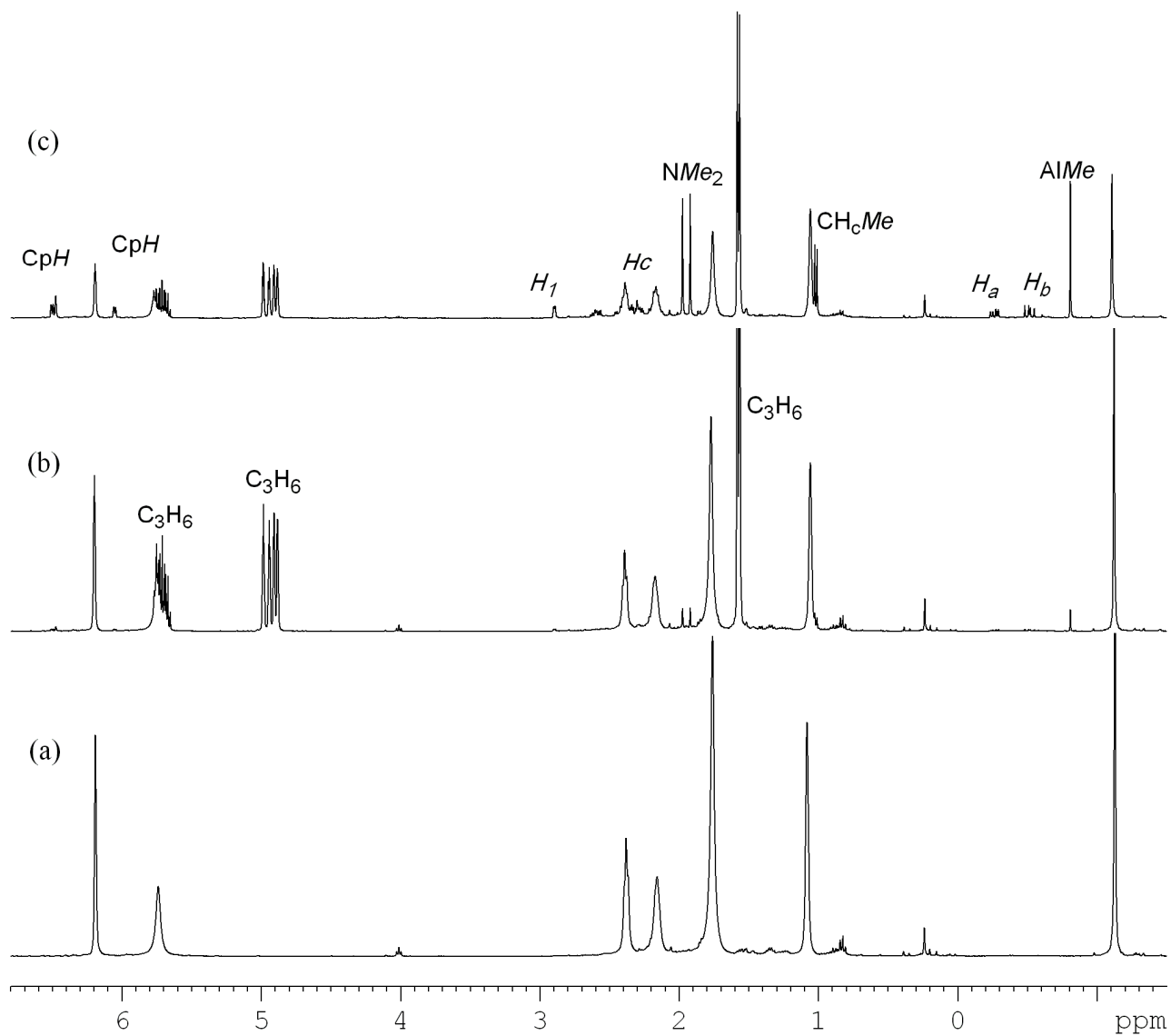


Figure I

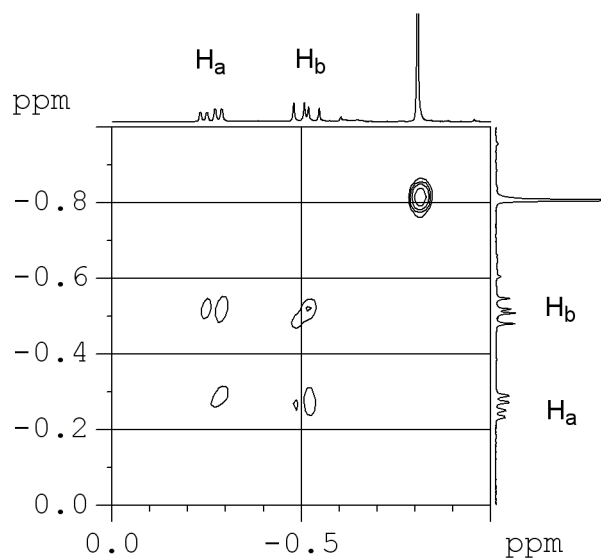


Figure II

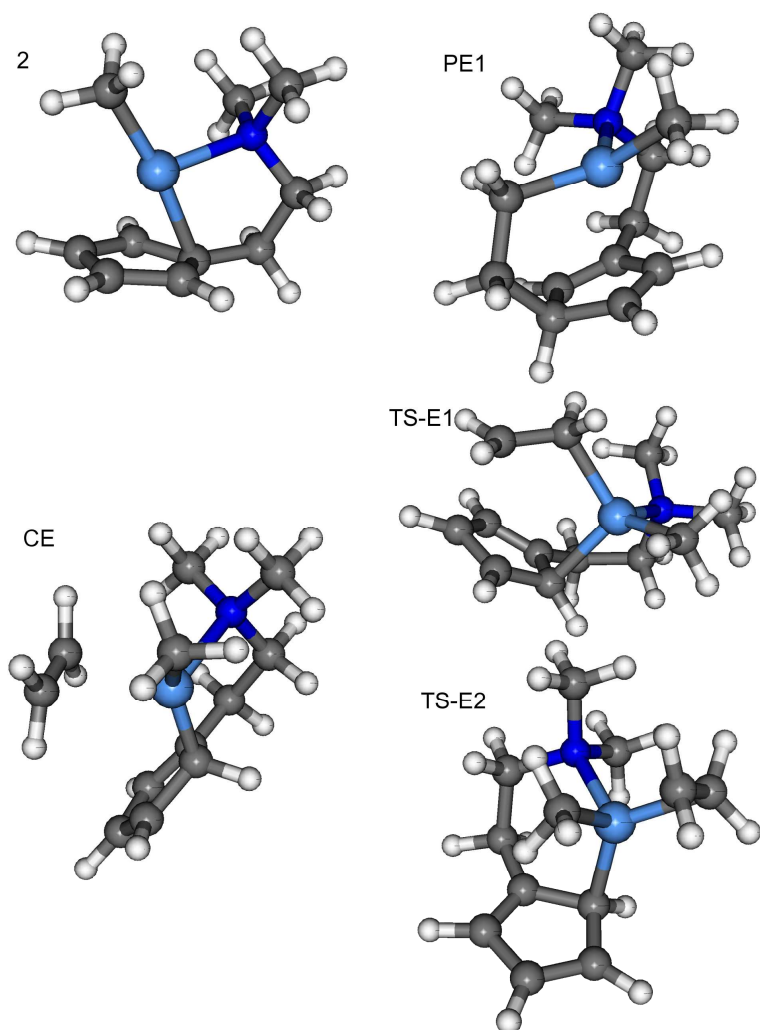


Figure III

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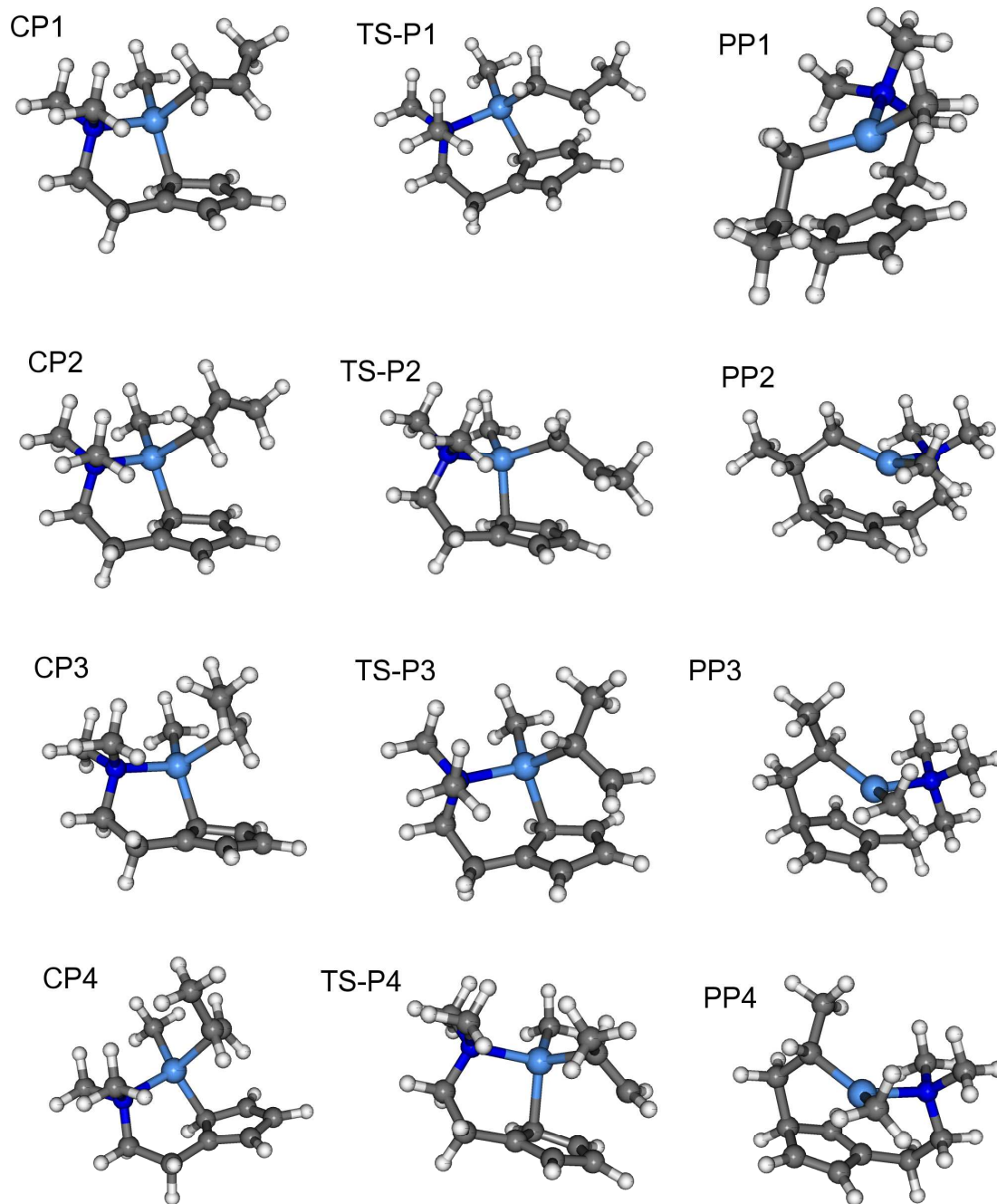


Figure IV

TS-HOMO E=-0.35968 hartree

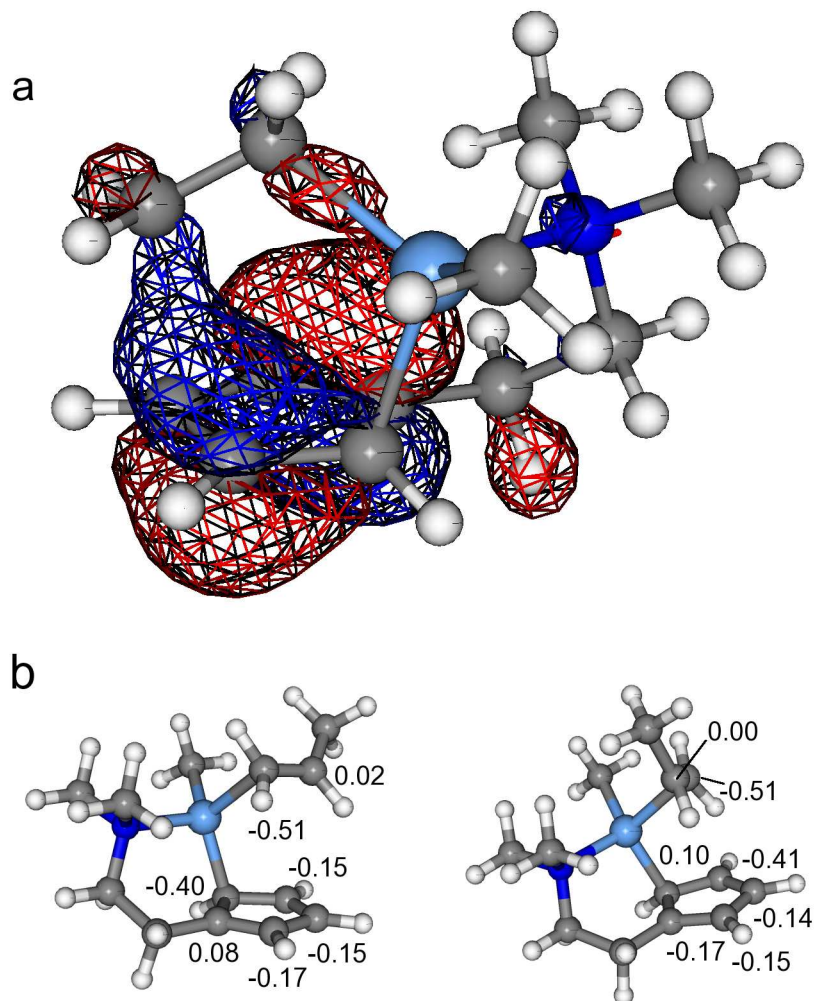


Figure V