

# A Journal of the Gesellschaft Deutscher Chemiker A Deutscher Chemiker GDCh International Edition www.angewandte.org

## **Accepted Article**

- Title: Silica-grafted Tris(neopentyl)aluminum: A Monomeric Aluminum Solid Co-Catalyst for Efficient Nickel-Catalyzed Ethene Dimerization
- Authors: Christophe Copéret, Ilia Moroz, Pierre Florian, Jasmine Viger Gravel, Christopher P Gordon, and Anne Lesage

This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: Angew. Chem. Int. Ed. 10.1002/anie.202006285

Link to VoR: https://doi.org/10.1002/anie.202006285

## WILEY-VCH

**RESEARCH ARTICLE** 

#### WILEY-VCH

## Silica-grafted Tris-(neopentyl)aluminum: A Monomeric Aluminum Solid Co-Catalyst for Efficient Nickel-Catalyzed Ethene Dimerization

Ilia B. Moroz,<sup>[a]</sup> Pierre Florian,<sup>[b]</sup> Jasmine Viger-Gravel,<sup>[c]</sup> Christopher P. Gordon,<sup>[a]</sup> Anne Lesage,<sup>[c]</sup> and Christophe Copéret<sup>\*[a]</sup>

[a]	Dr. I. B. Moroz, C. P. Gordon, Prof. Dr. C. Copéret	
	Department of Chemistry and Applied Biosciences, ETH Zürich	
	Vladimir-Prelog-Weg 1-5, 8093 Zürich, Switzerland	
	E-mail: ccoperet@ethz.ch	
[b]	Dr. P. Florian	
	CEMHTI CNRS UPR3079, Université d'Orléans	A 1
	1D Avenue de la Recherche-Scientifique, F-45071 Orléans Cedex 2, France	
[c]	Dr. J. Viger-Gravel, Dr. A. Lesage	
	Centre de RMN à Très Hauts Champs, Université de Lyon (CNRS/ENS Lyon/UCB Lyon 1)	
	69100 Villeurbanne, France	

Supporting information for this article is given via a link at the end of the document.

**Abstract:** A silica-supported monomeric alkylaluminum co-catalyst was prepared via Surface Organometallic Chemistry by contacting tris-(neopentyl)aluminum and partially dehydroxylated silica. This system, fully characterized by solid-state <sup>27</sup>Al NMR augmented by computational studies, efficiently activates (*n*Bu<sub>3</sub>P)<sub>2</sub>NiCl<sub>2</sub> towards dimerization of ethene demonstrating comparable activity to previously reported dimeric diethylaluminum chloride supported on silica. Three types of aluminum surface species have been identified: monografted tetracoordinated Al species as well as two types of bisgrafted Al species – tetra- and pentacoordinated. Of them, only the monografted Al species is proposed to be able to activate the (*n*Bu<sub>3</sub>P)<sub>2</sub>NiCl<sub>2</sub> complex and generate the active cationic species.

#### Introduction

The oligomerization of ethene is one of the key technologies for the production of α-olefins (e.g. 1-butene, 1-hexene, etc.) that are co-monomers for the synthesis of linear low-density polyethylene. This reaction is catalyzed by various homogeneous catalysts based on early- (Ti, Ta, Cr) or late-transition metals (Ni) and requires the addition of co-catalysts, typically alkyl aluminum reagents to generate the active species.<sup>[1]</sup> Of them, methylaluminoxane (MAO) shows the best co-catalytic performance,<sup>[2]</sup> though a very large excess of >100 equiv. of MAO with respect to the active metal is needed, making its use problematic in industry.<sup>[3]</sup> While trialkylaluminums (Al<sub>2</sub>R<sub>6</sub>, R = Me or Et) are used to activate Ti(OR')4-pre-catalyst (Alphabutol process) with only a small excess (<10 equiv. with respect to the metal) compared to MAO,<sup>[4]</sup> such co-catalysts are inefficient for Ni-based systems, and they need to be replaced by alkylaluminum chloride –  $Al_2R_{6-2n}Cl_{2n}$ , n = 1 or 2 – or the corresponding phenoxide - Al<sub>2</sub>R<sub>4</sub>(OR)<sub>2</sub>, that are all dimeric in solution.[5]

The inefficiency of  $Al_2R_6$  co-catalysts has been proposed to be associated with the formation of anionic dimeric [AIR<sub>3</sub>][AIR<sub>2</sub>Cl<sub>2</sub>]<sup>-</sup>

species upon reaction with the metal pre-catalysts, e.g. ("Bu<sub>3</sub>P)<sub>2</sub>NiCl<sub>2</sub>. Such species can further dissociate, and free monomeric AIR<sub>3</sub> species can react with putative active [LMR]<sup>+</sup> species to form a deactivated [LM( $\mu_2$ -R)<sub>2</sub>AIR<sub>2</sub>]<sup>+</sup> complex as shown in **Scheme 1**.<sup>[6]</sup>

 $\label{eq:Scheme 1} \begin{array}{l} \mbox{Scheme 1}. \mbox{ The proposed mechanisms of (a) pre-catalyst activation by dimeric trialkylaluminum co-catalysts, (b) dissociation of anionic co-catalyst species, (c) inhibition of pre-activated catalyst, where [LMCl_2] is a pre-catalyst, [AIR_3]_2 - a dimeric alkylaluminum co-catalyst. \end{figure}$ 

(a) Activation

$[LMCl_2] + [R_2Al(\mu_2-R)_2AlR_2] \longrightarrow$	[LMR] <sup>+</sup> [AIR <sub>3</sub> ][AIR <sub>2</sub> Cl <sub>2</sub> ] <sup>-</sup>

(b) Dissociation

 $[LMR]^+ [AIR_3][AIR_2Cl_2]^-$  [AIR<sub>3</sub>] +  $[LMR]^+ [AIR_2Cl_2]^-$ 

(c) Inhibition

 $[AIR_3] + [LMR]^+ [AIR_2Cl_2]^- \longrightarrow [LM(_2-R)_2AIR_2]^+ [AIR_2Cl_2]^-$ 

The presence of bridging CI ligands in alkylaluminum chloride (AIR<sub>3-n</sub>CI<sub>n</sub>, n = 1 or 2) prevents the inhibition of the activated cationic species. The same behavior has been observed for the corresponding silica-supported co-catalysts based on triethylaluminum (TEA) and diethylaluminum chloride (DEAC) that led to inactive and active Ni-oligomerization catalysts, respectively.<sup>[7]</sup> The combined <sup>27</sup>AI solid-state NMR and computational studies indicated the presence of various dimeric AI species on the surface, and the high catalytic performance of the DEAC-based system (unlike inactive TEA-based) was attributed to the preservation of  $\mu^2$ -CI bridging ligands between the two AI atoms that stabilize the AI dimeric surface structure thus preventing deactivation of the Ni catalyst.<sup>[6-7]</sup>

## **RESEARCH ARTICLE**

**Scheme 2.** Possible surface species resulting from a reaction of  $AI(CH_2/Bu)_3$  with a silica surface: (a) reaction of  $AI(CH_2/Bu)_3$  with a surface silanol leading to the formation of monografted species; (b) neopentyl transfer process leading to the formation of bis-grafted and tris-grafted AI species and Si–CH<sub>2</sub>/Bu surface moieties. d, d<sub>1</sub>, d<sub>2</sub>, and d<sub>3</sub> are AI–[O(Si=)<sub>2</sub>] bond lengths. The terms mono-, bis- and tris-grafted AI species refer to the number of bonds between AI and surface siloxy ligand (=Si-O<sup>-</sup>); it does not include an additional coordination of neutral siloxane bridges (=Si-O-Si=), that only contribute to coordination number.



We reasoned that monomeric alkylaluminum isolated on a silica surface should also be an efficient co-catalyst. They are predicted by DFT computations to be able to activate late-transition metal complexes,<sup>[6]</sup> their site-isolation should prevent the poisoning of tentative active species.

We thus decided to investigate the grafting of a base-free monomeric alkylaluminum, namely tris-(neopentyl)aluminum AI(CH<sub>2</sub><sup>t</sup>Bu)<sub>3</sub>, on a silica partially dehydroxylated at 700 °C, SiO<sub>2-700</sub>, that contains isolated OH groups. We show that such supported alkylaluminum can be an efficient solid co-catalyst for the Ni-catalyzed ethene oligomerization, whose co-catalytic activity is attributed to the presence of isolated alkylaluminum species by enabling the formation of cationic Ni alkyl species from (<sup>n</sup>Bu<sub>3</sub>P)<sub>2</sub>NiCl<sub>2</sub>.<sup>[8]</sup>

#### **Results and Discussion**

The aluminum precursor Al(CH<sub>2</sub><sup>t</sup>Bu)<sub>3</sub> was synthesized by reaction of AlBr<sub>3</sub> with 3 equiv. of LiCH<sub>2</sub><sup>t</sup>Bu in heptane, and isolated as a colorless liquid in 89% overall yield (see **Figure S1** for <sup>1</sup>H NMR); this compound is monomeric in the liquid state and in hydrocarbon solutions.<sup>[9]</sup>

Grafting of Al(CH<sub>2</sub>'Bu)<sub>3</sub> on SiO<sub>2-700</sub> (1.08 OH nm<sup>-2</sup>) in C<sub>6</sub>H<sub>6</sub> generates ~1 equiv. of 2,2-dimethylpropane per surface OH group. The resulting solid (material 1) contains 0.97 wt% Al and 4.55 wt% C that correspond to 1.08 Al nm<sup>-2</sup> and 10.6 C per Al atom. These data and the complete consumption of surface OH groups as observed by IR (see **Figure S2**) are consistent with a simple protonolysis of one Al–CH<sub>2</sub>'Bu bond of Al(CH<sub>2</sub>'Bu)<sub>3</sub> leading to the formation of the monografted dialkyl Al species (**Scheme 2a**). However, the grafting of alkylaluminum compounds on silica is often quite complex because of the possible subsequent reaction of the surface alkylaluminium species with adjacent siloxane bridges through the transfer of an alkyl group from Al to a Si atom

and the formation of an additional Al–OSi≡ bond.<sup>[7, 10]</sup> Since these processes lead to similar stoichiometries (evolution of 2,2-dimethylpropane and overall elemental analysis), one cannot preclude the formation of bis- (single alkyl transfer) and trisgrafted neopentyl-free (transfer of two alkyls) aluminum species (see **Scheme2b**).



Figure 1. <sup>27</sup>AI MAS NMR spectra (solid black lines) obtained at (a) 16.4 and (b) 23.5 T, along with three simulated components: site **S1** (dotted line), **S2** (dotdash line), and **S3** (dashed) as well as the resulting line shape (solid grey line).

Thus, in order to obtain information on the exact structure of Al species, we performed  $^{27}\text{Al}$  solid-state NMR measurements complemented by DFT computations. $^{[7, \ 10c]}$   $^{27}\text{Al}$  NMR parameters (chemical shift ( $\delta$ ) and quadrupolar coupling constants,  $C_Q$ ) are

## **RESEARCH ARTICLE**

highly sensitive to the local environment of <sup>27</sup>Al nuclei and allow the discrimination of possible mono- and dimeric sites as well as understanding the coordination sphere (which ligand and geometry).<sup>[7, 10c, 11] 27</sup>Al spin-echo spectra were acquired at two different high magnetic fields, namely 16.4 and 23.5 T, under very fast Magic Angle Spinning (MAS >50 kHz). The spectra show a broad line shape featuring resolved discontinuities, particularly at 16.4 T. Those features are highly dependent on the magnetic field: the line width sharply decreases with increasing magnetic field, as expected for signals dominated by quadrupolar broadening (**Figure 1**).

The simulation of the two data sets – carried out simultaneously (see the Supporting Information for a detailed discussion on the simulation of <sup>27</sup>Al NMR spectra) – reveals three significant contributions (**Figure 1** and **Table S1**) that are necessary to consistently model the two spectra with the exact same set of NMR parameters (*i.e.*  $\delta_{so}$ .  $C_Q$  and  $\eta_Q$ ): the site **S1** (cyan, 19% of total area, **Figure 1**) characterized by  $\delta_{so}$  / $C_Q$  / $\eta_Q$  of 154 ppm / 31 MHz / 0.4; the site **S2** (orange, 58%, **Figure 1**) – 101 ppm / 19 MHz / 0.7; and the site **S3** (purple, 23%, **Figure 1**) – 83 ppm / 19 MHz / 0.9. The need for three components, each characterized by a specific set of NMR parameters, to simulate the obtained <sup>27</sup>Al NMR spectra, indicates the presence of at least three types of surface Al species.



Figure 2. Optimized structures of alkylaluminum surface species (right) with a schematic representation of Al coordination spheres (left): (a) monografted tricoordinated species (**M**); (b) monografted tetracoordinated species (**M\_[O(Si=)**<sub>2</sub>]\_d) with Al–[O(Si=)<sub>2</sub>] bond length d of 1.9 Å as an example; (c) bisgrafted tri-coordinated species (**B**); (d) bis-grafted tetracoordinated species (**B\_[O(Si=)**<sub>2</sub>]\_d) with d of 1.9 Å; (e) bis-grafted pentacoordinated species (**B\_[O(Si=)**<sub>2</sub>]\_d, d) with d\_1 and d\_2 of 2.1 Å. Al, O, C, Si and H atoms are represented as violet, red, black, grey, and white balls, respectively.

To assign the observed <sup>27</sup>Al NMR features to specific Al species, we carried out DFT studies on cluster models representing various Al environments, that are expected to be formed upon reaction of Al(CH<sub>2</sub>'Bu)<sub>3</sub> with surface OH groups and reactive siloxane bridges present on SiO<sub>2-700</sub> (*vide supra*). Representative structures were optimized (**Figure 2**), and their NMR properties were calculated (**Figure 3**), in particular <sup>27</sup>Al  $\delta_{so}$  and  $C_Q$ , that are important signatures for Al coordination and geometry in aluminosilicates and related materials.<sup>[12]</sup> The computed NMR parameters are also given in **Table S2**.

First, the monografted tri-coordinated structure (**M**, see **Figure 2a**) shows both very high  $\delta_{iso}$  and  $C_Q$  values (209.9 ppm and 40.7

MHz), not matching any of the experimental values (**Figure 3** and **Table S2**). Coordination of a siloxane bridge (**M\_[O(Si=)**<sub>2</sub>]\_d) leads to a significant decrease of both  $\delta_{iso}$  and  $C_Q$ , and their values depend on the AI–[O(Si=)<sub>2</sub>] bond length d (see **Figure 2b**): varying d from 1.8 to 2.1 Å (around the bond length found by optimizing the geometry) gives  $\delta_{so}$  ranging from 154.8 to 173.5 ppm and  $C_Q$  – from 24.7 to 34.9 MHz (**Figure 3**).Note that the  $C_Q$  value is significantly affected upon varying the bond length, while the  $\delta_{iso}$  value is much less sensitive.<sup>[12b]</sup> The experimentally observed site **S1** ( $\delta_{iso} = 154$  ppm,  $C_Q = 31$  MHz) is most consistent with the structure **M\_[O(Si=)**<sub>2</sub>]\_d with a distance between AI and the oxygen of the siloxane bridge of ca. 1.9 Å (d = 1.9 Å).

The bis-grafted tri-coordinated structure (B, Figure 2c), which can be formed upon the reaction of the grafted neopentyl aluminum species with a nearby siloxane bridge, shows further decrease in  $\delta_{iso}$  down to 142.9 ppm, while  $C_Q$  remains significantly high – 36.4 MHz. Such combination of parameters does not match the experimental data. However, an increase of the Al coordination number from 3 to 4 by coordinating a siloxane bridge (B\_[O(Si=)2]\_d, Figure 2d) leads to δiso of ca. 105-107 ppm and  $C_Q$  of 18.3–25.8 MHz, the  $C_Q$  significantly depends on the Al-[O(Si=)2] bond length d (varied between 1.8 and 2.0 Å), as observed for the monografted structures. The <sup>27</sup>AI NMR parameters of site S2 ( $\delta_{iso}$  = 101 ppm, C<sub>Q</sub> = 19 MHz) match quite well those of B\_[O(Si=)2]\_d structure with the Al-[O(Si=)2] bond length being close to 1.8 Å (Figure 3). Thus, sites S1 and S2 can be assigned to tetracoordinated AI species, rather than tricoordinated, that are mono- and bis-grafted, respectively.



Figure 3. Graphical representation of NMR parameters  $C_0$  (horizontal axis) and  $\delta_{so}$  (vertical axis) of experimentally observed sites S1 (filled hexagon), S2 (filled triangle) and S3 (filled diamond), and calculated structures shown as open circles: monografted tri-coordinated M and tetracoordinated M\_[O(Si=)\_2]\_d structures (open circles), bis-grafted tri-coordinated B and tetracoordinated B\_[O(Si=)\_2]\_d structures (open triangles), bis-grafted pentacoordinated B\_[O(Si=)\_2]\_d tructures (open squares).

Regarding site **S3** ( $\delta_{so}$  = 83 ppm,  $C_Q$  = 19 MHz), one can propose that a second alkyl transfer from Al to Si occurs with the formation of tris-grafted alkyl-free Al species, however the calculated  $\delta_{iso}$  and  $C_Q$  values of neither tri-coordinated ( $\delta_{iso}$  = 70-80 ppm,  $C_Q$  = 31-35 MHz) nor tetracoordinated ( $\delta_{iso}$  = 61-65 ppm,  $C_Q$  = 7-21 MHz) tris-grafted Al structures match the observed experimental values due to too high  $C_Q$  or too low  $\delta_{iso}$ , respectively (**Figure** 

### **RESEARCH ARTICLE**

3).<sup>[12b]</sup> Noteworthy, site S3 is characterized by C<sub>Q</sub> value, very close to the one of site **S2**, but with a  $\delta_{iso}$  that is 20 ppm lower. Such 20-ppm-decrease in  $\delta_{iso}$  while maintaining similar  $C_Q$  values is typically observed upon addition of the second siloxane bridge in the coordination sphere of aluminum in a trans-position to the first siloxane, increasing coordination of AI from 4 to 5 and geometry from tetrahedral to trigonal changing the bipyramidal.<sup>[12b]</sup> Indeed, for bis-grafted pentacoordinated structures with two mutually trans siloxane bridges (B\_[O(Si≡)<sub>2</sub>]<sub>2</sub>\_d<sub>1</sub>\_d<sub>2</sub>, Figure 2e), the calculated *δ*<sub>iso</sub> is 69-74 ppm, which is rather close to the  $\delta_{iso}$  value of the site S3 (Figure 3).  $C_Q$ depends strongly on the Al-[O(Si=)2] bond lengths d1 and d2 (see Figure 2e) and varies between 11.5 ( $d_1$ =1.8 Å,  $d_2$  = 2.1 Å) and 20.5 (d<sub>1</sub> = 2.1 Å, d<sub>2</sub> = 2.1 Å) MHz (see Figure 3 and Table S2) Note that  $C_Q > 16$  MHz (observed for site S3, see Figure 3) is associated with both d1 and d2 longer than 2.0 Å. We thus assign the site S3 to bis-grafted pentacoordinated alkylaluminum species with the structure  $B_[O(Si=)_2]_2_d_1_d_2$  (Figure 2e) with long  $d_1$ and d<sub>2</sub> distances, greater than 2.0 Å.

The co-catalytic property of material **1** in the oligomerization of ethene was then examined by contacting material **1** with a solution of ( ${}^{n}Bu_{3}P)_{2}NiCl_{2}$  under constant ethene pressure of 5 bar at 30 °C (*in situ* formation of active species).<sup>[5c, 13]</sup> We have also isolated the pre-activated catalyst by reacting ( ${}^{n}Bu_{3}P)_{2}NiCl_{2}$  with material **1** (material **2**, *ex situ* activation, see the Supporting Information for synthetic details and **Figure S3** for IR spectra) and examined its catalytic performance under the same reaction conditions. An Al/Ni ratio of ca. 4.1 was used for material **1** that corresponds to the ratio found in material **2** based on elemental analysis. Compared to a previously reported Cl-free triethylaluminum on mesoporous silica SBA-15 (TEA@SBA), which was reported as inactive,<sup>[7]</sup> material **1** does activate ( ${}^{n}Bu_{3}P)_{2}NiCl_{2}$  complex converting 9400 mol(C<sub>2</sub>H<sub>4</sub>) per mol(Ni) after 1 h of reaction (see **Table S3**). Under the same conditions,

silica-supported AIEt2CI (DEAC@SiO2, see the Supporting Information for synthetic details) demonstrates turnover numbers (TON) of ca. 2800. Both systems show rather high selectivity in butenes: 93% for material 1 vs. 92% for DEAC@SiO2. Together with a desired product - 1-butene - a mixture of E/Z-2-butenes is formed, with selectivity in 1-butene of 37% (vs. 17% for DEAC@SiO<sub>2</sub>). The formation of E/Z-2-butenes is well-known for Ni-catalyzed oligomerization of ethene that is due to a favorable double-bond isomerization of 1-butene into thermodynamically more stable 2-butenes.<sup>[7, 14]</sup> Other minor by-products are mostly hexenes as identified by GC. The pre-activated material 2 also demonstrates catalytic activity in ethene oligomerization, reaching 3900 mol(C<sub>2</sub>H<sub>4</sub>) mol(Ni)<sup>-1</sup> after 1 h, and the selectivity in butenes of 96%. Note that the solution left after isolation of material 2 is inactive in the oligomerization of ethene, thus confirming that this catalytic system is heterogeneous.

We further studied the reaction of ("Bu<sub>3</sub>P)<sub>2</sub>NiCl<sub>2</sub> and its diamagnetic Pt equivalent with material 1 (1 equiv. of Ni or Pt per surface AI, as calculated based on EA of material 1) to better understand the activation process (see the Supporting Information for synthetic details). Based on elemental analysis, the resulting (catalytically active) material 2 contains 0.45 wt.% of Ni and 0.85 wt.% of AI that corresponds to an AI/Ni ratio of 4.1 as mentioned above. Material 2 also contains 0.59 wt.% of CI and 0.52 wt.% of P. This corresponds to a Cl/Ni and P/Ni ratio of 2.2 in both cases, as present in the initial Ni complex. <sup>1</sup>H NMR of combined benzene washings shows the presence of at least two compounds, both containing "Bu<sub>3</sub>P ligands, however their identification is not trivial due to overlapping NMR signals (Figure S9). <sup>31</sup>P NMR is usually very characteristic for the metal phosphine complexes, but the presence of paramagnetic species typical for 4-coordinated Ni(II) complexes leads to very broad signals that are difficult to interpret (Figure S11a).





We thus prepared the corresponding material from the diamagnetic cis-( $^{n}Bu_{3}P$ )<sub>2</sub>PtCl<sub>2</sub> complex (see **Figure S5** for IR spectra). In particular, the chemical shift and the magnitude of  $^{1}J(^{195}Pt, ^{31}P)$ , observed in  $^{31}P$  NMR spectra of Pt(II) phosphine complex, are known to be very sensitive to the nature of trans

ligand in square-planar Pt(II) complexes. The <sup>31</sup>P NMR spectrum of the combined washings exhibits two signals (**Figure S11b**): the first one with  $\delta(^{31}P) = 4.86$  ppm and  $^{1}J(^{195}Pt-^{31}P) = 2400$  Hz is characteristic of trans-( $^{n}Bu_{3}P)_{2}PtCl_{2}$ ,<sup>[15]</sup> which likely results from the isomerization of the initial compound, while the second one

## **RESEARCH ARTICLE**

(with  $\delta({}^{31}P) = 4.30$  ppm and  ${}^{1}J({}^{195}Pt-{}^{31}P) = 3000$  Hz) has a Jcoupling constant characteristic of the alkylated compound, namely trans-[("Bu3P)2PtRCI],[16] where R is neopentyl. This indicates that alkyl-chloride exchange takes place upon reaction of the supported (neopentyl)aluminum species and cis-(<sup>n</sup>Bu<sub>3</sub>P)<sub>2</sub>PtCl<sub>2</sub>. It is expected that a similar exchange occurs in the case of ("Bu<sub>3</sub>P)<sub>2</sub>NiCl<sub>2</sub>, that is in line with the presence of two Ni phosphine compounds observed in <sup>1</sup>H NMR of washings (vide supra). Note also, that <sup>31</sup>P MAS NMR of the obtained solid material contains signal at 7.3 ppm, which can be attributed to adsorbed ("Bu<sub>3</sub>P)<sub>2</sub>PtCl<sub>2</sub>, together with two shoulders at 15.7 and -1.5 ppm (see Figure S12b). While alkylchloride complexes [(R'<sub>3</sub>P)<sub>2</sub>Pt**R**Cl] are characterized by slightly more shielded  $\delta$ (<sup>31</sup>P) than their dichloride analogues [(R'3P)2PtCl2] (see Table S4), a deshielded signal at 15.7 ppm is likely associated with the formation of cationic alkyl complex [("Bu<sub>3</sub>P)<sub>2</sub>PtR]<sup>+</sup> on the surface. Indeed, according to DFT computations, [("Bu<sub>3</sub>P)<sub>2</sub>Pt(CH<sub>2</sub>'Bu)]<sup>+</sup> has ca. 15 ppm more deshielded <sup>31</sup>P chemical shift than ("Bu<sub>3</sub>P)<sub>2</sub>PtCl<sub>2</sub> (see Table S4). Formation of such cationic species in the case of Ni complex would be consistent with the catalytic properties of material 2 in ethene oligomerization.

To summarize, material **1** prepared by grafting Al(CH<sub>2</sub><sup>t</sup>Bu)<sub>3</sub> on SiO<sub>2-700</sub> contains three types of monomeric alkylaluminum species. The first type represents monografted di(neopentyl)aluminum species that are tetracoordinated because of the coordination of additional siloxane bridge to Al. These species are formed via protonolysis of one Al-CH2<sup>t</sup>Bu bond of Al(CH<sub>2</sub><sup>t</sup>Bu)<sub>3</sub> by surface OH groups, as expected for grafting of alkyl compounds on SiO<sub>2-700</sub>. However, only 19% of all Al on the surface belong to this type. Two other types represent bis-grafted mono(neopentyl)aluminum species that are tetra- (58%) and pentacoordinated (23%) due to the coordination of one or two additional siloxane bridges coordinated to Al, respectively. Taking into account the high isolation of OH groups on the surface of SiO<sub>2-700</sub> and C/AI ratio of 10.6 (ca. 2 neopentyl per surface AI), we propose that bis-grafted species result from transfer of a neopentyl group from Al to a Si atom of an adjacent siloxane bridge and the formation of additional Al–OSi≡ bond, that has been previously observed for other alkylaluminum compounds grafted on partially dehydroxylated silica (Scheme 2).[7, 10a-c, 10e, 10f] Material 1 was shown to activate in situ ("Bu<sub>3</sub>P)<sub>2</sub>NiCl<sub>2</sub> towards selective dimerization of ethene, demonstrating ca. 3.3 times higher TON and higher selectivity in 1-butene (37% vs. 17%) as compared to DEAC@SiO2 tested under the same conditions. These results suggest that tailor-made monomeric (neopentyl)aluminum species grafted on silica provide access to an efficient co-catalyst for Ni-catalyzed ethene dimerization. We believe that by stabilizing monomeric alkylaluminum species on the surface of silica, poisoning of the putative active species with free AIR<sub>3</sub> is likely avoided, and as a result, high catalytic performance of the system can be achieved.

We have also investigated activation of Ni pre-catalyst by cocatalyst **1**. Based on our results, material **1** can alkylate Ni precatalyst (*vide supra*), forming [(<sup>n</sup>Bu<sub>3</sub>P)<sub>2</sub>Ni(CH<sub>2</sub><sup>/</sup>Bu)Cl] complex, similar to the first step of activation with homogeneous cocatalysts (**Scheme 3a**).<sup>[17]</sup> The second step likely involves abstraction of Cl<sup>-</sup> by surface Al and formation of cationic nickelalkyl complex [(<sup>n</sup>Bu<sub>3</sub>P)<sub>2</sub>Ni(CH<sub>2</sub><sup>/</sup>Bu)]<sup>+</sup>, which is the proposed active species in this Ni-catalyzed ethene dimerization. It is expected that these species are strongly bound to the surface due to ionic interactions with anionic Al species. Noteworthy, only ca. 0.25 equiv. of Ni with respect to Al species was found in material **2**, suggesting that only 25% of (neopentyl)aluminum species can further react with [("Bu<sub>3</sub>P)<sub>2</sub>Ni(CH<sub>2</sub>'Bu)CI] complex and form an ionic pair with [("Bu<sub>3</sub>P)<sub>2</sub>Ni(CH<sub>2</sub>'Bu)]<sup>+</sup>. Taking into account that monografted tetracoordinated bis-alkyl Al species, representing ca. 20% of all Al species, are expected to be more reactive than bis-grafted pentacoordinated species (*vide supra*), we propose that the monografted alkyl aluminum species generate the active cationic species by abstraction of Cl<sup>-</sup> from [("Bu<sub>3</sub>P)<sub>2</sub>Ni(CH<sub>2</sub>'Bu)CI] (Scheme 3a), while bis-grafted species (ca. 80%) do not participate in the activation (Scheme 3b). The co-catalytic properties of material 1 are thus likely related to the presence of monografted di(neopentyl)aluminum species supported on silica.

#### Conclusion

In conclusion, we have shown that grafting of Al(CH<sub>2</sub><sup>t</sup>Bu)<sub>3</sub> on silica treated at 700 °C leads to the formation of supported monomeric Al species that activate the ("Bu<sub>3</sub>P)<sub>2</sub>NiCl<sub>2</sub> complex towards selective dimerization of ethene and demonstrates comparable catalytic performances with the previously reported supported dimeric DEAC co-catalyst systems. Three specific structures for the grafted monomer have been identified using <sup>27</sup>AI MAS NMR augmented by DFT computations of NMR parameters: (i) monografted di(neopentyl)aluminum species with coordinated siloxane bridge resulting from protonolysis of Al-CH2<sup>t</sup>Bu bond with surface OH groups; and (ii-iii) two bis-grafted mono(neopentyl)aluminum species having one and two siloxane bridges coordinated to AI, respectively that are likely formed by neopentyl transfer from Al to an adjacent siloxane bridge. Analysis of the reaction between well-defined co-catalyst and (<sup>n</sup>Bu<sub>3</sub>P)<sub>2</sub>NiCl<sub>2</sub> suggests that monografted species are responsible for the efficient catalytic properties of the material, while bisgrafted species are unlikely to activate the Ni complex. We are currently exploring approaches to directly observe the active species in these supported systems.

#### Acknowledgements

I.B.M. is grateful to Swiss Government Excellence scholarship for financial support. We thank M. Pucino and J. de Jesus Silva for their help with gas chromatography analyses and J. Meyet for his help with catalytic tests.

**Keywords**: co-catalysts • oligomerization of ethene • nickel • alkylaluminum • aluminum-27 solid state NMR • DFT computations

- a) E. Y. X. Chen, T. J. Marks, *Chem. Rev.* 2000, 100, 1391-1434; b) K.
  P. Bryliakov, E. P. Talsi, *Coord. Chem. Rev.* 2012, 256, 2994-3007; c) K.
  Ziegler, E. Holzkamp, H. Breil, H. Martin, *Angew. Chem.* 1955, 67, 426-426; d) R. Gao, W.-H. Sun, C. Redshaw, *Catal. Sci. Technol.* 2013, 3, 1172-1179.
- a) E. Zurek, T. Ziegler, *Prog. Polym. Sci.* 2004, 29, 107-148; b) H. Sinn,
  W. Kaminsky, H.-J. Vollmer, R. Woldt, *Angew. Chem.* 1980, 92, 396-402;
  c) W. Kaminsky, *Macromolecules* 2012, 45, 3289-3297.
- a) G. J. P. Britovsek, V. C. Gibson, D. F. Wass, *Angew. Chem., Int. Ed.* **1999**, *38*, 428-447; b) S. D. Ittel, L. K. Johnson, M. Brookhart, *Chem. Rev.* **2000**, *100*, 1169-1204; c) V. C. Gibson, S. K. Spitzmesser, *Chem. Rev.*

**Ianusc** 

## **RESEARCH ARTICLE**

**2003**, *103*, 283-316; d) D. S. McGuinness, *Chem. Rev.* **2011**, *111*, 2321-2341.

- [4] A. W. Al-Sa'doun, Appl. Catal., A 1993, 105, 1-40.
- a) A. Kermagoret, P. Braunstein, *Organometallics* 2008, 27, 88-99; b) M.
  Dötterl, H. G. Alt, *ChemCatChem* 2012, 4, 660-667; c) M. Eichmann, W.
  Keim, M. Haumann, B. U. Melcher, P. Wasserscheid, *J. Mol. Catal. A: Chem.* 2009, 314, 42-48; d) D. S. McGuinness, W. Mueller, P.
  Wasserscheid, K. J. Cavell, B. W. Skelton, A. H. White, U. Englert,
  *Organometallics* 2002, 21, 175-181.
- [6] Z. Boudene, A. Boudier, P. A. R. Breuil, H. Olivier-Bourbigou, P. Raybaud, H. Toulhoat, T. de Bruin, J. Catal. 2014, 317, 153-157.
- [7] A. Kermagoret, R. N. Kerber, M. P. Conley, E. Callens, P. Florian, D. Massiot, F. Delbecq, X. Rozanska, C. Copéret, P. Sautet, J. Catal. 2014, 313 46-54
- [8] F. Rascón, R. Wischert, C. Copéret, Chem. Sci. 2011, 2, 1449-1456.
- [9] O. T. Beachley, L. Victoriano, Organometallics **1988**, 7, 63-67.
- [10] a) J. Li, J. A. DiVerdi, G. E. Maciel, J. Am. Chem. Soc. 2006, 128, 17093-17101; b) R. Anwander, C. Palm, O. Groeger, G. Engelhardt, Organometallics 1998, 17, 2027-2036; c) R. N. Kerber, A. Kermagoret, E. Callens, P. Florian, D. Massiot, A. Lesage, C. Copéret, F. Delbecq, X. Rozanska, P. Sautet, J. Am. Chem. Soc. 2012, 134, 6767-6775; d) E. Mazoyer, J. Trébosc, A. Baudouin, O. Boyron, J. Pelletier, J.-M. Basset, M. J. Vitorino, C. P. Nicholas, R. M. Gauvin, M. Taoufik, L. Delevoye, Angew. Chem., Int. Ed. 2010, 49, 9854-9858; e) B. Werghi, A. Bendjeriou-Sedjerari, A. Jedidi, E. Abou-Hamad, L. Cavallo, J.-M. Basset, Organometallics 2016, 35, 3288-3294; f) J. Pelletier, J. Espinas, N. Vu, S. Norsic, A. Baudouin, L. Delevoye, J. Trébosc, E. Le Roux, C. Santini, J.-M. Basset, R. M. Gauvin, M. Taoufik, Chem. Commun. 2011, 47, 2979-2981.
- [11] A. Kermagoret, R. N. Kerber, M. P. Conley, E. Callens, P. Florian, D. Massiot, C. Copéret, F. Delbecq, X. Rozanska, P. Sautet, *Dalton Trans.* 2013, 42, 12681-12687.
- [12] a) J. A. Tang, J. D. Masuda, T. J. Boyle, R. W. Schurko, *ChemPhysChem* 2006, 7, 117-130; b) E. Lam, A. Comas-Vives, C. Copéret, *J. Phys. Chem. C* 2017, *121*, 19946-19957; c) E. Lam, C. Copéret, *Helv. Chim. Acta* 2018, *101*, e1800120.
- [13] A. Kermagoret, P. Braunstein, Dalton Trans. 2008, 1564-1573.
- [14] J. Zhang, H. Gao, Z. Ke, F. Bao, F. Zhu, Q. Wu, J. Mol. Catal. A: Chem. 2005, 231, 27-34.
- [15] A. Pidcock, R. E. Richards, L. M. Venanzi, J. Chem. Soc. A 1966, 1707-1710.
- [16] R. L. Brainard, T. M. Miller, G. M. Whitesides, Organometallics 1986, 5, 1481-1490.
- [17] I. E. Soshnikov, N. V. Semikolenova, K. P. Bryliakov, V. A. Zakharov, W.-H. Sun, E. P. Talsi, Organometallics 2015, 34, 3222-3227.

## **RESEARCH ARTICLE**

#### Entry for the Table of Contents



**Isolation for Activity.** Monomeric AI solid co-catalyst for Ni-catalyzed ethene dimerization was prepared by grafting AI(CH<sub>2</sub><sup>'</sup>Bu)<sub>3</sub> on partially dehydroxylated silica and characterized by <sup>27</sup>AI solid-state NMR augmented by DFT computations. The efficient co-catalytic properties of the material were assigned to the presence of monografted alkylaluminum species, representing 19 % of all AI species.