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## Single Site Silica Supported Tetramethyl Niobium by the SOMC Strategy: Synthesis, Characterization and Structure-Activity Relationship in Ethylene Oligomerization Reaction

Received 00th January 20xx,  
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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Silica supported Tetramethyl niobium complex  $[(\equiv\text{SiO})\text{NbMe}_4]$  **2** has been isolated by surface alkylation of  $[(\equiv\text{SiO})\text{NbCl}_3\text{Me}]$  **1** with dimethyl zinc in pentane. **1** can be easily synthesized by grafting of  $\text{NbCl}_3\text{Me}_2$  on to the surface of partially dehydroxylated silica by the SOMC strategy. Precise structural analysis was carried out by the FTIR, advance solid state NMR, elemental analysis and mass balance techniques (gas quantification after treating **2** with degassed water). Complex **1** was found to be active in the ethylene oligomerization to produce up to  $\text{C}_{30}$ , whereas to our surprise complex **2** selectively dimerizes ethylene into 1-butene in the absence of a co-catalyst at the same conversion levels.

Transition metal alkyl compounds are active intermediates in many catalytic reactions and are heavily used in industry,<sup>1-5</sup> though many of them have never been isolated or characterized yet.<sup>6-8</sup> These type of metal alkyl compounds usually are highly unstable, and prone to decompose via  $\beta$ -H abstraction or through bi-molecular pathway. Till date, only limited number of metal alkyl compounds of early transition metals are isolated which do not poses  $\beta$ -H due to their poor stability.<sup>9,10</sup>

Surface organometallic chemistry (SOMC) allows isolation, characterization and study of the catalytic properties of those organometallic compounds (Surface OrganoMetallic Fragments, SOMF) which are highly unstable at room temperature or below.<sup>11-13</sup> In addition, SOMC based catalysts are easily separated from the products which is highly preferable.<sup>14-16</sup> Another major advantage of SOMC based catalysts is the ability to isolate reaction intermediates, propose reaction mechanisms, and study the structure activity relationship.<sup>12, 17-20</sup> Recently, using this strategy we have

prepared a variety of tungsten,  $[(\equiv\text{SiO})\text{WMe}_5]$ <sup>11</sup> tantalum  $[(\equiv\text{SiO})\text{TaMe}_4]$ <sup>21</sup>,  $[(\equiv\text{SiO})\text{Ta}^{\vee}\text{Cl}_2\text{Me}_2]$ ,<sup>22</sup> and niobium<sup>23</sup> SOMC complexes and isolate the key intermediate for alkane metathesis reaction and trimerization of ethylene.

Very recently, we developed surface alkylation technique where a combination of surface coordination compounds and their alkylation lead us to isolate metal alkyl fragments (SOMF),<sup>24, 25</sup> especially those that are difficult to synthesized by homogeneous condition. Using this techniques we were able to synthesize  $[(\equiv\text{SiO})\text{W}(=\text{O})\text{Me}_3]$ <sup>26</sup> whereas the synthesis of the homogeneous counterpart  $[\text{W}(=\text{O})\text{Me}_4]$  is not known in the literature.<sup>27</sup>



Scheme 1: Grafting of  $\text{NbCl}_3\text{Me}_2$  on to the  $\text{SiO}_2\text{-700}$  to form complex **1**.

In a previous report we demonstrate that  $[(\equiv\text{SiO})\text{Ta}^{\vee}\text{Cl}_2\text{Me}_2]$  showed a high selectivity towards trimerization of ethylene into 1-hexene.<sup>28</sup> On the other hand, although the homoleptic tantalum and tungsten methyl SOMC complex was well explored, corresponding niobium complexes are not reported earlier. Thus, we decided here to chose niobium complex for our research. However, niobium alkyl compounds are less studied, probably because of their higher instability.<sup>29-31</sup> To our knowledge, homoleptic pentaalkyl or tetraalkyl niobiumhalides have not been isolated yet. Thus, we applied our surface alkylation strategy to isolate well-defined alkyl niobium complex.<sup>24, 26</sup>

In the present manuscript, we report the synthesis of silica supported tetramethyl niobium complex  $[(\equiv\text{SiO})\text{NbMe}_4]$  via the surface methylation of niobium monomethyl  $[(\equiv\text{SiO})\text{NbCl}_3\text{Me}]$  (**1**) SOMC complex. These surface niobium compounds were systematically characterized by the classical tools of SOMC.

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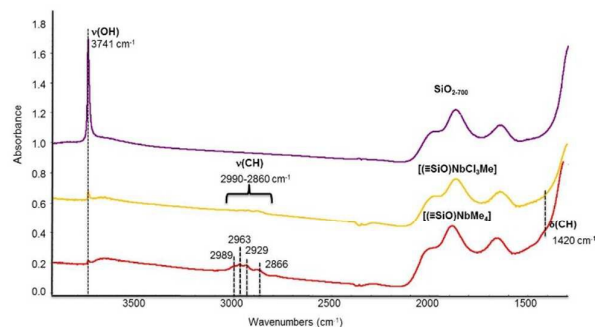
Electronic Supplementary Information (ESI) available: Spectroscopic data.

See DOI: 10.1039/x0xx00000x

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Niobium complex **1** was prepared by the grafting of  $\text{Nb}^{(V)}\text{Cl}_3\text{Me}_2$  on partially dehydroxylated silica (partial dehydroxylation was carried out at  $700^\circ\text{C}$  under high vacuum ( $10^{-5}$  bar) to form  $\text{SiO}_{2-700}$ ).  $\text{Nb}^{(V)}\text{Cl}_3\text{Me}_2$  was reacted with  $\text{SiO}_{2-700}$  at room temperature in dichloromethane or pentane for two hours under argon flow (Scheme 1), followed by washing with pentane and drying under high vacuum ( $10^{-5}$  bar) in the absence of light, giving **1** as a pale yellow powder. The grafting reaction leads to the release of one equivalent of methane and the formation of a major product, well-defined niobium complex  $[(\equiv\text{SiO})\text{NbCl}_3\text{Me}]$  **1** with traces of a byproduct probably as result of the reaction between the chloride of the niobium complex and the silanol. The structure of **1** was confirmed by means of FTIR, elemental analysis and solid state NMR ( $^1\text{H}$ ,  $^{13}\text{C}$ , DQ, TQ, and HETCOR). Infrared spectrum showed that the characteristic peak of free silanol in  $\text{SiO}_{2-700}$  at  $3743\text{ cm}^{-1}$  (Fig. 1) completely disappeared (Fig. 1, yellow) as a sign of a quasi complete grafting.



**Fig. 1:** FTIR spectra of  $\text{SiO}_{2-700}$  (purple), complex **1** (yellow) and complex **2** (red).

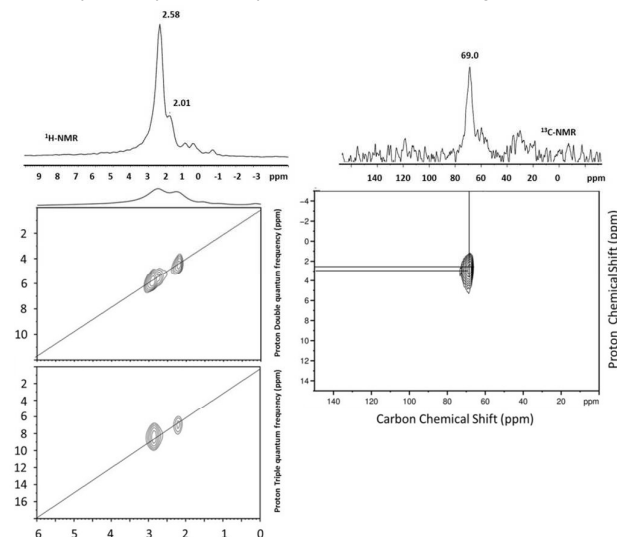
Elemental analysis of **1** gave 2.69 % Nb, 0.38 % C, 2.87 % Cl with a ratio of Nb:C:Cl=1:1.1:2.8 (Theoretical: Nb:C:Cl=1:1:3) where  $[(\equiv\text{SiO})\text{NbCl}_3\text{Me}]$  represents the major product.

The complex **1** was fully characterized by solid state NMR. The  $^1\text{H}$  magic-angle spinning (MAS) NMR spectra of **1** exhibit one main signal at 2.5 ppm with a small shoulder at 2.0 ppm. All the signals auto-correlate in the two-dimensional (2D) double-quantum (DQ) and triple-quantum (TQ) proving that they both belong to a  $\text{CH}_3$  group (Fig. 2). Similarly,  $^{13}\text{C}$  CP/MAS NMR spectrum of **1** displays only a single peak at 69 ppm. The 2D HETCOR spectrum of **1** with short contact time (0.5 ms) shows a clear correlation between the main methyl proton and the carbon peak at 69 ppm, allowing the assignment of the carbon–proton pairs to the individual methyl groups.



**Scheme 2:** Surface methylation of complex **1** by  $\text{ZnMe}_2$  to generate complex.

To fully methylate compound **1**  $[(\equiv\text{SiO})\text{NbCl}_3\text{Me}]$  we used

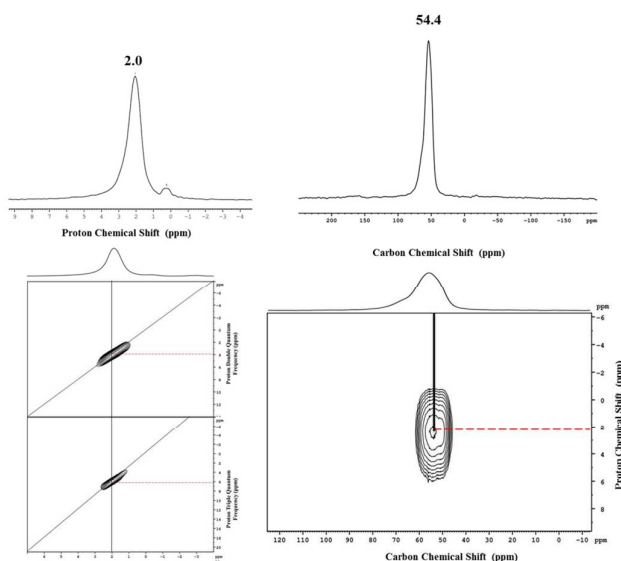


**Fig. 2:**  $^1\text{H}$  MAS NMR spectra of complex **1** b)  $2\text{D } ^1\text{H}-^1\text{H}$  DQ/SQ and c)  $^1\text{H}-^1\text{H}$  TQ/SQ NMR spectra of complex **1** c) One-dimensional  $^{13}\text{C}$  CP/MAS NMR spectra of complex **1** d)  $2\text{D}$  CP/MAS HETCOR NMR spectra of **1**.

surface methylation technique with dimethylzinc to form full alkylated complex  $[(\equiv\text{SiO})\text{NbMe}_4]$ . Complex **1**  $[(\equiv\text{SiO})\text{NbCl}_3\text{Me}]$  was taken in dichloromethane and then reacted with 1.5 equivalents (with respect to niobium) of dimethylzinc (solution in pentane) at room temperature for an hour (Scheme 2). The product was washed three time with pentane and then dried under high vacuum for 30 min ( $<10^{-5}$  bar) to form **2**. The FTIR shows characteristic peak of the niobium methyls by the increase of intensity of the bands in the range of  $3000\text{ cm}^{-1}$ ,  $\nu(\text{C}-\text{H})$ , and  $1540\text{ cm}^{-1}$ ,  $\delta(\text{C}-\text{H})$  assigned to an increase in the amount of methyl fragments (Fig. 1, red). Elemental analysis of **2** gave 2.59 % Nb, 1.28 % C, 1.32 % Cl, 1.11 % Zn with a ratio of Nb/C = 1/3.8 (Theoretical: Nb/C = 1/4). In addition, the structure was further proved by gas quantification method [adding degassed water to 100 mg of complex **2** releases 0.114 mmol of methane ( $4.2\text{ CH}_4/\text{Nb}$ ) after analyzing gas samples by gas chromatography (GC)]. This can be explained by the presence of  $[(\equiv\text{SiO})\text{NbMe}_4]$  as a major species.

Additionally, formulation of surface organometallic fragment (SOMF) **2** was elucidated by solid state NMR. The  $^1\text{H}$ -solid state NMR spectrum of **2** displays a main peak at 2.0 ppm along with a small peak at 0.3 ppm (Fig. 3). This peak shows a strong autocorrelation peak on the diagonal of both  $2\text{D } ^1\text{H}-^1\text{H}$  double and triple quantum (DQ, TQ). Thus, the peak at 2.0 ppm can be assigned to a methyl group.

Besides,  $^{13}\text{C}$  cross polarization magic-angle spinning (CP-MAS) of **2** shows a single peak at 54 ppm,  $^1\text{H}$ - $^{13}\text{C}$  HETCOR spectrum of **2** shows a correlation between the carbon peak at 54 ppm and the proton peak at 2.0 ppm (Fig. 3).



**Fig. 3:** a)  $^1\text{H}$  MAS NMR spectra of complex **2** b) 2D  $^1\text{H}$ - $^1\text{H}$  DQ/SQ and (c)  $^1\text{H}$ - $^1\text{H}$  TQ/SQ NMR spectra of complex **2** c) One-dimensional  $^{13}\text{C}$  CP/MAS NMR spectra of complex **2** d) 2D CP/MAS HETCOR NMR spectra of complex **2**

The alkylation reaction of **1** has been repeated with an excess amount of dimethylzinc (5 equivalents compared to Nb) keeping in mind to get fully converted tetramethyl niobium complex. After analyzing the formed product, the proton peak at 2.0 and the carbon peak at 54 are still intact, as well as new proton and carbon peaks appears at 0.3 and -20 ppm as expected due to the formation of  $[(\equiv\text{SiO})\text{ZnMe}]$  because of excess use of dimethyl zinc (SI, Fig. S1).

After systematic characterization, the reactivity of the surface niobium compounds was tested in ethylene oligomerization. complex **1** or **2** was taken inside a special glass reactor in dry toluene, followed by a high pressure introduction of ethylene (at constant pressure of 50 bars) at  $100^\circ\text{C}$ . Using **1**, oligomerization of ethylene into olefins ranging between  $\text{C}_4$  and  $\text{C}_{32}$  (with a difference of two carbons between two consecutive products). In this reaction  $\text{C}_4$  (38.8%) and  $\text{C}_6$  (36.5%) share equally up to 76 % of the total amount of the formed oligomers. However, the same catalytic test was carried out with complex **2**, a dramatic change in the selectivity was observed. Only butenes and hexenes are formed (Table 1). In contrast to previously reported tantalum complex  $[(\equiv\text{SiO})\text{Ta}^{\text{V}}\text{Cl}_2\text{Me}_2]$  that forms hexenes ( $\approx 90\%$ ), complex **2** forms butenes selectively in the range between 80-92%. It is important to note that changing the reaction condition by lowering the pressure of ethylene did not change

the selectivity of both complexes **1** and **2**. The pre-catalysts **1** and **2** were deactivated likely due to the formation of polymer on the active sites. This difference of selectivity between **1** and **2** is likely due to different coordination sphere and their ability to abstract the  $\beta$ -hydrogen from the growing chain.

**Table 1:** Oligomerization of ethylene catalyzed with complex  $[(\equiv\text{SiO})\text{NbCl}_3\text{Me}]$  **1**, complex  $[(\equiv\text{SiO})\text{NbMe}_4]$  **2** and previously reported tantalum complex  $[(\equiv\text{SiO})\text{TaCl}_2\text{Me}_2]$ .

Complex	Butenes Selectivity (1-butene %)	Hexenes Selectivity (1-hexen %)	Activity <sup>a</sup>
$[(\equiv\text{SiO})\text{NbCl}_3\text{Me}]^{\text{b}}$	38.8(82)	36.5(66)	1150
$[(\equiv\text{SiO})\text{NbCl}_3\text{Me}]^{\text{c}}$	40.1(83)	34.4(54)	934
$[(\equiv\text{SiO})\text{NbMe}_4]^{\text{b}}$	91.9(94)	7.8(54)	1050
$[(\equiv\text{SiO})\text{NbMe}_4]^{\text{c}}$	87.2(93)	10.5(45)	977
$[(\equiv\text{SiO})\text{TaCl}_2\text{Me}_2]$	9.6	82.7	375

[a] Turnovers mol(ethylene)/mol(Nb)/h

[b] Ethylene pressure =50 bars

[c] Ethylene pressure=40 bars

In conclusion, we have succeeded to prepare the first niobium tetramethyl complex on a silica support  $[(\equiv\text{SiO})\text{NbMe}_4]$  using SOMC-approach combined by surface alkylation tool. Complex  $[(\equiv\text{SiO})\text{NbMe}_4]$  **2** was synthesized by alkylating  $[(\equiv\text{SiO})\text{NbCl}_3\text{Me}]$  **1** with dimethylzinc. Complexes **1** and **2** were fully characterized by advance solid state NMR, FTIR, elemental analysis and mass balance. Finally, we revealed that **2** exhibits good activity and high selectivity in the dimerization of ethylene into 1-butene.

This work was supported by funds from King Abdullah University of Science and Technology (KAUST) office of sponsored research (OSR).

## Notes and references

- J. Klosin, P. P. Fontaine and R. Figueroa, *Accounts Chem. Res.*, 2015, **48**, 2004-2016.
- J. R. Zoeller, V. H. Agreda, S. L. Cook, N. L. Lafferty, S. W. Polichnowski and D. M. Pond, *Catal. Today*, 1992, **13**, 73-91.
- M. Beller, B. Cornils, C. D. Frohning and C. W. Kohlpaintner, *J. Mol. Catal. a-Chem.*, 1995, **104**, 17-85.
- R. Jira, *Angew. Chem. Int. Edit*, 2009, **48**, 9034-9037.
- D. R. Patel and R. N. Ram, *J. Mol. Catal. a-Chem.*, 1998, **130**, 57-64.
- J. R. M. Kress, M. J. M. Russell, M. G. Wesolek and J. A. Osborn, *J. Chem. Soc. Chem. Comm.*, 1980, **10**, 431-432.

## COMMUNICATION

Journal Name

7. F. S. Dyachkovskii and N. E. Khrushch, *Zh. Obshch. Khim.*, 1971, **41**, 1779-1781.
8. J. F. Hartwig, *J. Am. Chem. Soc.*, 1996, **118**, 7010-7011.
9. Shortlan, A. J. and Wilkinson, G., *J. Chem. Soc. Dalton*, 1973, , 872-876.
10. P. J. Chirik, *Organometallics*, 2010, **29**, 1500-1517.
11. M. K. Samantaray, E. Callens, E. Abou-Hamad, A. J. Rossini, C. M. Widdifield, R. Dey, L. Emsley and J. M. Basset, *J. Am. Chem. Soc.*, 2014, **136**, 1054-1061.
12. Y. Chen, E. Abou-hamad, A. Hamieh, B. Hamzaoui, L. Emsley and J. M. Basset, *J. Am. Chem. Soc.*, 2015, **137**, 588-591.
13. J. D. A. Pelletier and J. M. Basset, *Accounts Chem. Res.*, 2016, **49**, 664-677.
14. V. Salinier, G. P. Niccolai, V. Dufaud and J. M. Basset, *Adv. Synth. Catal.*, 2009, **351**, 2168-2177.
15. E. Mazoyer, N. Merle, A. de Mallmann, J. M. Basset, E. Berrier, L. Delevoye, J. F. Paul, C. P. Nicholas, R. M. Gauvin and M. Taoufik, *Chem. Commun.*, 2010, **46**, 8944-8946.
16. N. Merle, F. Le Quemener, Y. Bouhoute, K. C. Szeto, A. De Mallmann, S. Barman, M. K. Samantaray, L. Delevoye, R. M. Gauvin, M. Taoufik and J. M. Basset, *J. Am. Chem. Soc.*, 2017, **139**, 2144-2147.
17. M. K. Samantaray, R. Dey, E. Abou-Hamad, A. Hamieh and J. M. Basset, *Chem-Eur. J.*, 2015, **21**, 6100-6106.
18. E. Kuntz, J. M. Basset, D. Bouchu, G. Godard, F. Lefebvre, N. Legagneux, C. Lucas and D. Michelet, *Organometallics*, 2010, **29**, 523-526.
19. J. M. Basset, C. Coperet, D. Soulivong, M. Taoufik and J. T. Cazat, *Accounts Chem. Res.*, 2010, **43**, 323-334.
20. C. Coperet, M. Chabanas, R. P. Saint-Arroman and J. M. Basset, *Angew. Chem. Int. Edit*, 2003, **42**, 156-181.
21. Y. Chen, S. Ould-Chikh, E. Abou-Hamad, E. Callens, J. C. Mohandas, S. Khalid and J. M. Basset, *Organometallics*, 2014, **33**, 1205-1211.
22. Y. Chen, R. Credendino, E. Callens, M. Atiqullah, M. A. Al-Harthi, L. Cavallo and J. M. Basset, *Acs Catal.*, 2013, **3**, 1360-1364.
23. P. Zhang, A. D'Elia, W. V. Delsolaro and K. Artoos, *Nucl. Instrum. Meth. A*, 2015, **797**, 101-109.
24. A. Hamieh, R. Dey, M. K. Samantaray, S. Abdel-Azeim, E. Abou-Hamad, Y. Chen, J. D. A. Pelletier, L. Cavallo and J. M. Basset, *Organometallics*, 2016, **35**, 2524-2531.
25. Y. Bouhoute, A. Garron, D. Grekov, N. Merle, K. C. Szeto, A. De Mallmann, I. Del Rosal, L. Maron, G. Girard, R. M. Gauvin, L. Delevoye and M. Taoufik, *ACS Catal.*, 2014, **4**, 4232-4241.
26. A. Hamieh, Y. Chen, S. Abdel-Azeim, E. Abou-hamad, S. Goh, M. Samantaray, R. Dey, L. Cavallo and J. M. Basset, *ACS Catal.*, 2015, **5**, 2164-2171.
27. P. Stavropoulos, G. Wilkinson, M. Motevalli and M. B. Hursthouse, *Polyhedron*, 1987, **6**, 1081-1087.
28. Y. Chen, E. Callens, E. Abou-Hamad, N. Merle, A. J. P. White, M. Taoufik, C. Coperet, E. Le Roux and J. M. Basset, *Angew. Chem. Int. Edit*, 2012, **51**, 11886-11889.
29. R. R. Schrock and P. Meakin, *J. Am. Chem. Soc.*, 1974, **96**, 5288-5290.
30. Y. D. Wu, K. W. K. Chan and Z. Xue, *J. Am. Chem. Soc.*, 1995, **117**, 9259-9264.
31. R. R. Schrock, *J. Organomet. Chem.*, 1976, **122**, 209-225.

We describe herein a facile approach to synthesize silica grafted niobium tetramethyl complex from its chloride analogue. Those two complexes shows different selectivity in the ethylene oligomerization reaction, where the fully alkylated species is highly selective toward the dimerization of ethylene.

