This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the **Information for Authors**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard **Terms & Conditions** and the **Ethical guidelines** still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Journal Name

COMMUNICATION

Direct observation of supported W bis-methylidene from supported W-methyl/methylidyne species

E. Callens,* E. Abou-Hamad, N. Riache and J. M. Basset*

Extensive solid-state NMR analyses determine unambiguously the formation of silica supported W bis-methylidene methyl species by reaction of the corresponding methyl carbyne wih trimethylphosphine or cyclic olefin.

Transition metals alkylidene species are involved in olefin metathesis and assumed to be key intermediates in alkane metathesis.[1, 2] Alkane metathesis is a reaction widely studied employing two catalytic systems: dual catalysts operating in tandem[3] and single supported multifunctional catalysts.[1] For the single catalytic system, it is generally assumed that a metal alkylidene hydride or metal alkylidene alkyl belonging typically to group V and VI with a pendant alkyl group is needed to convert alkanes. This transformation occurs *via* a multistep mechanism (C-H bond activation, olefin metathesis...) Olefins were found to be key intermediates in this reaction forming metallacyclobutane.[4, 5] In the past, several approaches to synthesize W methylidene species have been used. Initially, it was postulated that direct protonation of the carbynic W≡C bond by surface Bronsted acids should provide methylidene tungsten species.[6, 7] The lack of results on this approach leads to the direct substitution of one ligand of a complex possessing already the alkylidene moiety, followed by cycloaddition of ethylene.[8] Non alkyls ligands (imido, oxo, phenolate) are generally required to stabilize this alkylidene species explaining that these surface organometallic species are generally restricted for olefin metathesis.[9] Additionally, direct methanation of W polyhydrides complex followed by α-H abstraction on the methyl ligand provides encouraging results for the obtention of W methylidene complex.[10] Therefore, we recently synthesized a well-defined silica supported W pentamethyl complex **1** possessing no β-H which upon thermal treatment is transformed into W methylidyne species **2a** and **2b** (Chart 1).[11]
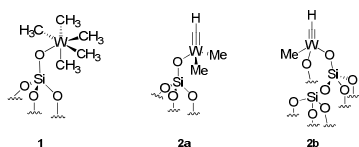

Chart 1: Well-defined supported W methyl catalysts

These species were found to be active for propane metathesis giving lower and higher linear homologues. These results are in contrast to the silica supported Schrock complex possessing neopentyl/neopentylidyne group which found to be much less active for propane metathesis than **2**.[12] Nevertheless, this complex (≡SiO)W(≡CtBu)(CH₂tBu)₂ was very active for the propene metathesis.[13] To account for the observed reactivity, the formation of a W bis-alkylidene was suggested without experimental evidence.

Herein, we wish to report the isolation and characterization at the molecular level of well-defined W methylidene methyl species promoted by PMe₃ from the tautomerization of W methylidyne methyl species. Its activity towards cycloalkane metathesis would also be disclosed.

Xue and co-workers have observed by NMR spectroscopy that W-alkyl/alkylidyne with a pendant silyl groups could undergo a tautomerization *via* an α-H migration to form a d⁰ W bis(alkylidene) species in homogeneous phase.[14-17] Additionally, they calculated by DFT that the equilibrium between hypothetical molecular Me₃W≡CH and its corresponding W bis-methylidene has an energy barrier of only 5 kcal/mol at room temperature (Scheme 1).[18]
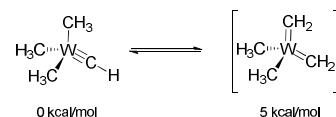
Scheme 1: Equilibrium between molecular W-methylidyne and W bis-methylidene

Furthermore, they found that the equilibrium between these W alkylidyne alkyl and W bis-alkylidene species could be catalyzed by coordination of trimethylphosphine. Addition of PMe₃ on (Me₃SiCH₂)₃W≡CSiMe₃ promotes an observable exchange to give W bis-alkylidene tautomer (Me₃SiCH₂)₂W(=CHSiMe₃)₂(PMe₃) and (Me₃SiCH₂)₃W≡CSiMe₃(PMe₃) at room temperature.[18] Thus, we envisage that **2a** and **2b** could evolve to W bis-methylidene species *via* H-transfer of a pendant methyl ligand under our alkane metathesis conditions. These species **2a** and **2b** were fully characterized by NMR spectroscopy in our previous work: ¹³C CP/MAS spectrum displays four signals at 298, 48, 44 and 40 ppm

(Figure 1-IA).[11] The carbon signal at 298 ppm, confirmed by DFT calculations, is assigned to a methylidyne moiety (W≡CH), which the corresponding protons signal shows no autocorrelation in ^{1}H-^{1}H double quantum and triple quantum. The carbon resonances at 44 and 48 ppm correspond to the two methyl groups of monopodal species **2a** and the carbon signal at 48 ppm correspond to the methyl group of bipodal species **2b**.

In the work described herein, a vapor pressure of PMe$_3$ was introduced on silica supported ^{13}C enriched **2a** and **2b**. The ^{13}C CP/MAS solid state NMR spectroscopy of the resulting powder shows the disappearance of the signal at 298 ppm and the appearance of two signals at 356 ppm and 252 ppm (Figure 1-IB). The other signal at 33 ppm corresponds likely to PMe$_3$ physisorbed on dehydroxylated silica (see the experimental evidence on ESI). Furthermore, the carbon resonance at 252 ppm shows a correlation with proton chemical shifts centered at 4.2 ppm in the 2D ^{1}H-^{13}C Heteronuclear (HETCOR) NMR experiment (Figure 1-II) with a short contact time (0.2 ms), attributed to a typical W alkylidene species. The carbon resonance at 356 ppm correlates with the proton chemical shifts centered at 7 ppm (Figure 1-II), that corresponds to the W methylidyne. These observed ^{13}C chemical shifts are matching those obtained of W methylidyne and methylidene species in liquid phase of the molecular complex (Me$_3$SiCH$_2$)$_3$W≡CSiMe$_3$ in the presence of PMe$_3$ in toluene *d*8.[18] Note that several resonances centered at 33 ppm correlating with protons between 1.9 and 1.2 ppm correspond probably to different orientations of the methyl groups.
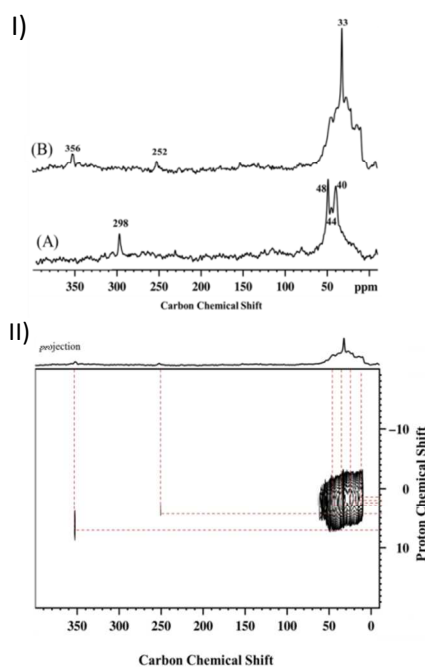

Figure 1: I) (A) ^{13}C CP/MAS spectrum of **2**; (B) W methylidyne and W bis-methylidene PMe$_3$ adducts (both acquired at 9.4 T (ν$_0$ (^{1}H) = 400 MHz) with a 10 kHz MAS frequency, 10.000 scans. A 4 s repetition delay and a 2 ms contact time. Exponential line broadening of 80 Hz was applied prior to Fourier transformation). II) 2D ^{1}H-^{13}C CP/MAS dipolar HETCOR spectrum of W methylidyne and W bis-methylidene PMe$_3$ adducts (acquired at 9.4 T with an 8.5 kHz MAS frequency, 4000 scans per t_1 increment, a 4 s repetition delay, 32 individual increments and 0.2 ms contact time).

Additionally, ^{31}P solid state NMR was also undertaken since its natural isotopic abundance allows fast acquisition. ^{31}P NMR spectrum shows two signals at -21 and -47 ppm (figure 2A). The latter corresponds to the PMe$_3$ physisorbed on silica (see ESI). Thus, the phosphorous resonance at -21 ppm corresponds likely to an average of the different W supported tautomers species coordinated with PMe$_3$. The ^{31}P-^{31}P spin-diffusion shows no correlation between the two phosphorus signals confirming the existence of two distinct coordination sites of PMe$_3$: coordination to W atom and physisorbed on silica (figure 2B).[19, 20] While, in the 2D ^{1}H-^{31}P HETCOR NMR spectrum (Figure 2C) with a contact time (1 ms) the two ^{31}P signals at -21 and -47 ppm correlate with methyl protons between 1.6 and 2.1 ppm. To determine whether two phosphorous ligands could coordinate to the W metal center, we also study 1D INADEQUATE (Incredible Natural Abundance Double Quantum Transfer Experiment).[21-23] This is a NMR method to identify pairs of bonded nuclei, including when the two nuclei have the same isotropic chemical shift.[24-27] The 1D refocused INADEQUATE spectrum shows no signal at -21 ppm (see ESI). This result strongly supports that only one molecule of PMe$_3$ is coordinated per tungsten. Schrock and Clark reported that (Me$_3$CCH$_2$)$_3$W≡CCMe$_3$ reacts with neat PMe$_3$ to form (Me$_3$CCH$_2$)W(=CHCMe$_3$)(≡CCMe$_3$)(PMe$_3$)$_2$ through CMe$_4$ elimination at 100 °C in a sealed tube.[28] Thus, 2D ^{13}C-^{13}C double-quantum was performed to confirm the assignment of W bis-methylidene supported species. The DQ frequency in the w_1 dimension corresponds to the sum of two single quantum (SQ) frequencies of the two coupled carbon and correlates in the w_2 dimension with the two corresponding carbon resonances.[29] Conversely, carbon groups with spins that are not dipolar coupled will give no signals. The projection on the w_2 dimension of the ^{13}C-^{13}C double-quantum MAS spectrum of species **2** in the presence of PMe$_3$ shows the appearance of a signal at 252 ppm confirming the presence of two neighboring equivalent methylidene groups (Figure 3).
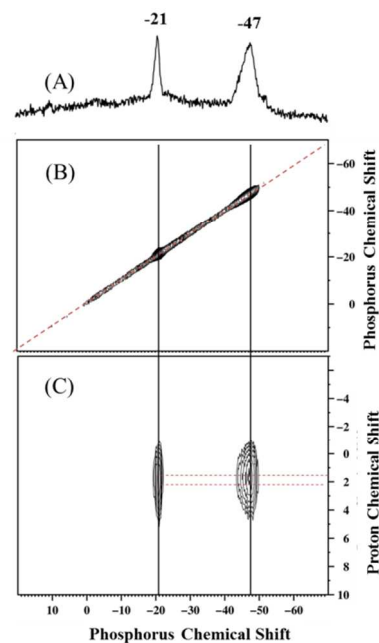

Figure 2: (A) ^{31}P CP/MAS spectrum of W methylidyne and W bis-methylidene PMe$_3$ adducts (acquired at 9.4 T (ν0 (^{1}H) = 400 MHz) with a 10 kHz MAS frequency, 500 scans, 4 s repetition delay and a 2 ms contact time. Exponential

line broadening of 20 Hz was applied prior to Fourier transformation). (B) 2D [31]P-^{31}P spin-diffusion with DARR (dipolar-assisted rotational resonance) obtaining with a mixing time τ_{mix}=40 ms.[19, 20] Sequence begins with CP using a ramped pulse on the ^{31}P channel (acquired at 9.4 T with an 10 kHz MAS frequency, 400 scans per t_1 increment, a 4 s repetition delay, 128 individual increments and 4 ms contact time) and (C) 2D [1]H-^{31}P CP/MAS dipolar HETCOR spectrum of W methylidyne and W bis-methylidene PMe$_3$ adducts (acquired at 9.4 T with an 10 kHz MAS frequency, 400 scans per t_1 increment, a 4 s repetition delay, 32 individual increments and 1 ms contact time).
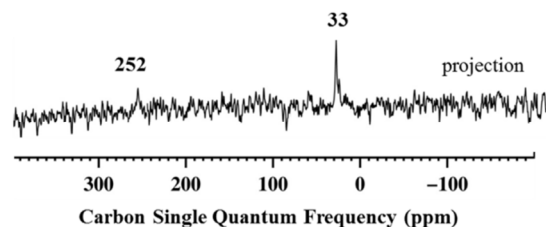

Figure 3: Projection in the w_2 dimension of the 2D [13]C-^{13}C double-quantum DQ/single Quantum (SQ) with cross polarization for weak dipole-dipole couplings, compensated for pulse imperfection of) W methylidyne and W bis-methylidene PMe$_3$ adducts (acquired at 9.4 T with an 10 kHz MAS frequency, 1000 scans per t_1 increment, a 4 s repetition delay, 256 individual increments and 3 ms contact time).

This result strongly supports that grafted W methylidyne species **2** undergo tautomerization to form W bis-methylidene species **4** in the presence of PMe$_3$ see scheme 2.
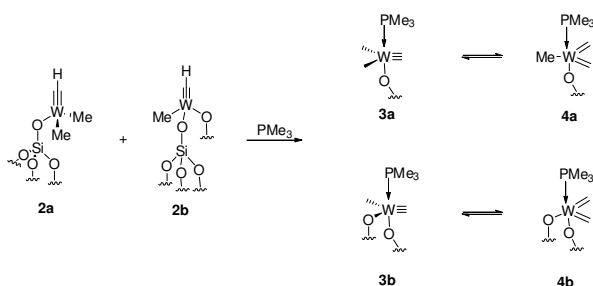
Scheme 2: Formation of W bis-methylidene species **4**

In order to have a better understanding of their reactivity, these supported catalysts were studied in the metathesis of cyclooctane.[30] Cyclooctane metathesis reaction using catalyst precursor **1** or **2** found to be very similar in terms of reactivity and selectivity. TONs are respectively 311 and 362 for this alkane metathesis after 340h. Conversions reached respectively 50% and 57% (Figure 4). Supported species **3** and **4** were found to be inactive for this cyclooctane metathesis because an open coordination site is taken by the added phosphine ligand or the strong σ–donor property of PMe$_3$ decreases the electrophilic character of the W metal.
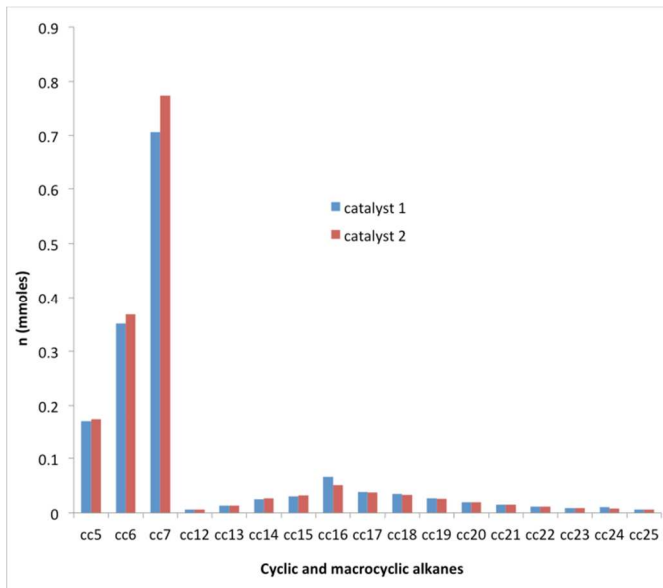

Figure 4: Products distribution of cyclooctane metathesis catalyzed by **1** and **2**. Reaction conditions: batch reactor, **1** and **2**, cyclooctane (0.5 mL, 3.7 mmol), 150°C.

As observed in our previous work, this cyclooctane metathesis transformation involves the formation of olefin intermediate that would undergo a metathesis step.[29] Having demonstrated earlier that cyclooctene would undergo a facile ring opening metathesis polymerization, we studied whether a coordination of cyclohexene (well-known to be difficult for ROMP)[31] on the W metal sphere could also evolve to a W bis-methylidene species. Contacting cyclohexene to **2** lead to several carbon resonances at 307, 252, 144, 59 and 44 ppm in ^{13}C NMR spectroscopy (see ESI). The signal at 252 ppm indicates the presence of the two methylidene ligands, demonstrating that an olefin could act as PMe$_3$ by promoting the tautomerization.[32]

Conclusions

Extensive solid-state NMR allows the evidence of the first supported W bis-methylidene species, upon treatment of supported W methylidyne with either PMe$_3$ or an olefin. This result is important to a better comprehension of alkane metathesis catalyzed with supported single catalytic system. We are currently exploring the reactivity of such supported complexes in alkene metathesis.
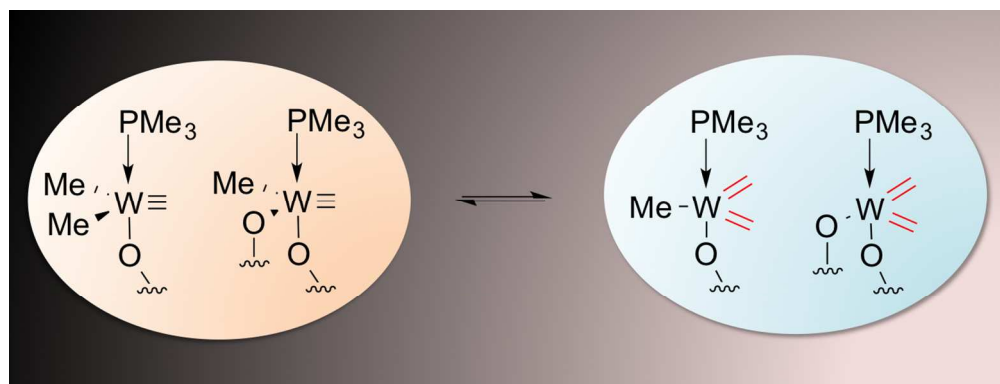
Acknowledgements

Notes and references

KAUST Catalyst Center, Physical Sciences and Engineering Division, King Abdullah University of Science and Technology, Thuwal, 23955-6900, Saudi Arabia. E-mail: Emmanuel.callens@kaust.edu.sa, Jean-Marie.Basset@kaust.edu.sa

1.   J. M. Basset, C. Coperet, D. Soulivong, M. Taoufik and J. T. Cazat, *Accounts Chem Res*, 2010, **43**, 323-334.
2.   F. Rascon and C. Coperet, *J Organomet Chem*, 2011, **696**, 4121-4131.
3.   M. C. Haibach, S. Kundu, M. Brookhart and A. S. Goldman, *Accounts Chem Res*, 2012, **45**, 947-958.
4.   J. M. Basset, C. Coperet, L. Lefort, B. M. Maunders, O. Maury, E. Le Roux, G. Saggio, S. Soignier, D. Soulivong, G. J. Sunley, M. Taoufik and J. Thivolle-Cazat, *J Am Chem Soc*, 2005, **127**, 8604-8605.
5.   M. Leconte and J. M. Basset, *J Am Chem Soc*, 1979, **101**, 7296-7302.
6.   R. Buffon, M. Leconte, A. Choplin and J. M. Basset, *J Chem Soc Chem Comm*, 1993, 361-362.
7.   R. Buffon, M. Leconte, A. Choplin and J. M. Basset, *J Chem Soc Dalton*, 1994, 1723-1729.
8.   F. Blanc, R. Berthoud, C. Coperet, A. Lesage, L. Emsley, R. Singh, T. Kreickmann and R. R. Schrock, *P Natl Acad Sci USA*, 2008, **105**, 12123-12127.
9.   M. P. Conley, V. Mougel, D. V. Peryshkov, W. P. Forrest, D. Gajan, A. Lesage, L. Emsley, C. Copéret and R. R. Schrock, *J Am Chem Soc*, 2013, **135**, 19068-19070.
10. K. C. Szeto, S. Norsic, L. Hardou, E. Le Roux, S. Chakka, J. Thivolle-Cazat, A. Baudouin, C. Papaioannou, J. M. Basset and M. Taoufik, *Chem Commun*, 2010, **46**, 3985-3987.
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. E. Le Roux, M. Taoufik, A. Baudouin, C. Coperet, J. Thivolle-Cazat, J. M. Basset, B. M. Maunders and G. J. Sunley, *Adv Synth Catal*, 2007, **349**, 231-237.
13. E. Le Roux, M. Taoufik, M. Chabanas, D. Alcor, A. Baudouin, C. Coperet, J. Thivolle-Cazat, J. M. Basset, A. Lesage, S. Hediger and L. Emsley, *Organometallics*, 2005, **24**, 4274-4279.
14. L. A. Morton, R. T. Wang, X. H. Yu, C. F. Campana, I. A. Guzei, G. P. A. Yap and Z. L. Xue, *Organometallics*, 2006, **25**, 427-434.
15. L. A. Morton, S. J. Chen, H. Qiu and Z. L. Xue, *J Am Chem Soc*, 2007, **129**, 7277-7283.
16. Z. L. Xue and L. A. Morton, *J Organomet Chem*, 2011, **696**, 3924-3934.
17. K. G. Caulton, M. H. Chisholm, W. E. Streib and Z. L. Xue, *J Am Chem Soc*, 1991, **113**, 6082-6090.
18. L. A. Morton, X. H. Zhang, R. T. Wang, Z. Y. Lin, Y. D. Wu and Z. L. Xue, *J Am Chem Soc*, 2004, **126**, 10208-10209.
19. K. Takeda, K. Takegoshi and T. Terao, *J Chem Phys*, 2002, **117**, 4940-4946.
20. K. Takegoshi, S. Nakamura and T. Terao, *Chemical Physics Letters*, 2001, **344**, 631-637.
21. E. Ciampi, M. I. C. Furby, L. Brennan, J. W. Emsley, A. Lesage and L. Emsley, *Liq Cryst*, 1999, **26**, 109-125.
22. F. Fayon, G. Le Saout, L. Emsley and D. Massiot, *Chem Commun*, 2002, 1702-1703.
23. S. Cadars, J. Sein, L. Duma, A. Lesage, T. N. Pham, J. H. Baltisberger, S. P. Brown and L. Emsley, *J Magn Reson*, 2007, **188**, 24-34.
24. L. Duma, W. C. Lai, M. Carravetta, L. Emsley, S. P. Brown and M. H. Levitt, *Chemphyschem*, 2004, **5**, 815-833.
25. F. Fayon, D. Massiot, M. H. Levitt, J. J. Titman, D. H. Gregory, L. Duma, L. Emsley and S. P. Brown, *J Chem Phys*, 2005, **122**.
26. M. M. Maricq and J. S. Waugh, *J Chem Phys*, 1979, **70**, 3300-3316.
27. D. Gajan, D. Levine, E. Zocher, C. Coperet, A. Lesage and L. Emsley, *Chem Sci*, 2011, **2**, 928-931.
28. D. N. Clark and R. R. Schrock, *J Am Chem Soc*, 1978, **100**, 6774-6776.
29. M. Feike, D. E. Demco, R. Graf, J. Gottwald, S. Hafner and H. W. Spiess, *J Magn Reson Ser A*, 1996, **122**, 214-221.
30. N. riache et al. Cyclooctane metathesis catalyzed by silica supported tungsten pentamethyl ($\equiv$SiO)W(Me)5: distribution of macrocyclic alkanes, submitted to JACS.
31. G. Natta, G. Dallasta, I. W. Bassi and G. Carella, *Makromolekul Chem*, 1966, **91**, 87-&.
32. The signals at 307 and 142 ppm are respectively assigned to methylidyne moiety (W$\equiv$CH) and the CH of the sp2 carbons of cyclohexene. The one at 59 could correspond to a W-metallacycle adopting a square bipyramidal geometry and the methyl groups at 44 pm.

ChemComm Accepted Manuscript

Direct observation of supported W bis-methylidene from supported W methyl/methylidyne species