

Cationic Tungsten(VI) Penta-Methyl Complex: Synthesis, Characterization and its Application in Olefin Metathesis Reaction

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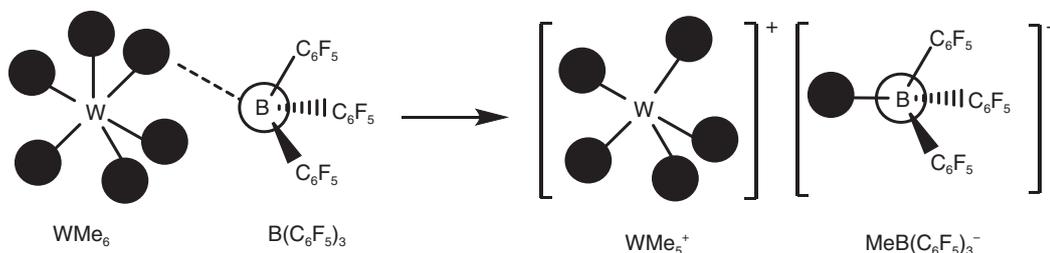
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Abstract — Tungsten-hexa-methyl readily reacts with $B(C_6F_5)_3$ in dichloromethane and generates the corresponding well-defined cationic tungsten-penta-methyl complex which was identified precisely by 1H NMR, ^{13}C NMR, 1H - ^{13}C NMR correlation spectroscopy. Unlike WMe_6 , this cationic complex has low energy barrier to form tungsten carbene intermediate, which was further supported by the fact that WMe_6 alone has no activity in olefin metathesis reaction whereas the cationic complex shows catalytic activity for self-metathesis of 1-octene.



Résumé — **Complexe pentaméthyle de tungstène(VI) cationique : synthèse, caractérisation et son application dans la réaction de métathèse des oléfines** — L'hexaméthyle de tungstène réagit avec le $B(C_6F_5)_3$ dans du dichlorométhane et génère le complexe pentaméthyle de tungstène cationique bien défini qui a été précisément identifié par spectroscopie de corrélation 1H RMN, ^{13}C RMN, 1H - ^{13}C RMN. À la différence du WMe_6 , ce complexe cationique a une barrière énergétique faible pour former un intermédiaire de carbène tungstène, ce qui a été ultérieurement étayé par le fait que le WMe_6 seul n'a pas d'activité dans la réaction de métathèse des oléfines, tandis que le complexe cationique montre une activité catalytique pour l'autométathèse d'1-octène.

INTRODUCTION

In 1973, Shortlan and Wilkinson described the first report on Tungsten hexamethyl [1], [2–4]. After its synthesis, the structure was established in 1996 by Seppelt [5], [6, 7] and Kaupp [8]. The geometry was calculated by Demolliens *et al.* [9] and Kang *et al.* [10]. However, until 2015 and to our knowledge there was no report on the catalytic activity of this homoleptic complex. WMe_6 is indeed difficult to prepare, extremely unstable, and very sensitive to even few ppm levels of oxygen or moisture. Handling this compound is challenging due to its explosive nature as reported by Shortlan and Wilkinson [1, 2], Galyer *et al.* [3], Galyer and Wilkinson [4]. In our previous communication, we demonstrated that grafting this unstable WMe_6 to the silica surface by SOMC (Surface Organometallic Chemistry) strategy and methodology at -80°C can enhance its thermal stability due to the formation of the stable grafted complex, $[\equiv\text{SiO-W}(\text{Me})_5]$ which proved to be a nice precursor of alkane metathesis catalysts via the formation of surface monopodal tungsten carbyne [11]. This carbyne is in equilibrium with a bis carbene upon addition of a donor ligand [12] (Scheme 1). Also, we demonstrated that WMe_6 on silica-alumina shows relatively higher reactivity than on silica because of the formation of very reactive cationic intermediate [13]. Let us recall that Kress and Osborn were the first to report the synthesis of a cationic W-carbene very active in olefin metathesis [14]. Based on the above fact we speculate that in order to prepare more reactive catalysts in terms of reactivity and selectivity a higher electrophilicity on tungsten center is essential.

However, high oxidation state cationic complexes of tungsten are very rare, especially those which do not contain a coordinating ligand [15] and these complexes are expected to be more reactive than the corresponding neutral complexes [14]. Cationic tungsten complex containing one or more stabilizing ligands *e.g.* oxygen, nitrogen, or oxygen, nitrogen, phosphorous containing ligand, cyclopentadienyl ligand are relatively stable and are described in the literature [14, 16–20]. Very recently, Schowner *et al.* have reported the synthesis of first cationic tungsten-oxo-alkylidene-N-heterocyclic-carbene complexes where the cationic metal center was stabilized by N-heterocyclic carbene [20].

To the best of our knowledge, the only example for homoleptic cationic tungsten-alkyl complex was reported in the literature by Wilkinson *et al.* Even in this paper they mentioned the reaction of WMe_6 with AlCl_3 which would lead to the formation of WMe_5^+ but without any proof [1–4].

1 EXPERIMENTAL

All experiments were carried out by using standard Schlenk and glovebox techniques under an inert nitrogen

atmosphere. The syntheses and the treatments of the surface species were carried out using high-vacuum lines ($<10^{-5}$ mbar) and glovebox techniques. Pentane was distilled from a Na/K alloy under N_2 and dichloromethane from CaH_2 . Both solvents were degassed through freeze–pump–thaw cycles. SiO_{2-700} was prepared by calcination at 300°C in the presence of air followed by dehydroxylation at 700°C under high vacuum ($<10^{-5}$ mbar) for 24 h. It contained 0.5–0.7 OH per nm^2 .

^1H NMR spectra were recorded at 600 MHz in CD_2Cl_2 unless otherwise stated. Chemical shifts are reported in ppm with the solvent resonance (CD_2Cl_2 : 5.32 ppm). Data are reported as follows: chemical shift, integration, and coupling constants (Hz). ^{13}C NMR were recorded at 150 MHz in CD_2Cl_2 unless otherwise stated with complete proton decoupling. Chemical shifts are reported in ppm from solvent peak as the standard (CD_2Cl_2 : 53.84 ppm).

1.1 1-Octene Metathesis

A mixture of catalytic species and dry 1-octene were mixed inside the glovebox. The ampoules were sealed under vacuum, kept at room temperature for 12 h. At the end of the reaction, the ampoules were frozen under liquid nitrogen. Then, the catalytic run was quenched by addition of a fixed amount of CH_2Cl_2 and after filtration the resulting solution was analyzed by GC and GC/MS.

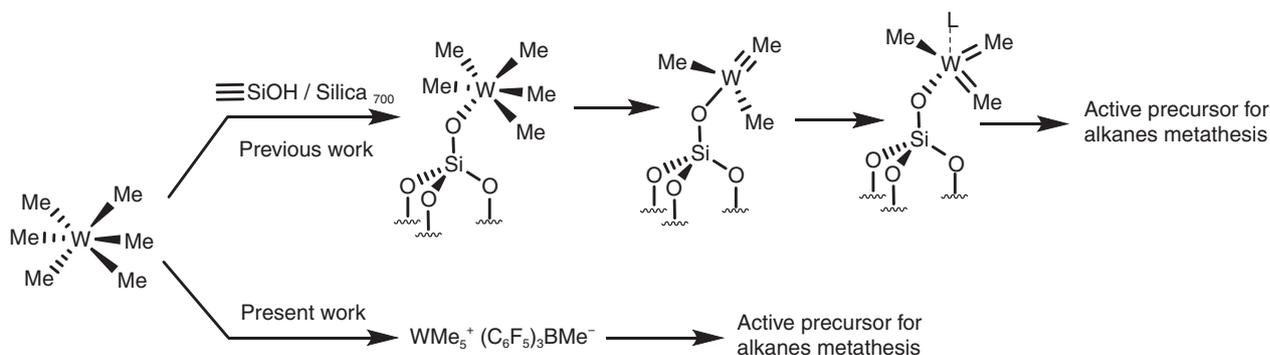
GC measurements were performed with an Agilent 7890 A Series (FID detection). Method for GC analyses: column HP-5; 30 m length 0.32 mm ID X 0.25 mm film thickness; flow rate: $1\text{ mL}\cdot\text{min}^{-1}$ (N_2); split ratio: 50/1; inlet temperature: 250°C ; detector temperature: 250°C ; temperature program: 40°C (3 min), $40\text{--}250^\circ\text{C}$ ($12^\circ\text{C}\cdot\text{min}^{-1}$), 250°C (3 min), $250\text{--}300^\circ\text{C}$ ($10^\circ\text{C}\cdot\text{min}^{-1}$), 300°C (3 min); *n*-decane retention time: $t_R = 9.6$.

1.2 Preparation of Hexamethyltungsten, WMe_6

The molecular precursor WMe_6 was prepared from WCl_6 and $(\text{CH}_3)_2\text{Zn}$, following the literature procedure [1, 6]. To a mixture of WCl_6 (1.80 g, 4.5 mmol) in dichloromethane (25 mL) was added $(\text{CH}_3)_2\text{Zn}$ (13.6 mmol, 1.0 M in heptane) at -80°C , and after addition, the reaction mixture was warmed to -35°C and stirred at this temperature for another 30 min. After successive filtrations with pentane and removal of the solvent, the red solid corresponding to WMe_6 was obtained (0.16 g, 12%).

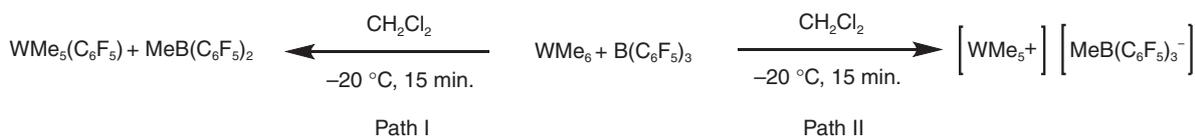
Caution! This $12e^-$ compound is highly unstable and is prone to violent decomposition [1].

^1H NMR (CD_2Cl_2 , 600 MHz): δ (ppm) 1.65 (s, 18H, WCH_3). ^{13}C NMR (CD_2Cl_2 , 150 MHz): δ (ppm) 82 (s, 6C, $J_{183\text{W-}^{13}\text{C}} = 47\text{ Hz}$, WCH_3). HSQC (Heteronuclear Single Quantum Coherence) confirms the correlation between the ^1H and ^{13}C NMR signals.



Scheme 1

Application of WMe_6 in SOMC and in solution (present work).



Scheme 2

Possible reaction between WMe_6 and $B(C_6F_5)_3$.

The ^{13}C -enriched $W(^{13}CH_3)_6$ was synthesised as described below: ^{13}C -enriched $(^{13}CH_3)_2Zn$ was prepared from a suspension of $^{13}CH_3Li$ and $ZnCl_2$ (2/1), with subsequent synthetic steps being analogous to those provided above.

1.3 Preparation of $[WMe_5^+ B(C_6F_5)_3Me^-]$

A cold solution ($-20\text{ }^\circ\text{C}$) of $B(C_6F_5)_3$ (100 mg) in dichloromethane was added drop wise to the cold ($-20\text{ }^\circ\text{C}$) solution of hexamethyltungsten (55 mg, 1 equiv. with respect to $B(C_6F_5)_3$) in dichloromethane. The mixture was stirred for 15 min at $-20\text{ }^\circ\text{C}$. Color of the solution intensified to reddish indicating the formation of ionic complex. At temperature below $-60\text{ }^\circ\text{C}$, this ionic complex is precipitated out from the solution however this $10e^-$ compound is highly unstable and decompose into black tungsten powder while drying.

Caution! This $10e^-$ compound is highly unstable and is prone to violent decomposition.

1H -NMR(600 MHz) δ (ppm) 0.5 (s, 3H, BCH_3), 2.7 (s, 15H, WCH_3). ^{13}C NMR(150 MHz) δ (ppm) 10.8 (s, 1C, BCH_3), 103.2 (s, 5C, WCH_3).

1.4 Grafting of $[WMe_5^+ B(C_6F_5)_3Me^-]$ on Silica₇₀₀

A solution of $[WMe_5^+ B(C_6F_5)_3Me^-]$ (85 mg, 1.2 equiv. with respect to WMe_6 and with respect to the amount of

surface-accessible silanols) in dichloromethane (15 mL) was mixed with silica (SiO_{2-700} ; 1.0 g) at $-50\text{ }^\circ\text{C}$ for one hour, allowed to warm to $-30\text{ }^\circ\text{C}$, and then stirred for an additional 2 h. At the end of the reaction, the resulting brown solid was washed with pentane ($3 \times 20\text{ mL}$) and dried under dynamic vacuum (1 mPa, 1 h).

1H solid-state NMR(400 MHz): δ (ppm) 2.0 (b, $W-CH_3$). ^{13}C CP/MAS solid-state NMR(100 MHz): δ (ppm) 83.0 ($W-CH_3$), 46.0($W-CH_3$) [11].

2 RESULTS AND DISCUSSION

As a part of our continuing program to explore the novel applications of tungsten hexamethyl, we report here the synthesis of the cationic tungsten-penta-methyl complex $[WMe_5]^+[MeB(C_6F_5)_3]^-$, starting from WMe_6 and its application in olefin metathesis. The experimental procedure is very simple. Simple mixing of bulky and non-coordinating Lewis acid, $B(C_6F_5)_3$ with WMe_6 at very low temperature ($-20\text{ }^\circ\text{C}$) generates quantitatively the cationic tungsten-penta-methyl complex $[WMe_5]^+[MeB(C_6F_5)_3]^-$.

In a preliminary study, we tried to synthesise WMe_5^+ according to literature reference using $AlCl_3$ as a de-methylating reagent but after several attempts we were unable to get the desired product [1-4]. Subsequently, we switched to tris(pentafluorophenyl)-boron which is known to form a

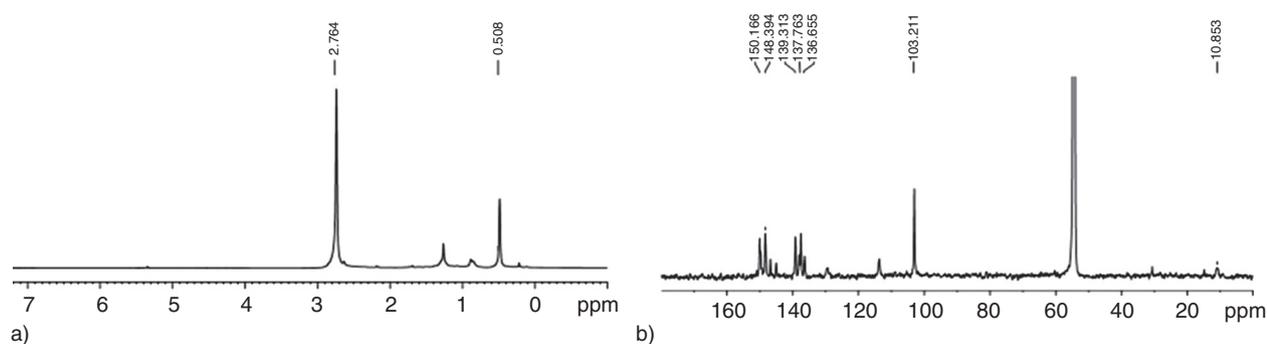
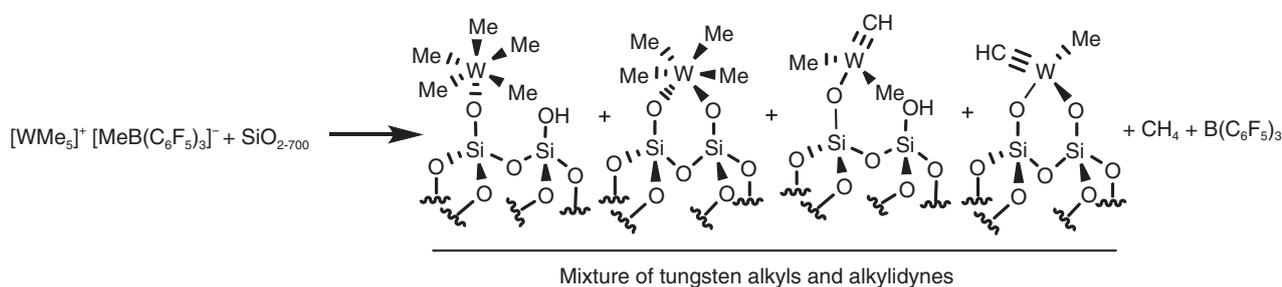


Figure 1

a) ^1H NMR spectra, b) ^{13}C NMR spectra of $[\text{WMe}_5]^+[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$.



Scheme 3

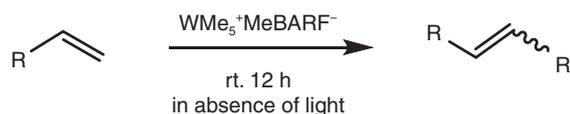
Grafting of $[\text{WMe}_5]^+[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$ onto the silica₇₀₀ support.

non-nucleophilic anion after de-methylation reaction. When the reaction was monitored by NMR at $-20\text{ }^\circ\text{C}$, it was found that the reaction between WMe_6 and $\text{B}(\text{C}_6\text{F}_5)_3$ was very fast and the peak corresponding to WMe_6 at 1.75 ppm in ^1H -NMR almost completely disappeared in less than 15 minutes and two new peaks at 2.68 ppm and 0.48 ppm were formed (Fig. 1). The product generated by the above reaction has a fair stability below $-40\text{ }^\circ\text{C}$ in the absence of light. However, upon warming this reaction mixture to $0\text{ }^\circ\text{C}$ from $-40\text{ }^\circ\text{C}$, a very first decomposition of the cationic complex was observed with release of gaseous methane. Based on the above experimental facts, one can assume the two possibilities; where Path I (Scheme 2) is the formation of neutral tungsten complex by the ligand metathetical exchange and Path II (Scheme 2) is de-methylation from WMe_6 , formation of cationic tungsten complex.

The ^1H -NMR chemical shift at +0.5 ppm corresponds to $[\text{CH}_3\text{-B}(\text{C}_6\text{F}_5)_3]^-$ which is well documented in the literature [21, 22] and as expected the resonance for the methyl proton of WMe_6 at 1.75 ppm is shifted downfield to 2.7 ppm, and ascribed to $[\text{WMe}_5]^+$. Similarly the ^{13}C -NMR spectra also clearly shows that the peak at 83 ppm of WMe_6 is

also completely replaced by two peaks at 10.8 ppm $[\text{CH}_3\text{-B}(\text{C}_6\text{F}_5)_3]^-$ and 103.2 ppm corresponding to $[\text{W}(\text{CH}_3)_5]^+$ which is good agreement with the literature value reported for $[\text{CH}_3\text{-B}(\text{C}_6\text{F}_5)_3]^-$ (Fig. 1). We also found in the ^1H - ^{13}C correlation spectra that the peak at 0.5 ppm in ^1H -NMR was correlating with the peak at 10.8 ppm in ^{13}C -NMR and the peak at 2.7 ppm in ^1H -NMR was correlating with the peak at 103.2 ppm in ^{13}C -NMR. These spectroscopic data strongly support the formation of $[\text{WMe}_5]^+[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$. In separate experiments, we synthesised ^{13}C label $\text{W}(\text{C}^{13}\text{H}_3)_6$ and upon treatment with $\text{B}(\text{C}_6\text{F}_5)_3$ we have thus identified incorporation of the labeled methyl in the final $[(\text{C}^{13}\text{H}_3)\text{B}(\text{C}_6\text{F}_5)_3]^-$ anion. The above experiment clearly indicates that in $[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$, 'CH₃' came from WMe_6 and strongly supports Path II (Scheme 2).

We then tried to graft cationic complex on the surface of silica₇₀₀, in order to get a cationic tungsten catalyst onto the heterogeneous support. However, after several attempts we were unable to identify any well define heterogeneous cationic tungsten complex except a mixture of neutral tungsten-methyl complex (Scheme 3).



Substrate	Product	Yield
1-octene	7-tetradecene	40%(E/Z= 3/1)
2-octene	no reaction	-----
Cyclooctene	Polyoctenamer	90%(E/Z= 7/3)

Scheme 4

Metathesis of olefin by cationic tungsten-methyl complex.

BARF⁻ = B(C₆F₅)₃

Tungsten cationic complex was found to be very effective for the metathesis of 1-octene and ROMP (Ring Opening Metathesis Polymerization) for cyclooctene. Cyclooctene was polymerized to polyoctenamer by ROMP at even $-40\text{ }^{\circ}\text{C}$ by this cationic tungsten complex. However, this complex was inactive for metathesis of trans 2-octene (Scheme 4). The detailed mechanism and the precise nature of the active catalytic species are still unknown for this catalytic system. However from the control experiment, we found that WMe₆ does not metathesise cyclooctene nor 1-octene. From the above experiments, we can assume that the formation of a tungsten carbene intermediate is more favoured when starting from the cationic complex rather than neutral WMe₆. A very similar observation was reported by Kress and Osborn, where they showed that cationic complexes are more active towards olefin metathesis than the corresponding neutral complexes [14]. Based on this, we speculate that a tetra coordinated cationic $[\text{WMe}_5(\text{=CH}_2)]^+[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$ intermediate is formed from $[\text{WMe}_5]^+[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$ by α -H transfer into neighbouring methyl groups. However, we have never seen any carbene intermediates by NMR during the decomposition of $[\text{WMe}_5]^+[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$ while the experiments were carried out inside the NMR instrument for long time.

CONCLUSION

In summary, we have developed a straight forward strategy for the synthesis of extremely unstable high oxidation state cationic tungsten(VI)-methyl complex in a precise way, starting from WMe₆. We fully characterised this unstable ionic species by ¹H-NMR, ¹³C-NMR, ¹H-¹³C correlation, etc., and also, we showed that this cationic complex is

reactive in olefin metathesis reaction. To the best of our knowledge, this is the first example of a well defined cationic tungsten complex. Further studies are in progress to assess the reactivity of this tungsten complex and its application in other catalysis.

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