Synthesis and Characterization of Cationic Tetramethyl Tantalum(V) Complex

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Abstract: A novel method for the synthesis of the homogeneous homoleptic cationic tantalum(V)tetramethyl complex $[(TaMe_4)^+ MeB(C_6F_5)_3^-]$ from neutral tantalumpentamethyl $(TaMe_5)$ has been described, by direct demethylation using $B(C_6F_5)_3$ reagent. The aforesaid higher valent cationic tantalum complex was characterized precisely by liquid state ^{1}H-NMR, ^{13}C-NMR, and ^{1}H-^{13}C-NMR correlation spectroscopy.

Keywords: tantalum; cationic; tungsten; DFT calculations; homoleptic; reaction mechanism; boron

1. Introduction

Tantalum alkyl complexes are of vital importance in current organometallic chemistry, from the point of view of stoichiometric reactions and mainly in catalysis [1–4]. Since 1974, tantalumpentamethyl $(TaMe_5, \mathbf{1})$ has the honour to be the simplest homoleptic complex of this class of compounds [5,6]. **1** was discovered by Richard Schrock and the structure was not unravelled until 1992 by Albright [7] and Haaland et al. [8]. $TaMe_5$ is rather unstable thermally and, consequently, **1** is highly prone to autocatalytically degradation [6]. Recently, in our previous communication [9], we checked that grafting this unstable $TaMe_5$ complex to the silica surface by a Surface Organometallic Chemistry (SOMC) strategy enhances its thermal stability due to the formation of the stable grafted $(\equiv Si-O-)TaMe_4$. The latter complex proved to be a nice precursor for alkane metathesis, leading to the formation of a surface monopodal tantalum methylidene dimethyl catalyst [9,10].

With the precedents of Buchmeiser and co-workers who developed the first cationic tungsten-oxo-alkylidene-NHC complex (NHC = *N*-heterocyclic carbene) [11,12], where the NHC was introduced to stabilize the cationic metal centre, together with the also tungsten based cationic complex WMe_5^+ [13], to improve the catalysts in terms of reactivity and selectivity, and taking into account the idea of increasing the electrophilicity on metal centre, we deepened into the idea of generating the cationic species of $TaMe_5$. This change planned to enter the field of predictive catalysis. Unfortunately, the drawback for tantalum with respect to tungsten is that the similar cationic Ta-complexes are scarce in literature [14–16], whereas there are several examples with stable cationic

tantalum complexes containing one or more nitrogen [17], phosphorous [18] and cyclopentadienyl containing ligands [19–21].

2. Results

As a part of our continuing research program to explore any novel application of tantalumpentamethyl complex, we report here a method for the synthesis of the homogeneous cationic $[TaMe_4]^+$ together with $[MeB(C_6F_5)_3^-]$ anion (**2**), starting from the neutral $TaMe_5$. The experimental procedure was straightforward: The simple mixture of bulky and non-coordinating boron Lewis acid, $B(C_6F_5)_3$, with **1**, at low temperature ($-40\ ^\circ C$) generates the cationic complex **2** (see Scheme 1), since above this temperature the undesired phenomenon of degradation appears in a rather facile way.
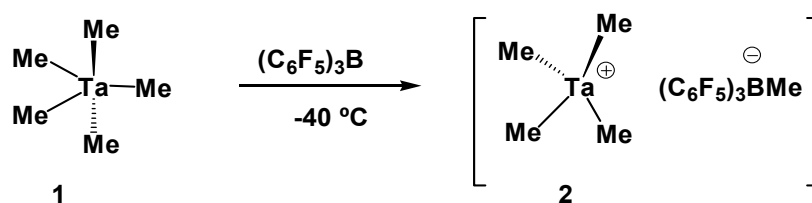
Scheme 1. Demethylation of homoleptic $TaMe_5$ complexes by strong electrophilic $B(C_6F_5)_3$.

Preliminarily, we tried the synthesis of $TaMe_4^+$ using an organic Lewis acid, tris(pentafluorophenyl)boron. The latter species is known to form a non-nucleophilic anion after demethylation reaction, a strategy that it is valid also with titanium [22,23], zirconium [24], or hafnium [24–26]. When the reaction was monitored by nuclear magnetic resonance (NMR) spectroscopy, at $-40\ ^\circ C$, the peak corresponding to $TaMe_5$ at 0.9 ppm in ^{1}H-NMR (Figure 1a) almost completely disappeared in less than 15 min due to the fast reaction between $TaMe_5$ and $B(C_6F_5)_3$, and two new peaks at 2.6 ppm and 0.5 ppm appeared (Figure 1b) [27].

Based on the above observations one can assume two possibilities (Scheme 2); path I consists of simple demethylation by the $B(C_6F_5)_3$ from $TaMe_5$ leading to the formation of cationic tantalum complex; whereas in path II there would be a chance for the formation of a neutral tantalum complex by simple ligand exchange. Path II could take place in a one-step mechanism from the original $TaMe_5$, however it seems more plausible after path I.
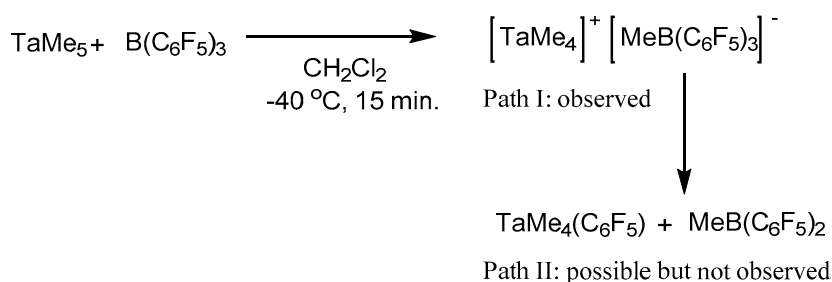

Scheme 2. Possible reaction between $TaMe_5$ and $B(C_6F_5)_3$.

Looking in detail at the ^{1}H-NMR chemical shift at +0.5 ppm, it is confirmed that it corresponds to $[Me-B(C_6F_5)_3]^-$, in agreement with past studies [13,25,26]. The peak at 2.6 ppm corresponded to the cationic tantalum complex $[TaMe_4]^+$, upfield with respect to the signal at 0.9 ppm assigned to the resonance for the methyl proton of $TaMe_5$.
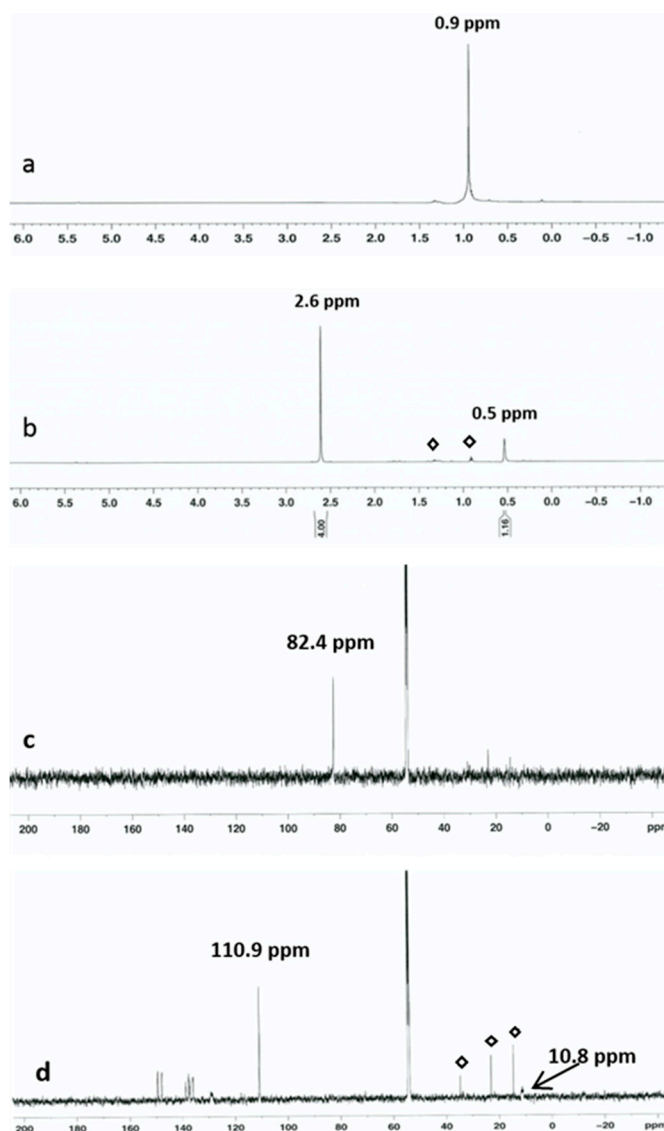
Figure 1. (**a**) ^{1}H-NMR spectra of TaMe$_5$; (**b**) ^{1}H-NMR spectra of [TaMe$_4$]$^+$[MeB(C$_6$F$_5$)$_3$]$^-$; (**c**) ^{13}C-NMR spectrum of TaMe$_5$; (**d**) ^{13}C-NMR spectrum of [TaMe$_4$]$^+$[MeB(C$_6$F$_5$)$_3$]$^-$, (at $-40\,°$C, peak marked by ($\Diamond$) is due to the slight amounts of pentane vapor which was used as a coolant during the low temperature reaction in the glovebox).

Switching to ^{13}C-NMR, the spectrum also clearly showed that the peak corresponding to TaMe$_5$ at 82.4 ppm (Figure 1c) was completely replaced by two peaks at 110.9 ppm [TaMe$_4$]$^+$ and 10.8 ppm (Figure 1d) corresponding to the [Me-B(C$_6$F$_5$)$_3$]$^-$ anion which is in good agreement with the literature value reported for the [Me-B(C$_6$F$_5$)$_3$]$^-$ anion [26]. We also found in the ^{1}H-^{13}C correlation spectra that the peak at 0.5 ppm in ^{1}H-NMR correlates with the peak at 10.8 ppm in ^{13}C-NMR and the peak at 2.6 ppm in ^{1}H-NMR correlated with the peak at 110.9 ppm in ^{13}C-NMR (Supplementary Materials Figure S1). In separate experiments we synthesised ^{13}C labelled Ta(^{13}CH$_3$)$_5$ and upon treatment with B(C$_6$F$_5$)$_3$ in dichloromethane solution, we identified incorporation of the labelled methyl in [(^{13}CH$_3$)B(C$_6$F$_5$)$_3$]$^-$ anion in the final product. The above experiment clearly indicates that in [MeB(C$_6$F$_5$)$_3$]$^-$, 'Me' came from TaMe$_5$. These spectroscopic data strongly support the formation of cationic complex **2** and is in favour of path I. The ionic product generated by the reaction was fairly stable at temperatures below $-40\,°$C and in the absence of light. However, upon warming a dichloromethane solution of **2** from $-40\,°$C to $0\,°$C, a very fast decomposition of the cationic complex was observed with the release of gaseous methane.

Density Functional Theory (DFT) calculations (M06/Def2TZVPP(smd)//PBE0-d3bj/SVP [28], at temperature = 298.15 °C and pressure = 1354 atm [29–31] to remove the overestimation of the entropy [32–34]) were envisaged to unravel the mechanistic insights of the first demethylation of $TaMe_5$. The energy barrier to overcome was found to be 6.8 kcal/mol (Figure 2a), releasing 15.4 kcal/mol (see Table 1), thus the favourable kinetic and thermodynamic character of the reaction, respectively, confirmed the observed experimental facile demethylation. Furthermore, the energy barrier for this reaction was even 2.3 kcal/mol lower with respect to the recent homologous process studied for WMe_6, together with a release of 1.6 kcal/mol more energy as well, confirms the experimental more facile demethylation by Ta than W based complexes [13]. It is worth pointing out that for $TaMe_5$, the radical demethylation was not in competition with the anion demethylation, because $TaMe_4 \cdot$radical was located 44.1 kcal/mol over $TaMe_5$, and thus enormously disfavoured by 25.3 kcal/mol with respect to the homologous WMe_5. Surprisingly, $TaMe_5$ is able to allocate easily a sixth anion like chloride, with an energy stabilization of 5.8 kcal/mol, compared with the destabilisation by 3.6 kcal/mol for WMe_6, due to steric hindrance in the metal centre of the WMe_6Cl^- anion.


(**a**)　　　　　　　　　　　　　　　　　　　　　　　　　（**b**)
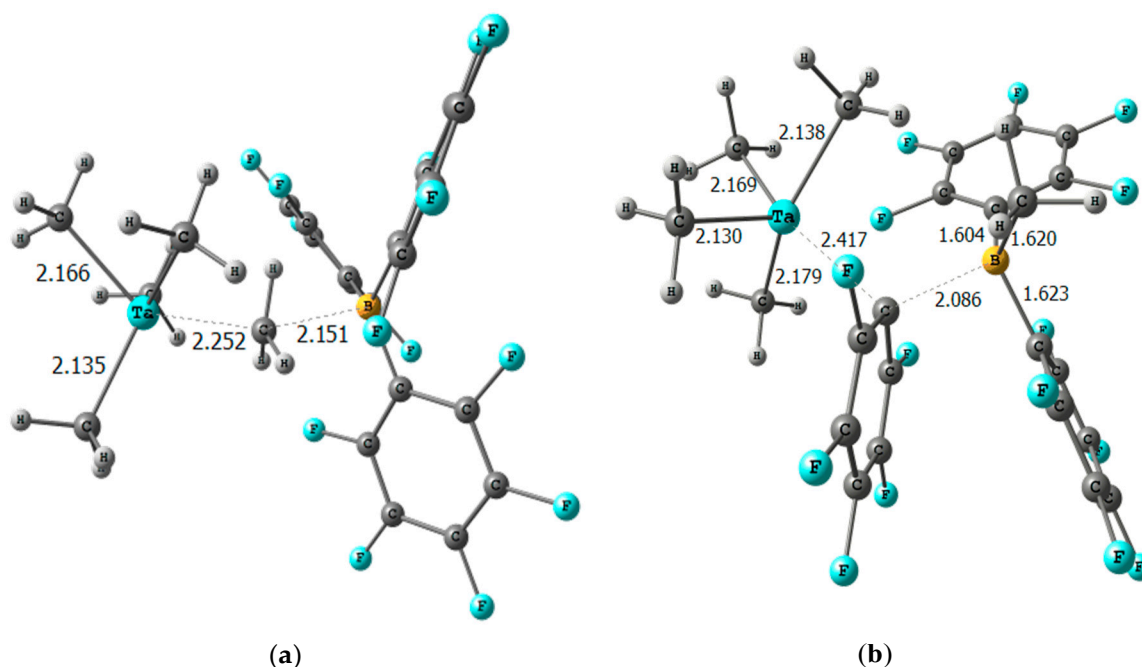
Figure 2. Transition states for (**a**) the demethylation of $TaMe_5$ by $B(C_6F_5)_3$ and (**b**) $(C_6F_5)^-$ transfer from $B(Me)(C_6F_5)_3{}^-$ to $TaMe_4{}^+$, main distances are shown in Å.

Table 1. Gibbs energy values (in kcal/mol) for (**a**) the energy barrier of the transition state of the anion demethylation in the reaction $[MMe_x \rightarrow MMe_{(x-1)}{}^+ + Me^-$, (**b**) the relative stability of the next demethylated anion $MMe_{(x-1)}{}^+$, (**c**) the intermediate $MMe_{(x-1)} \cdot$ after the loose of a radical methyl and (**d**) the addition of a chloride anion that leads to MMe_xCl^- (M = Ta or W).

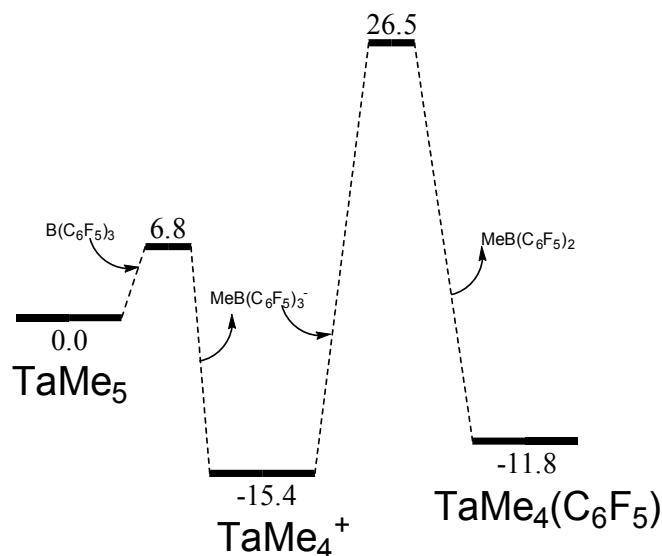| Catalyst	(a)	(b)	(c)	(d)
$TaMe_5$	6.8	−15.4	44.1	−5.8
WMe_6	9.1	−13.8	18.8	3.6

Here, steric effects play a key role, and the more sterically crowded W centre provides less space for a seventh coordination around the metal centre, and at the same time facilitates the loose of a methyl ligand. To evaluate the steric hindrance around the metal, SambVca steric maps were used [35–37]. The %Vbur was 74.5% for $TaMe_5$ and 79.9% for WMe_6. It is worth pointing out that the quadrants for the latter hexamethylated complex were not equally occupied (see Figure 3), ranging from 75.8% to

84.0%, with 76.1% and 83.8% in between. Anyway, none of the quadrants was less occupied than the equally distributed TaMe$_5$ ones [38].
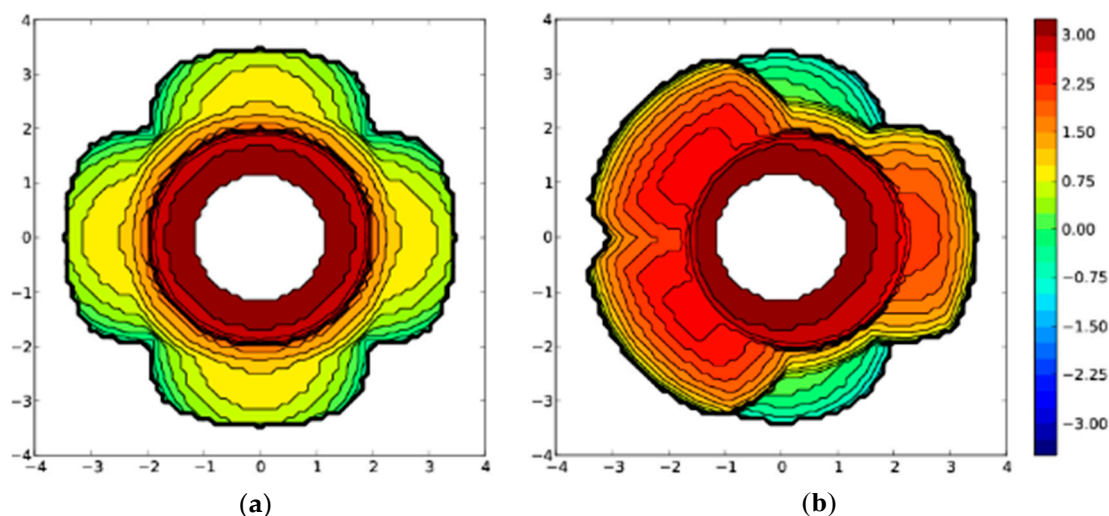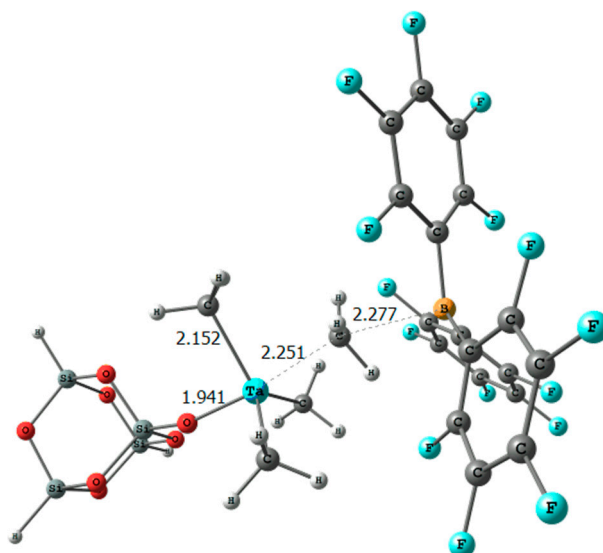

Figure 3. Topographic steric maps (xy plane) of the metal centres of (**a**) TaMe$_5$ and (**b**) WMe$_6$. The corresponding metal is at the origin and one methyl of TaMe$_5$ is on the z axis. The isocontour curves of the steric maps are given in Å.

On the other hand, the substitution of a methyl ligand by a perfluorobenzene ligand from B(C$_6$F$_5$)$_3$, i.e., path II in Scheme 2, requires to overcome an energy barrier that is placed at 26.8 kcal/mol with respect to TaMe$_5$. However, from [MeB(C$_6$F$_5$)$_3$]$^-$ an unaffordable energy barrier of 41.9 kcal/mol must be overcome (see Figure 2b). The overall reaction pathway following paths I and II in Scheme 2 is displayed in Figure 4. Consequently, the huge kinetic cost of path II confirms that once TaMe$_5$ is demethylated, the next cation intermediate TaMe$_4$$^+$ cannot recover an anionic ligand, i.e., (C$_6$F$_5$)$^-$, from [MeB(C$_6$F$_5$)$_3$]$^-$, even though the next intermediate TaMe$_4$(C$_6$F$_5$) is 11.8 kcal/mol lower in energy than TaMe$_5$.

Figure 4. Reaction pathway for the demethylation of TaMe$_5$ with B(C$_6$F$_5$)$_3$ and next C$_6$F$_5$ anionic transfer (Gibbs energies in kcal/mol referred to TaMe$_5$).

Switching to the grafted system ($\equiv$Si-O-)TaMe$_4$, the demethylation process requires to overcome an energy barrier of 9.8 kcal/mol (see Figure 5 for the corresponding transition state) and the next intermediate is 5.1 kcal/mol lower in energy than the initial supported catalyst. Here the difference with tungsten is significant, because apart from facing a more facile barrier by 4.8 kcal/mol, the relative stability of the next intermediate excludes the reversibility of the demethylation observed only for W. Overall, kinetically and thermodynamically, the demethylation process is more prone with Ta based systems. Consequently, we then prepared the surface complex of TaMe$_5$ after grafting on to the dehydroxylated Aerosil SiO$_{2(700)}$ (Figure S2). Synthesized ($\equiv$Si-O-)TaMe$_4$ was treated with B(C$_6$F$_5$)$_3$ in order to get a cationic tantalum-methyl complex anchored on the surface of silica, [($\equiv$Si-O-)TaMe$_3$]$^+$. However, after several attempts (varying reaction temperature, reaction time and solvents) we were unable to identify any well-defined heterogeneous cationic tantalum methyl complex [13], except for a mixture of decomposed tantalum methyl complex with a ^{13}C-NMR signal corresponding to the formation of the anionic [MeB(C$_6$F$_5$)$_3$]$^-$ (see Figures S3 and S4), indicating a probable formation of surface cationic species. The surface cationic complex decomposed much more rapidly, and it was difficult to characterize it by solid state NMR. This may be due to the unstable nature of 8 e$^-$ [($\equiv$Si-O-)TaMe$_3$]$^+$ complex.

Figure 5. Transition state for the demethylation by B(C$_6$F$_5$)$_3$ of ($\equiv$Si-O-)TaMe$_4$, main distances are shown in Å.

3. Conclusions

In summary, the cationic homoleptic tantalum (V)-methyl complex has been synthesized via a straightforward strategy to address the will to get a more electrophilic metal centre, generating the first tantalum-based species with such a property. The delicate equilibrium between stability and degradation was enforced to work at low temperature, and the high oxidation state cationic tantalum complex **2** was defined by liquid ^{1}H-NMR, ^{13}C-NMR and ^{1}H-^{13}C correlation spectroscopy; together with DFT calculations. Ongoing experimental studies are being undertaken in order to understand the null activity in alkane metathesis of the grafted tantalum system and will be disclosed in due time.

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Conflicts of Interest: The authors declare no competing financial interests.

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27. Preparation of [TaMe$_4$$^+$ B(C$_6$F$_5$)$_3$Me$^-$](**2**): A cold solution (-40 °C) of B(C$_6$F$_5$)$_3$ (125 mg, 0.25 mmol) in dichloromethane was added drop wise to the cold (-40 °C) solution of tantalumpentamethyl (50 mg, 0.2 mmol) in dichloromethane. The mixture was stirred for another 15 minutes. Colour of the solution intensified to dark yellowish which indicated the formation of the ionic complex. ^{1}H-NMR(600 MHz) δ (ppm) 0.5(s, 3H, BC<u>H</u>$_3$), 2.6(s, 12H, TaC<u>H</u>$_3$). ^{13}C-NMR(150 MHz) δ (ppm) 10.8(s, 1C, B<u>C</u>H$_3$), 110.9 (s, 4C, Ta<u>C</u>H$_3$). (Caution! This 8e- compound is highly unstable and decomposes into black tantalum power while drying.).

28. All the DFT calculations were performed with the Gaussian09, using the PBE0 functional, corrected by the D3 Grimme pairwise scheme, using the SVP basis set except for the metals the standard SDD. Single-point energy calculations in solution (SMD) were performed with the M06 functional and the Def2TZVPP basis set for main group atoms and again the same SDD pseudopotential for the metals.

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