Supplementary Information's

Synthesis and Characterization of Homoleptic Cationic Tungsten(VI)-Methyl Complex: Application in Olefin Metathesis Reaction

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General experimental procedure:

All experiments were performed using standard Schlenk and glovebox techniques under an inert nitrogen atmosphere. Syntheses and treatments of the surface species were completed using high-vacuum lines ($<10^{-5}$ mbar) and glovebox. All solvents were dried, degassed and freshly distilled prior use according to classical methods (over CaH_2 for dichloromethane, over Na/benzophenone for pentane). 1-octene was dried before use by passing it through a mixture of freshly regenerated molecular sieves (3 Å). Gas-phase analysis of alkanes was performed using an Agilent 6850 gas chromatography column with a split injector coupled with an FID (flame ionization detector). An HP-PLOT Al_2O_3 KCl 30 m × 0.53 mm, 20.00 mm capillary column coated with a stationary phase of aluminum oxide deactivated with KCl was used with helium as the carrier gas at 32.1 kPa. Each analysis was executed under the same conditions: a flow rate of 1.5 ml/min and an isotherm at 80 °C.

Nuclear Magnetic Resonance Spectroscopy

One-dimensional ^1H MAS and ^{13}C CP/MAS solid-state NMR spectra were recorded on Bruker AVANCE III spectrometers operating at 400 MHz or 600 MHz reso-nance frequencies for ^1H. 400 MHz experiments employed a conventional double resonance 4mm CP/MAS probe while experiments at 600 MHz utilized a 3.2 mm HCN triple resonance probe. In all cases, the samples were packed into rotors under inert atmosphere inside glove boxes. Dry nitrogen gas was utilized for sample spinning to prevent degradation of the samples. NMR chemical shifts are reported with respect to the external references, TMS, and adamantane. ^{13}C CP/MAS NMR experiments used the following sequence–90 0 pulses on the proton (pulse length 2.4 s), then a cross-polarization step with a contact time of typically 2 ms, and finally acquisition of the ^{13}C signal under high-power proton decoupling. The delay between the scans was set to 5 s to allow the complete relaxation of the ^{1}H nuclei and the number of scans ranged between 5000 and 10000 for ^{13}C and was 32 for ^{1}H. An exponential apodization function corresponding to a line broadening of 80 Hz was applied to the Fourier transformations.

$SiO_{2\text{-}700}$ were prepared from Aerosil silica from degussa (specific area of 200 $m^{2}g^{-1}$), and were partly dehydroxylated at 700 ^{o}C under high vacuum (< 10^{-5} mbar) for 24 h to give a white solid having a specific surface area of 190 $m^{2}g^{-1}$ and containing 0.3 mmol of Si-OH gm^{-1}.

^{1}H 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).

Preparation of hexamethyltungsten, WMe_6: The molecular precursor WMe_6 was prepared from WCl_6 and $(CH_3)_2Zn$. To a solution of WCl_6 (1.80g, 4.5 mmol) in dichloromethane (25 mL), $(CH_3)_2Zn$ (13.6 mmol, 1.0 M in heptane) was added at −80 °C, and after the addition, the reaction mixture was stirred for 2h. After that 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}H NMR (CD_2Cl_2, 600 MHz): δ (ppm) 1.65 (s, 18H, $WC\underline{H}_3$). ^{13}C NMR (CD_2Cl_2, 150 MHz): δ (ppm) 82 (s, 6C, $J^{183}{}_{W-}{}^{13}{}_{C}$ = 47 Hz, $W\underline{C}H_3$). HSQC confirms the correlation between the ^{1}H and ^{13}C NMR signals.

Preparation of ^{13}C label hexamethyltungsten, W(Me*)$_6$: The labelled ^{13}C molecular precursor of WMe$_6$ was prepared from WCl$_6$ using labelled ^{13}C, (C^{13}H$_3$)$_2$Zn. To a solution of WCl$_6$ (1.80g, 4.5 mmol) in dichloromethane (25 mL) label (C^{13}H$_3$)$_2$Zn (13.6 mmol, in pentane) was added at −80 °C, and after the addition, the reaction mixture was stirred for 2h. After that 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 label WMe$_6$ was obtained (0.16 g, 12%).

Preparation of ^{13}C label dimethylzinc, Zn(Me*)$_2$: A suspension of ^{13}CH$_3$Li(2 mmol) and ZnCl$_2$ (1 mmol)), in pentane are allowed to stirred for 3 days at room temperature. After the completion of the reaction a simple filtration by a double Schleck techniques provides ^{13}C-enriched (^{13}CH$_3$)$_2$Zn.

Preparation of [WMe$_5^+$ B(C$_6$F$_5$)$_3$Me$^-$]: A cold solution (-20 ^{o}C) of B(C$_6$F$_5$)$_3$ (100 mg, 0.2 mmol) in dichloromethane was added drop wise to the cold (-20 ^{o}C) solution of hexamethyltungsten (55 mg, 0.2 mmol) in dichloromethane. The mixture was stirred for 15 minutes at -20 ^{o}C. Color of the solution intensified to reddish and indicating the formation of an ionic complex. NMR study shows that this compound is 98 % pure. At temperature below -60 ^{o}C this cationic complex is precipitated out from the solution, however this 10e$^-$ compound is highly unstable and decomposes into black tungsten powder while drying at this temperature. In absence of light half-life of the cationic complex is around 3.5 hr at -20 ^{o}C (the half-life study was performed using liquid state NMR) and the decomposition is faster in presence of light.

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

^{1}H-NMR(600 MHz) δ (ppm) 0.5(s, 3H, BC$\underline{H}_3$), 2.7(s, 15H, WC$\underline{H}_3$). ^{13}C NMR(150 MHz) δ (ppm) 10.8(s, 1C, B$\underline{C}$H$_3$), 103.2 ((s, 5C, $J^{183}{}_{W-}{}^{13}{}_{C}$ = 54 Hz, W$\underline{C}$H$_3$)

Grafting of [WMe_5^+ $B(C_6F_5)_3Me^-$] on Silica$_{700}$: A solution of [WMe_5^+ $B(C_6F_5)_3Me^-$] (85 mg, 1.2 equivalents with respect to WMe_6 and with respect to the amount of surface-accessible silanols) in dichloromethane (15 mL) was mixed with silica ($SiO_{2\text{-}700}$; 1.0 g) at -50 ^{o}C for one hour, allowed to warm to -30^{o}C, and then stirred for an additional 2 h. At the end of the reaction, the resulting brown solid was washed with pentane (3x20 mL) and dried under dynamic vacuum (1 mPa, 1 h).

^{1}H 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$_3$), 55.0(W-CH$_3$).[5]

Preparation of WMe_6 on $SiO_{2\text{-}700}$: A solution of 1 in pentane (150 mg, 1.2 equiv with respect to the amount of surface-accessible silanols) was reacted with 1.8 g of Aerosil $SiO_{2\text{-}700}$ at −50 °C for 1 h, was warmed to −30 °C, and was stirred for an additional 2 h. At the end of the reaction, the resulting yellow solid was washed with pentane (3 × 20 mL) and dried under dynamic vacuum (<10−5 Torr, 1 h). IR data (cm^{-1}): 3742, 3014, 2981, 2946, 2878, 1410. ^{1}H solid-state NMR (400 MHz): δ (ppm) 2.0 (W−CH$_3$). ^{13}C CP/MAS solid-state NMR (100 MHz): δ (ppm) 82.0 (W−CH$_3$). Elemental analysis found: W, 3.50 wt% (purity 98%); C, 1.12 wt%. The C/W ratio obtained was 4.9 ± 0.1 (5 was expected).

Preparation of [$SiO_2\text{-}WMe_4^+$ $B(C_6F_5)_3Me^-$]: A solution of $B(C_6F_5)_3$ (100 mg, 0.2 mmol) in dichloromethane was added drop wise to the yellow solid of $SiO_2\text{-}WMe_5$ (1 gm, W loading 3.5) in dichloromethane. The mixture was stirred another 4h at rt. The resulting solid was washed with pentane (3x20 mL) and dried under dynamic vacuum (1 mPa, 1 h) to get a mixture of desired cationic product **2** (≈30 %) and unreacted starting material **3** along with decomposed product (≈70 %).

^{1}H solid-state NMR(400 MHz): δ (ppm) 2.0 (b, W-Me). ^{13}C CP/MAS solid-state NMR(100 MHz): δ (ppm) 149.0(C, $B(C_6F_5)_3$), 102.0(W-Me in WMe_4^+), 83.0 (W-Me in WMe_5), 55.0(W-Me decompose).

Alkene metathesis: A mixture of catalytic species and dry alkene were mixed inside the glovebox. The ampoules were sealed under vacuum, keep it 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 mLmin^{-1} (N_2); split ratio: 50/1; inlet temperature: 250 ^{o}C, detector temperature: 250 ^{o}C; temperature program: 40 ^{o}C (3 min), 40-250 ^{o}C (12 ^{o}C min^{-1}), 250 ^{o}C (3 min), 250-300 ^{o}C (10 ^{o}C min^{-1}), 300^{o}C (3 min); n-decane retention time: ^{t}R=9.6.

ROMP of CycloOctene: A mixture of catalytic species (0.1 mmol) and dry cyclooctene (20 mmol, 2.2 gm) were mixed inside the glovebox (S/C = 200/1). The ampoules were keep 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 adding DCM. The polymer was soluble in DCM and after purification 1.98 mg polymer (TON = 180) was obtained. During the analysis of the polymer Mn =172 KDa and PDI = 2.68 was obtained by the gel permeation chromatography.

NMR Spectroscopic Data:

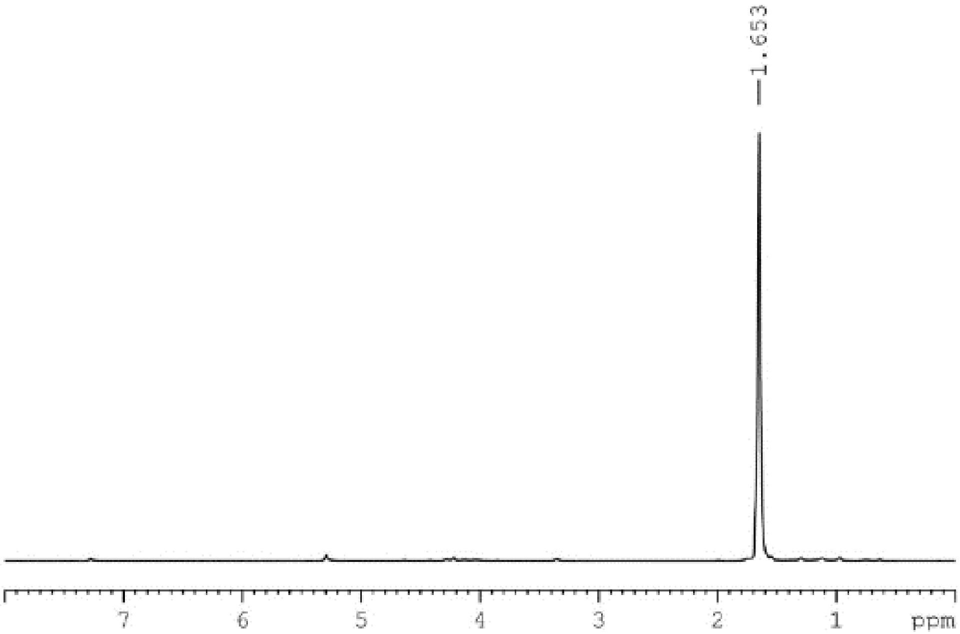


Figure S1: ^{1}H NMR spectrum of WMe_6 in CD_2Cl_2.

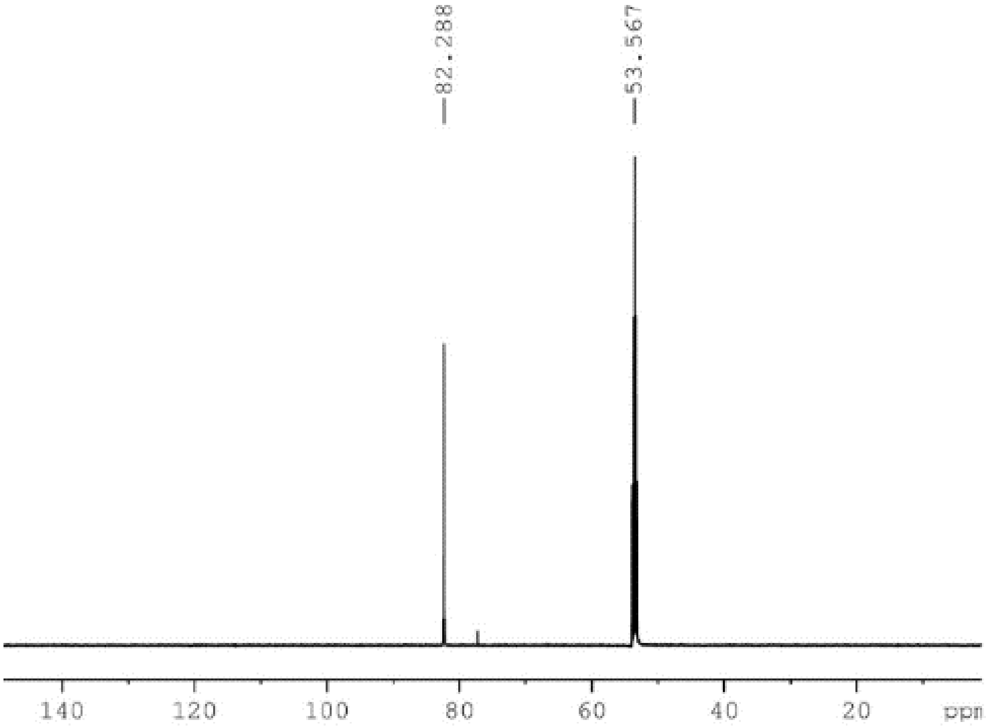


Figure S2: Solution ^{13}C NMR spectrum of WMe_6 in CD_2Cl_2.

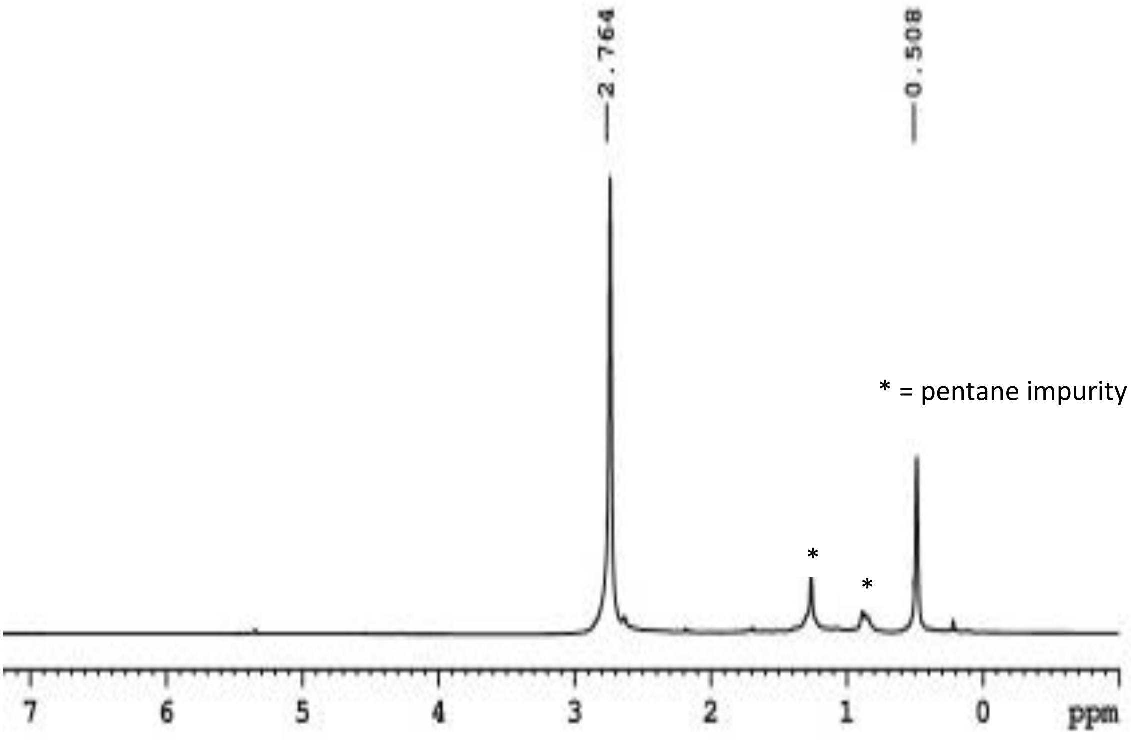


Figure S3: H^1 NMR spectrum of $[WMe_5{}^+B(C_6F_5)_3Me^-]$ in CD_2Cl_2.

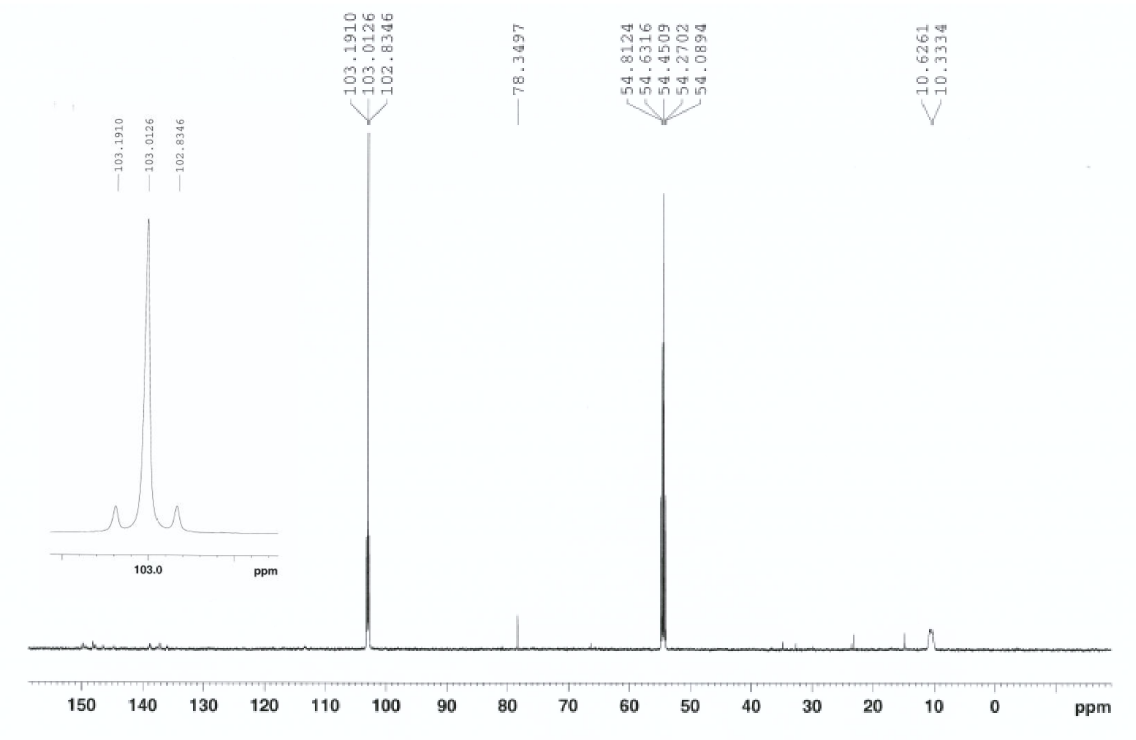


Figure S4: ^{13}C NMR spectrum of $[WMe_5{}^+B(C_6F_5)_3Me^-]$ in CD_2Cl_2.

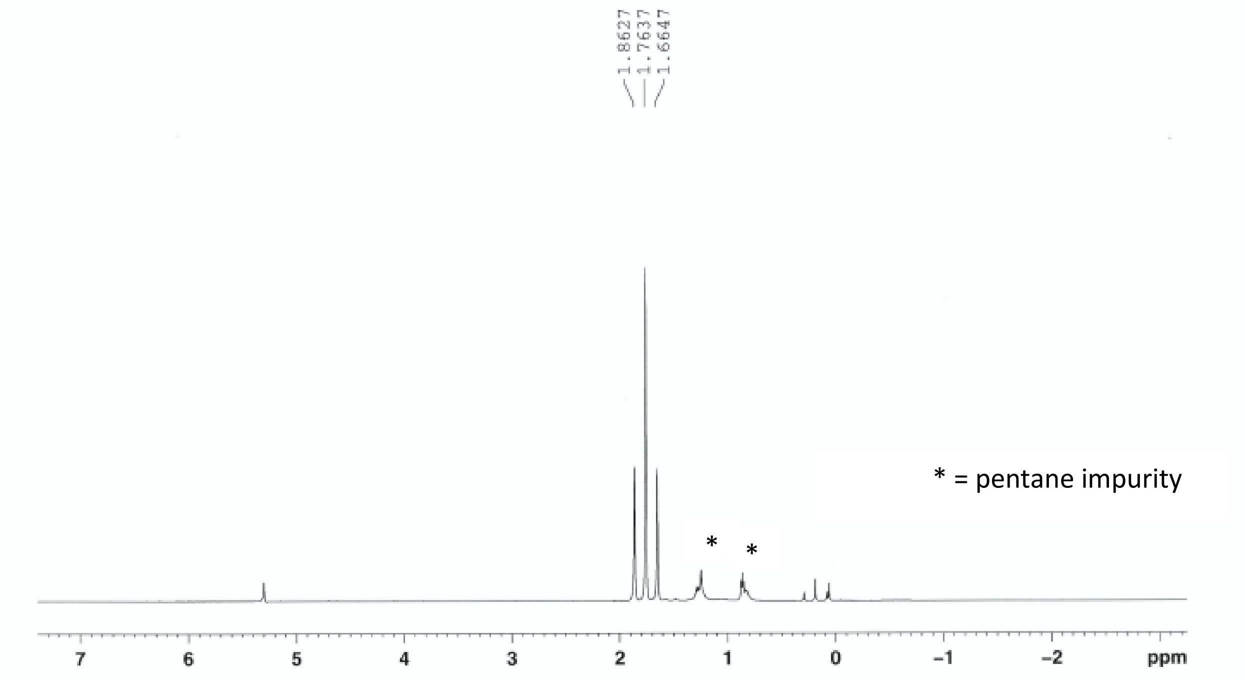


Figure S5: ^{1}H NMR spectrum of partially ^{13}C labeled WMe_6 in CD_2Cl_2 (singlet peak at 1.76 ppm is correspond for ^{12}C coupling with H and a doublet at 1.86-1.66 ppm for ^{13}C coupling with H).

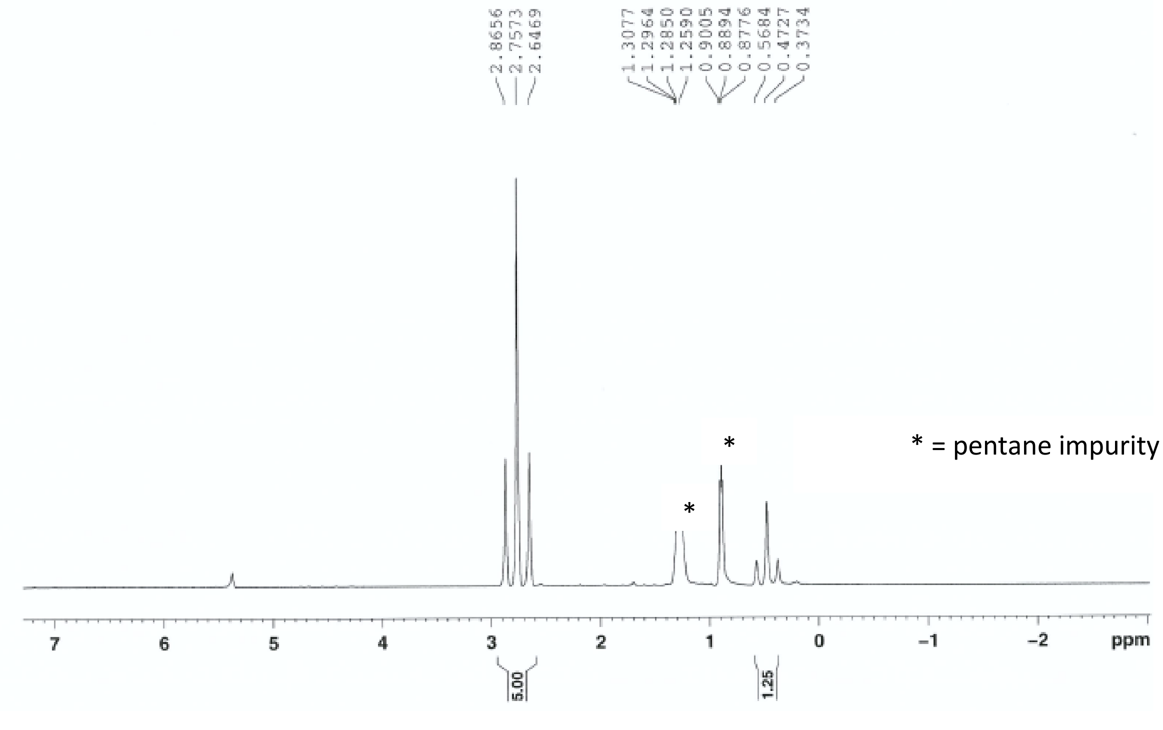


Figure S6: ^{1}H NMR spectrum of partially ^{13}C labeled $[WMe_5{}^{+}B(C_6F_5)_3Me^{-}]$ in CD_2Cl_2 (singlet peak at 2.76 ppm and 0.47 ppm is correspond for ^{12}C coupling with H and a doublet at 2.86-2.65 ppm and 0.56- 0.37 ppm for ^{13}C coupling with H)

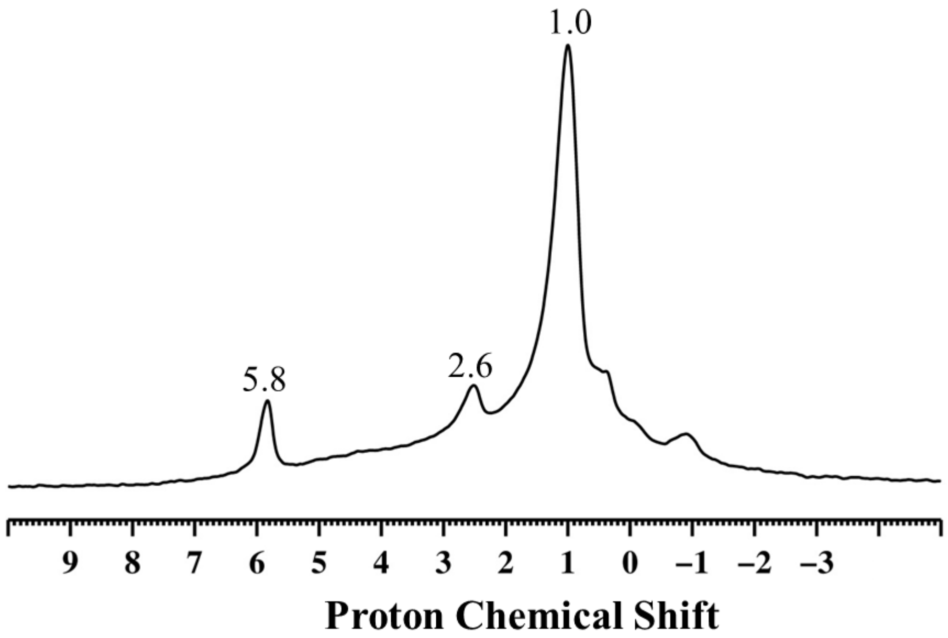


Figure S7: Solid state ^{1}H NMR spectra of [≡SiO-WMe$_4^+$ (C$_6$F$_5$)$_3$BMe$^-$].

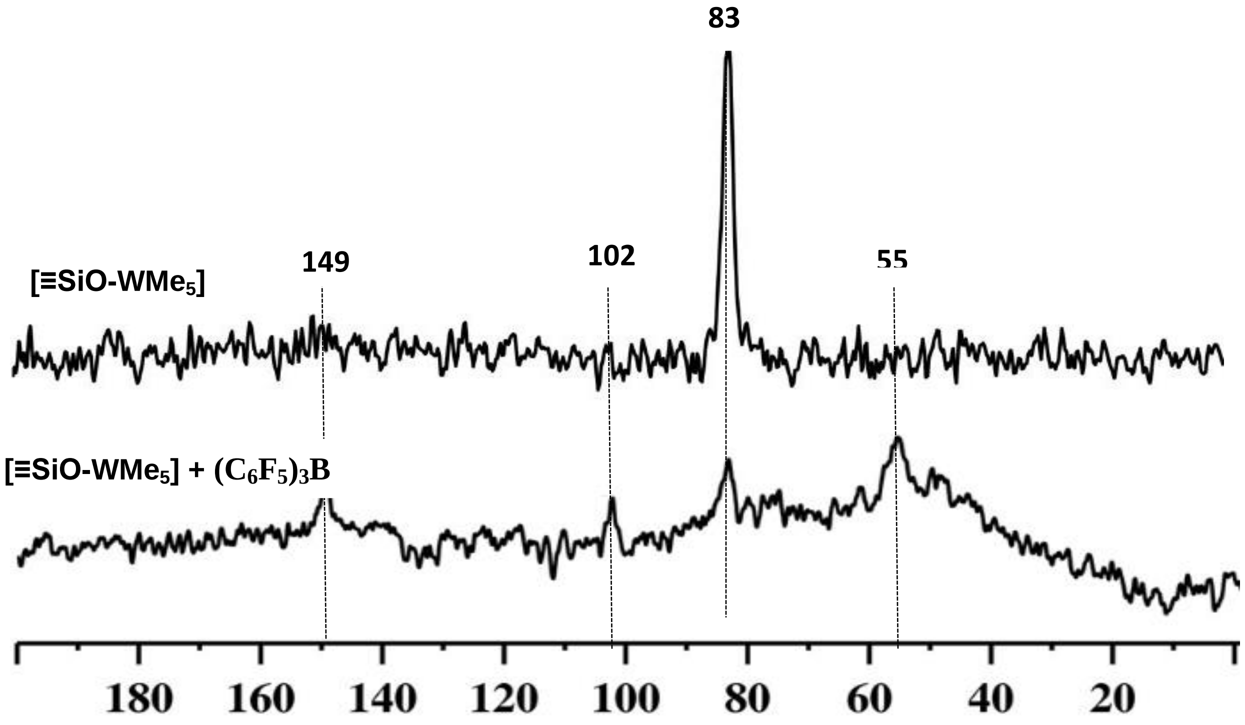


Figure S8: a) ^{13}C CP/MAS NMR spectra of ^{13}C labeled (50% ^{13}C) [≡SiO-WMe$_5$]. b) ^{13}C CP/MAS NMR spectra of [≡SiO-WMe$_4^+$ (C$_6$F$_5$)$_3$BMe$^-$]. Both spectra were acquired at 400 MHz with a 10 kHz MAS frequency, 1000 scans, a 4 s, repetition delay, and a 2 ms contact time and ambient sample temperature. An exponential line broadening of 80 Hz was applied prior to Fourier transform**.**

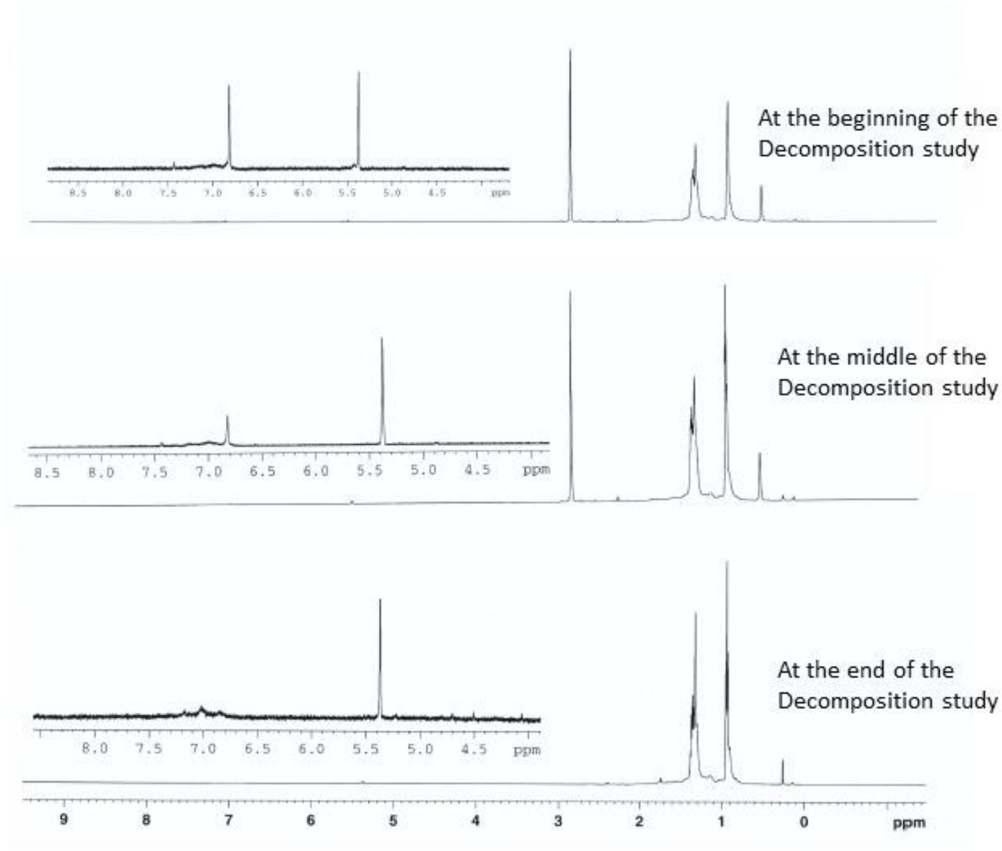


Figure S9: ^{1}H-NMR spectra of the intermediates produce during the decomposition of the [WMe_5^+ $B(C_6F_5)_3Me^-$] in CD_2Cl_2 at -20 °C.

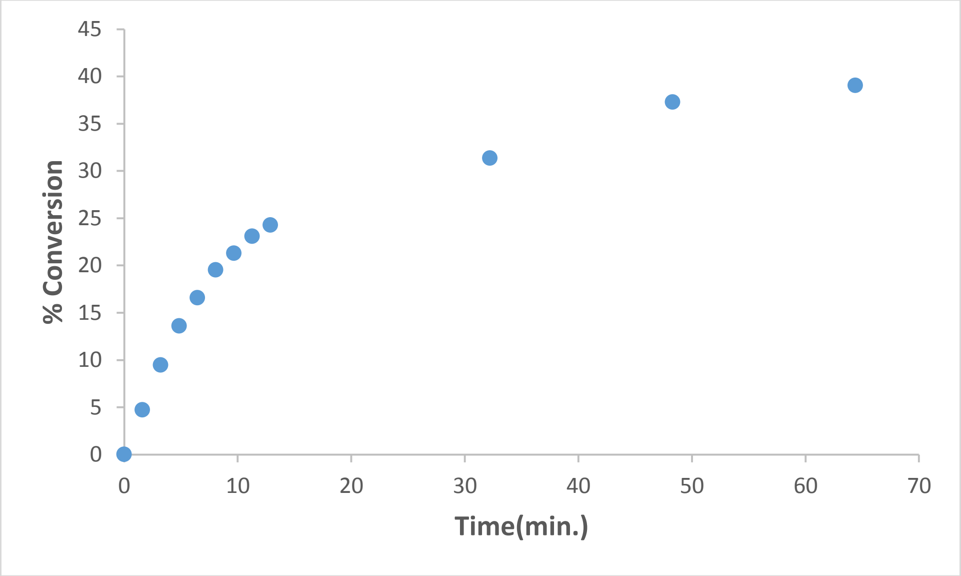


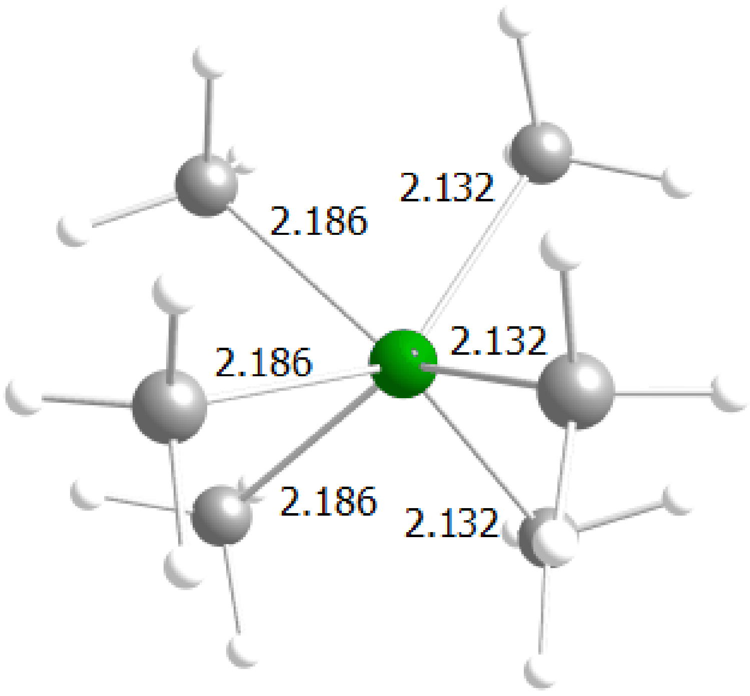
Figure S10: Kinetic plot for the cyclooctene conversion with time

Computational details

All the DFT static calculations were performed at the GGA level with the Gaussian09 set of programs,[1] using the PBE0 functional,[2] corrected by the D3 Grimme pairwise scheme.[3] The electronic configuration of the molecular systems was described with the standard split-valence basis set with a polarization function of Ahlrichs and co-workers for H, B, C, Si, O, and F (SVP keyword in Gaussian).[4] For W we used the small-core, quasi-relativistic Stuttgart/Dresden effective core potential, with an associated valence basis set contracted (standard SDD keywords in gaussian09).[5] The geometry optimizations were performed without symmetry constraints, and the characterization of the located stationary points was performed by analytical frequency calculations. The complete reaction pathways for all the mechanisms discussed in this study were verified using IRC analysis for all transition states. Structures at the last IRC points were optimized to positively identify the reactants and products to which each transition state is connected. We checked the role of low-lying vibrational harmonic frequencies on thermosstatistical entropy calculations.[6] Zero point energies and thermal corrections were calculated at the PBE0 level. Single-point energy calculations in solution were performed with the Def2TZVPP basis set[7] for main group atoms and again the same SDD pseudopotential for W. Solvent effects were included with the polarizable continuous solvation model SMD using dichloromethane as solvent.[8] Since entropic contribution calculated within the ideal gas approximation at P = 1 atm is likely exaggerating the expected values for the dissociative steps in the condensed phase,[9,10] all the thermochemical analysis was performed at P = 1354 atm, as suggested by Martin et al,[11] and T = 253.15 K.

Coordinates: Coordinate data sets and absolute energy (in a.u.), 3D structure for DFT optimized complexes with selected distances (in Å).

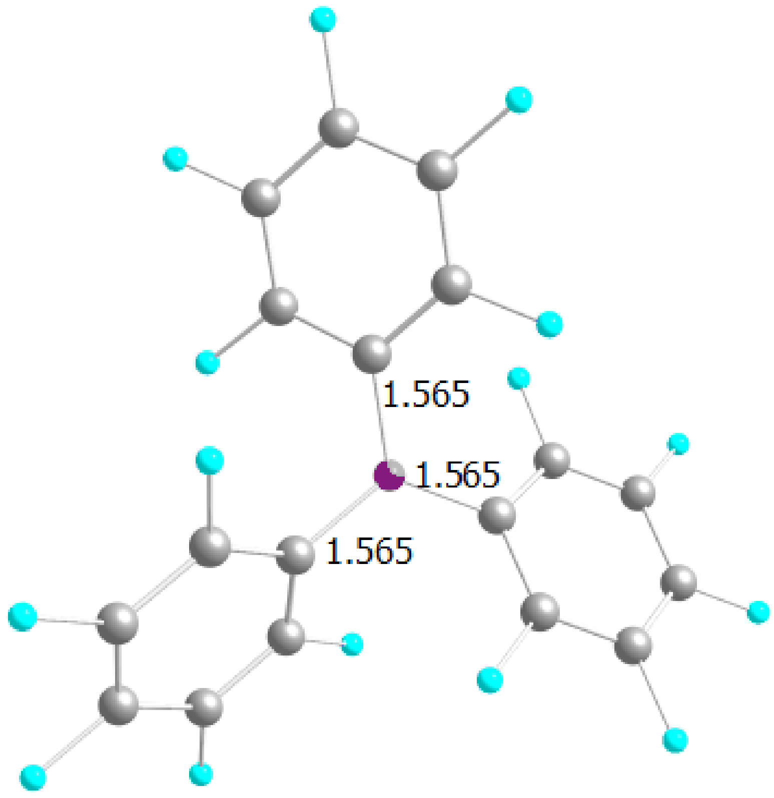
WMe$_6$



Zero-point correction= 0.216727 (Hartree/Particle)
Thermal correction to Energy= 0.230479
Thermal correction to Enthalpy= 0.231424
Thermal correction to Gibbs Free Energy= 0.178235
Sum of electronic and zero-point Energies= -305.782389
Sum of electronic and thermal Energies= -305.768636
Sum of electronic and thermal Enthalpies= -305.767692
Sum of electronic and thermal Free Energies= -305.820881

W	-0.084185	0.000081	0.000135
C	1.448183	-0.319355	-1.526044
C	1.450571	-1.161776	1.036765
C	1.452049	1.478296	0.484984
C	-1.218488	-0.287458	-1.782594
C	-1.215878	-1.400535	1.142348
C	-1.214067	1.690165	0.643522
H	2.491890	-0.209929	-1.207520
H	1.262835	0.364054	-2.372432
H	1.300525	-1.352423	-1.890234
H	2.493682	-0.940795	0.780254
H	1.264743	-2.236568	0.869195
H	1.305424	-0.959915	2.113720
H	2.494974	1.145696	0.418575
H	1.269070	1.869218	1.500598
H	1.304935	2.310960	-0.226825
H	-2.271345	-0.304663	-1.440711
H	-1.020942	-1.221405	-2.329609
H	-1.106799	0.558073	-2.481399
H	-2.269036	-1.095079	0.989866
H	-1.015137	-1.409373	2.224058
H	-1.105804	-2.427829	0.757240
H	-2.267782	1.404483	0.459824
H	-1.015617	2.629870	0.106749
H	-1.100161	1.873591	1.724750

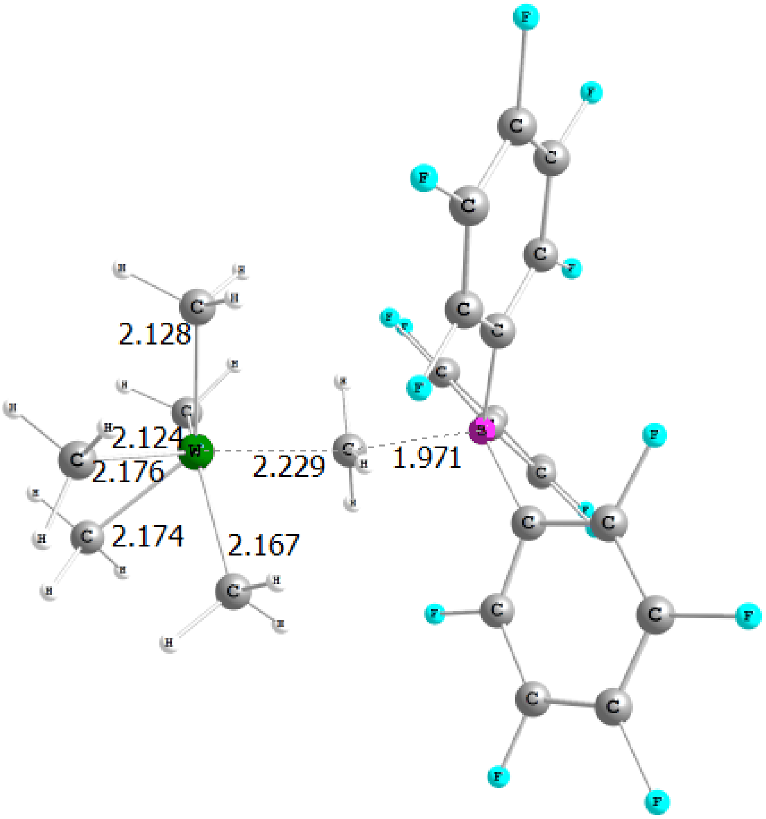
$B(C_6F_5)_3$



Zero-point correction= 0.157559 (Hartree/Particle)
Thermal correction to Energy= 0.186308
Thermal correction to Enthalpy= 0.187252
Thermal correction to Gibbs Free Energy= 0.096037
Sum of electronic and zero-point Energies= -2204.303943
Sum of electronic and thermal Energies= -2204.275194
Sum of electronic and thermal Enthalpies= -2204.274250
Sum of electronic and thermal Free Energies= -2204.365465

B	0.000225	-0.000279	0.000029
C	-0.455548	1.497016	-0.000038
C	0.237268	2.481097	0.716207
C	-1.579219	1.927990	-0.716311
C	-0.158787	3.813692	0.735504
C	-1.993016	3.255186	-0.735650
C	-1.278406	4.199513	-0.000072
C	-1.068788	-1.143406	0.000179
C	-0.880199	-2.332620	-0.715131
C	-2.267914	-1.034449	0.715517
C	-1.823053	-3.354237	-0.734314
C	-3.224347	-2.043365	0.734914
C	-2.998626	-3.206514	0.000326
C	1.524772	-0.354199	-0.000097
C	2.459987	0.404357	-0.715281
C	2.030566	-1.447038	0.715002
C	3.816299	0.099271	-0.734633
C	3.382679	-1.770256	0.734196
C	4.276730	-0.992587	-0.000244
F	-2.522775	0.049303	1.434678
F	-4.335535	-1.912384	1.434771
F	-3.896877	-4.166807	0.000384
F	-1.618324	-4.454270	-1.434106
F	0.218044	-2.514613	-1.434424
F	-2.284945	1.067710	-1.436422
F	-3.047498	3.627648	-1.436397
F	-1.661424	5.457419	-0.000080
F	0.509210	4.710626	1.436215
F	1.302658	2.160137	1.436342
F	2.067984	1.446443	-1.434331
F	4.666198	0.827175	-1.434291
F	5.557630	-1.289734	-0.000310
F	3.825384	-2.798011	1.433785
F	1.219879	-2.210120	1.434119

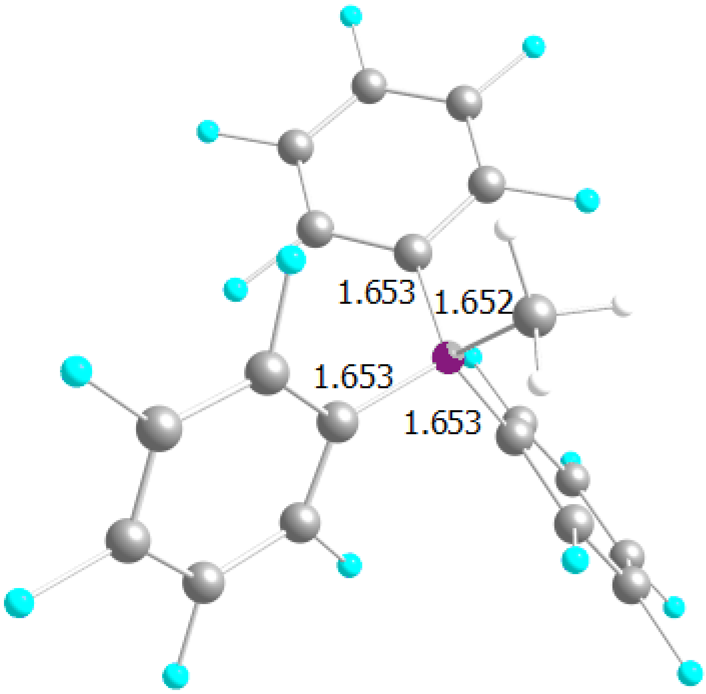
$WMe_5—CH_3^-—B(C_6F_5)_3$



Zero-point correction= 0.376218 (Hartree/Particle)
Thermal correction to Energy= 0.419313
Thermal correction to Enthalpy= 0.420258
Thermal correction to Gibbs Free Energy= 0.298044
Sum of electronic and zero-point Energies= -2510.088874
Sum of electronic and thermal Energies= -2510.045778
Sum of electronic and thermal Enthalpies= -2510.044834
Sum of electronic and thermal Free Energies= -2510.167048

B	-1.002339	0.002956	0.202208
C	-0.762029	-0.639433	1.669129
C	0.200904	-0.129618	2.542708
C	-1.463346	-1.744326	2.156163
C	0.519924	-0.696060	3.769627
C	-1.191170	-2.336596	3.389888
C	-0.188947	-1.814201	4.200577
C	-1.766649	-0.940966	-0.863662
C	-2.926044	-0.558244	-1.542363
C	-1.298795	-2.219121	-1.181678
C	-3.552777	-1.363718	-2.494428
C	-1.884080	-3.051600	-2.126244
C	-3.028201	-2.616434	-2.791103
C	-1.414437	1.565396	0.192588
C	-1.951229	2.221085	1.302187
C	-1.244985	2.366450	-0.939102
C	-2.256964	3.582287	1.308203
C	-1.525906	3.726326	-0.975912
C	-2.039887	4.340900	0.163399
F	-0.224374	-2.719470	-0.549408
F	-1.376658	-4.244746	-2.386979
F	-3.609311	-3.388452	-3.688558
F	-4.645420	-0.946073	-3.108964
F	-3.510255	0.609953	-1.303173
F	-2.448251	-2.294184	1.455322
F	-1.882647	-3.386978	3.795133
F	0.085330	-2.368642	5.365197
F	1.481556	-0.183002	4.520003
F	0.893460	0.973971	2.213325
F	-2.210704	1.563822	2.427823
F	-2.757680	4.152179	2.390556
F	-2.322781	5.629178	0.153248
F	-1.322751	4.430848	-2.076421
F	-0.795655	1.830183	-2.081766
W	3.033973	-0.013149	-0.859731
C	4.342530	0.481223	-2.524149
C	4.791220	0.898796	0.042772
C	2.584790	2.090378	-1.120101
C	2.819842	-1.686367	-2.151004
C	3.302489	-1.131174	0.930750
C	0.829992	0.003723	-0.524473
H	4.883726	1.432238	-2.463240
H	3.695264	0.499187	-3.418977
H	5.076847	-0.331873	-2.654177
H	5.171367	1.807651	-0.437922
H	5.592384	0.138620	0.030126
H	4.552680	1.123145	1.096235
H	3.420200	2.708472	-1.467580
H	2.260621	2.468100	-0.132627
H	1.740415	2.200151	-1.821099
H	2.100492	-2.359266	-1.648831
H	3.767465	-2.233686	-2.278431
H	2.416527	-1.441969	-3.145739
H	2.599637	-1.983119	0.862877
H	3.030777	-0.541081	1.821109
H	4.315280	-1.536494	1.071164
H	0.872514	-1.047958	-0.239480
H	0.495108	0.259117	-1.530163
H	0.944180	0.777471	0.235114

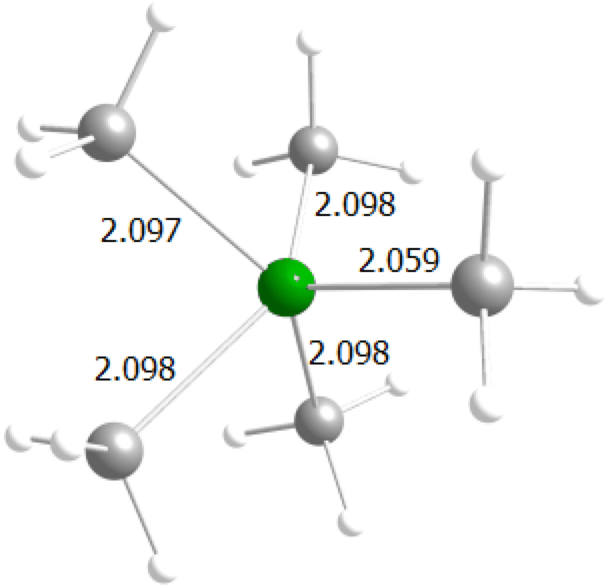
$[CH_3B(C_6F_5)_3]^-$



Zero-point correction= 0.194039 (Hartree/Particle)
Thermal correction to Energy= 0.224614
Thermal correction to Enthalpy= 0.225558
Thermal correction to Gibbs Free Energy= 0.129808
Sum of electronic and zero-point Energies= -2244.211795
Sum of electronic and thermal Energies= -2244.181220
Sum of electronic and thermal Enthalpies= -2244.180276
Sum of electronic and thermal Free Energies= -2244.276026

B	0.000596	0.000291	0.844237
C	-0.399872	-1.519014	0.331472
C	-1.514817	-2.161442	0.874828
C	0.300483	-2.279470	-0.603042
C	-1.896507	-3.462025	0.559290
C	-0.039349	-3.589599	-0.945799
C	-1.145809	-4.188166	-0.359058
C	1.516427	0.413369	0.331244
C	1.824412	1.400996	-0.602467
C	2.630578	-0.231109	0.873877
C	3.128791	1.762199	-0.945397
C	3.947585	0.089001	0.558090
C	4.200674	1.102915	-0.359591
C	-1.115353	1.106142	0.331154
C	-2.122688	0.879211	-0.604727
C	-1.116659	2.392537	0.875385
C	-3.088283	1.827466	-0.948015
C	-2.053135	3.372328	0.559387
C	-3.055856	3.084608	-0.360366
F	2.473520	-1.250794	1.721575
F	4.964987	-0.568273	1.111347
F	5.450786	1.429459	-0.676307
F	3.355376	2.724161	-1.837672
F	0.868190	2.067132	-1.255203
F	1.354748	-1.784314	-1.256902
F	0.679471	-4.266796	-1.838872
F	-1.488471	-5.433990	-0.675645
F	-2.973987	-4.014417	1.113472
F	-2.318473	-1.515475	1.723321
F	-2.218614	-0.281026	-1.259558
F	-4.032673	1.542828	-1.842437
F	-3.964315	4.003263	-0.677378
F	-1.995019	4.581353	1.114449
F	-0.156936	2.766418	1.725176
C	0.000652	0.000351	2.495964
H	0.386996	-0.947410	2.900230
H	0.628264	0.808736	2.900430
H	-1.013207	0.139650	2.900489

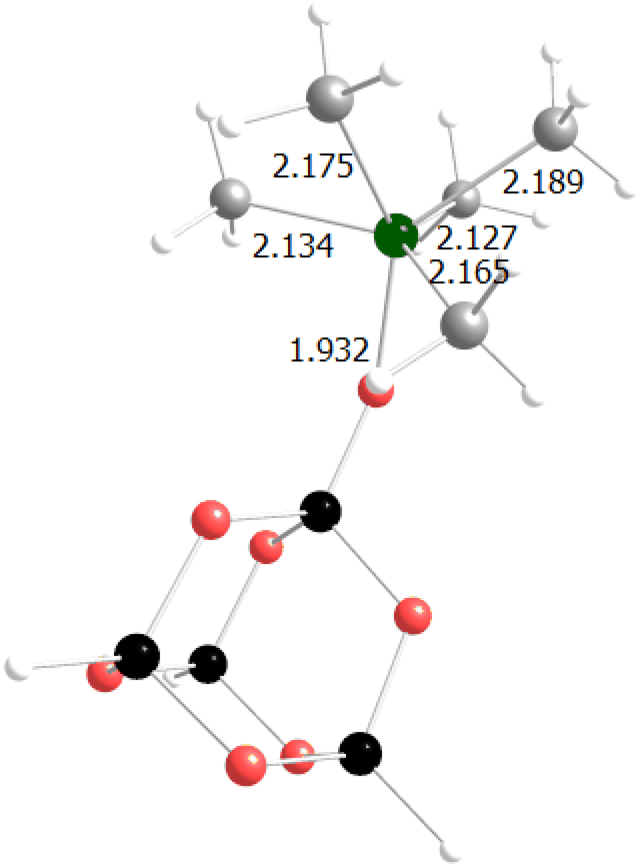
WMe$_5^+$



Zero-point correction= 0.177999 (Hartree/Particle)
Thermal correction to Energy= 0.189606
Thermal correction to Enthalpy= 0.190550
Thermal correction to Gibbs Free Energy= 0.141543
Sum of electronic and zero-point Energies= -265.763280
Sum of electronic and thermal Energies= -265.751674
Sum of electronic and thermal Enthalpies= -265.750729
Sum of electronic and thermal Free Energies= -265.799736

W	0.001852	0.001640	0.091149
C	-0.450995	-1.903226	-0.661463
C	-1.919410	0.406293	-0.645768
C	0.116310	0.056391	2.146223
C	1.848866	-0.438508	-0.801762
C	0.388691	1.867169	-0.786911
H	-1.331844	-2.225867	-0.073339
H	0.375792	-2.595408	-0.430955
H	-0.689219	-1.959255	-1.733945
H	-2.600866	-0.395750	-0.314532
H	-2.005953	0.536463	-1.734746
H	-2.231409	1.339621	-0.140441
H	1.037280	0.581072	2.466817
H	0.137491	-0.968959	2.564111
H	-0.754830	0.588334	2.575358
H	2.557785	0.385568	-0.619431
H	1.830247	-0.675933	-1.875725
H	2.209338	-1.321899	-0.239182
H	1.325099	2.213513	-0.309769
H	-0.411206	2.570844	-0.501382
H	0.514462	1.877574	-1.879809

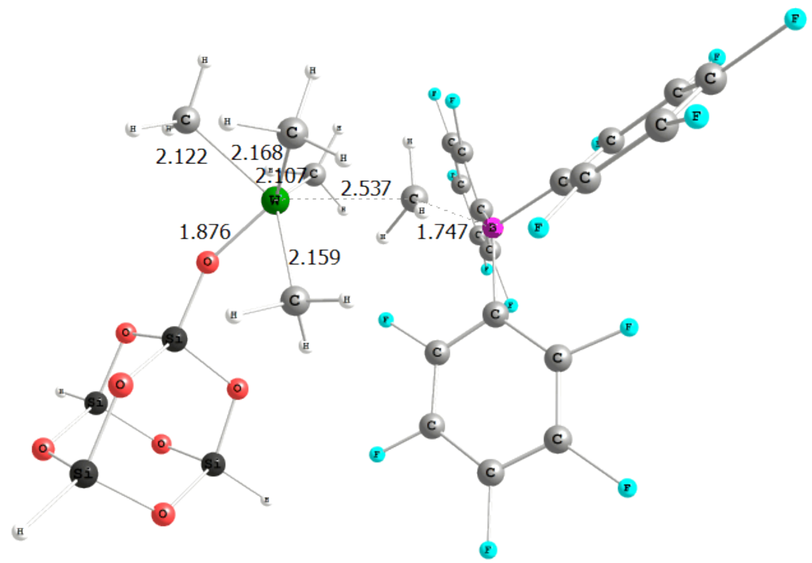
(≡SiO_2-)WMe_5



Zero-point correction= 0.248086 (Hartree/Particle)
Thermal correction to Energy= 0.270209
Thermal correction to Enthalpy= 0.271153
Thermal correction to Gibbs Free Energy= 0.194712
Sum of electronic and zero-point Energies= -1951.152328
Sum of electronic and thermal Energies= -1951.130205
Sum of electronic and thermal Enthalpies= -1951.129261
Sum of electronic and thermal Free Energies= -1951.205702

W	-2.293817	-0.080753	-0.018444
C	-3.326583	0.947836	1.596333
C	-3.962725	0.935173	-1.005289
C	-1.553211	1.938407	-0.263219
C	-2.088364	-1.398814	1.647760
C	-3.112143	-1.563374	-1.304980
H	-3.660186	1.972194	1.390480
H	-2.707018	0.949742	2.508294
H	-4.222197	0.332942	1.807898
H	-4.204981	1.942622	-0.645209
H	-4.875850	0.318000	-0.957688
H	-3.669432	1.008222	-2.068543
H	-2.264708	2.756865	-0.112471
H	-1.112445	2.011335	-1.272464
H	-0.737538	2.026173	0.479303
H	-1.685124	-2.332804	1.214974
H	-3.005454	-1.627919	2.207920
H	-1.333443	-1.001192	2.346628
H	-2.388885	-2.396869	-1.246494
H	-3.240330	-1.281883	-2.359371
H	-4.080803	-1.911447	-0.908139
Si	1.090934	-0.234868	-0.317201
O	-0.485292	-0.467119	-0.578086
O	1.967839	-1.649541	-0.345306
O	1.391053	0.453816	1.177234
O	1.813763	0.773167	-1.429277
Si	3.445076	1.072971	-1.223442
Si	2.994106	0.731151	1.564823
Si	3.610358	-1.519740	-0.063229
H	3.999865	1.964969	-2.246528
H	3.167977	1.334927	2.890011
H	4.303652	-2.811044	-0.108964
O	3.599038	1.677845	0.327737
O	4.178461	-0.429173	-1.195471
O	3.754001	-0.749951	1.414203

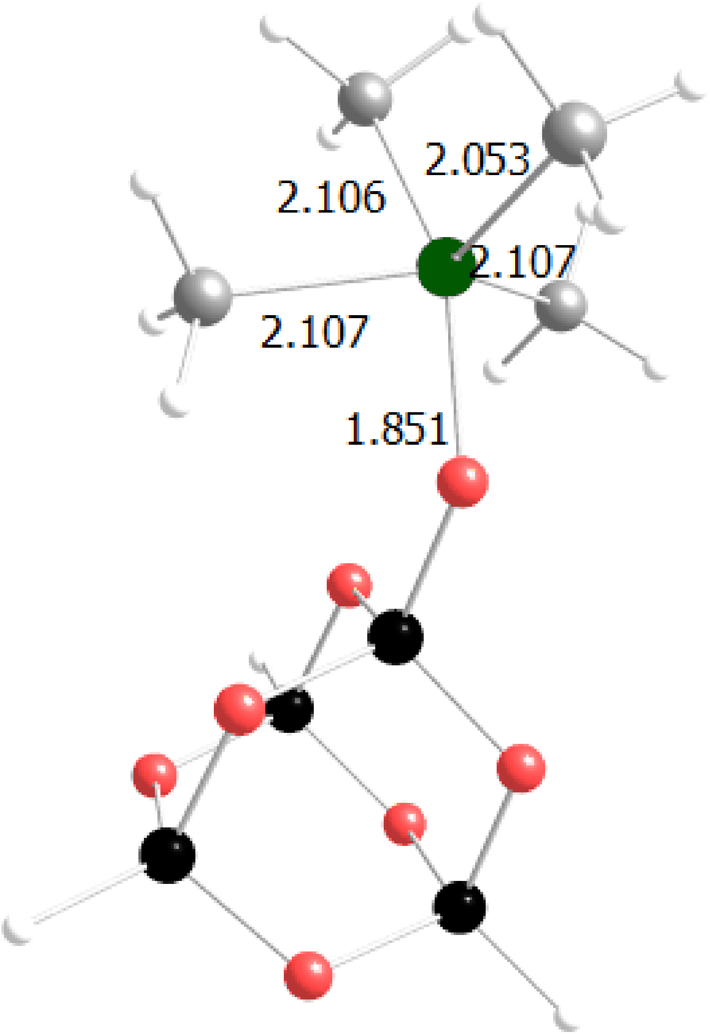
$(\equiv SiO_2\text{-})WMe_4\text{—}CH_3^{-}\text{—}B(C_6F_5)_3$



Zero-point correction= 0.409107 (Hartree/Particle)
Thermal correction to Energy= 0.459050
Thermal correction to Enthalpy= 0.459994
Thermal correction to Gibbs Free Energy= 0.324697
Sum of electronic and zero-point Energies= -4155.455593
Sum of electronic and thermal Energies= -4155.405650
Sum of electronic and thermal Enthalpies= -4155.404706
Sum of electronic and thermal Free Energies= -4155.540003

W	-0.997024	-1.309824	-1.717154
C	-0.009106	-0.745191	-3.562498
C	-1.335443	0.822208	-1.716292
C	-1.670004	-2.744397	-3.129090
C	-0.283648	-2.675586	-0.280551
H	0.524292	0.212149	-3.551771
H	-0.719486	-0.747656	-4.402357
H	0.734324	-1.544445	-3.747677
H	-0.494398	1.457824	-2.008686
H	-1.661565	1.096574	-0.698693
H	-2.176140	0.971189	-2.415244
H	-2.223448	-3.486002	-2.527390
H	-0.843479	-3.243910	-3.655117
H	-2.360708	-2.313024	-3.868687
H	-1.102958	-3.416615	-0.243155
H	-0.118992	-2.274263	0.730408
H	0.638862	-3.175539	-0.617246
Si	-4.073881	-0.529809	-0.476674
O	-2.770823	-1.296985	-1.107116
O	-5.265187	-1.578050	-0.011381
O	-4.753505	0.537488	-1.550866
O	-3.636165	0.343583	0.859930
Si	-4.863281	1.200564	1.619293
Si	-6.068853	1.405777	-0.963501
Si	-6.616783	-0.857701	0.685065
H	-4.424160	1.945212	2.799269
H	-6.625925	2.328098	-1.956522
H	-7.634570	-1.835325	1.078408
O	-5.518076	2.162465	0.417305
O	-6.032427	0.051069	1.955820
O	-7.154638	0.244863	-0.449672
B	2.322542	0.210971	0.244883
C	3.708830	0.541109	-0.556111
C	3.710256	1.362613	-1.687414
C	4.963018	0.033346	-0.211629
C	4.836762	1.639589	-2.452538
C	6.121743	0.283731	-0.948784
C	6.059584	1.089144	-2.079233
C	2.474688	-0.976665	1.359390
C	2.332834	-0.788827	2.735364
C	2.748594	-2.293364	0.985596
C	2.401021	-1.828301	3.664603
C	2.818928	-3.362277	1.870336
C	2.639473	-3.126884	3.230232
C	1.571271	1.542139	0.842997
C	2.135989	2.815804	0.920152
C	0.253780	1.473326	1.298680
C	1.432710	3.941651	1.353580
C	-0.491263	2.562931	1.730017
C	0.108136	3.818223	1.756976
F	2.967042	-2.599236	-0.304104
F	3.050108	-4.590865	1.431196
F	2.701653	-4.123203	4.095391
F	2.245380	-1.585023	4.955897
F	2.128258	0.421355	3.249240
F	5.132245	-0.722530	0.870348
F	7.280138	-0.234055	-0.572552
F	7.147464	1.337393	-2.786540
F	4.759754	2.426289	-3.515168
F	2.581156	1.971891	-2.082103
F	3.403711	3.030159	0.586134
F	2.021394	5.125055	1.392082
F	-0.571606	4.874167	2.167147
F	-1.752461	2.420481	2.121016
F	-0.377600	0.280457	1.347193
C	1.247995	-0.365172	-1.006349
H	1.683832	-1.301939	-1.360992
H	0.405245	-0.431736	-0.301924
H	1.225474	0.446492	-1.719555

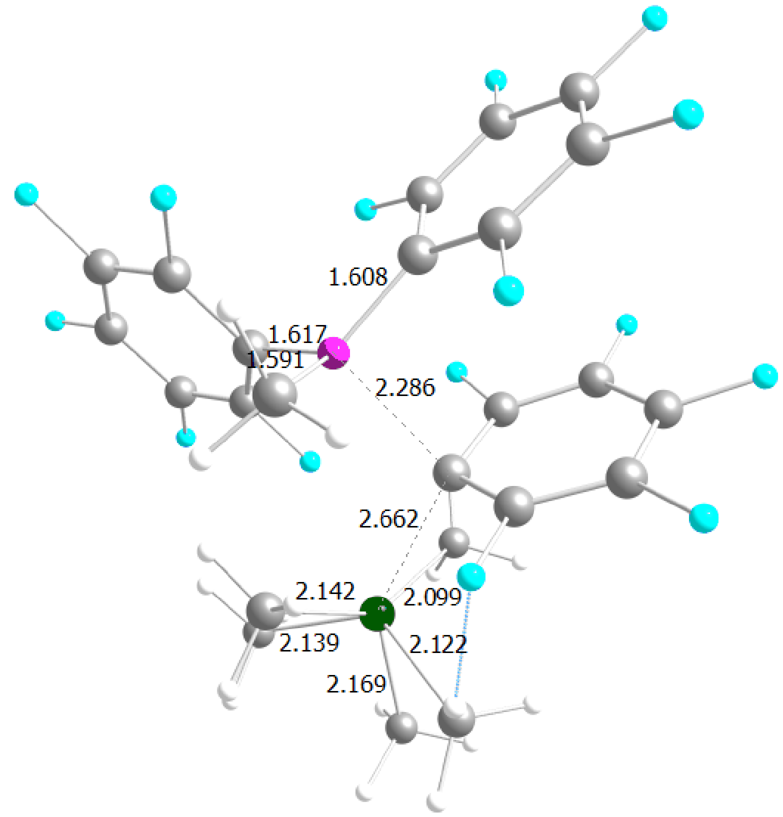
$(\equiv SiO_2\text{-})WMe_4^+$



Zero-point correction= 0.209390 (Hartree/Particle)
Thermal correction to Energy= 0.230132
Thermal correction to Enthalpy= 0.231076
Thermal correction to Gibbs Free Energy= 0.158594
Sum of electronic and zero-point Energies= -1911.131931
Sum of electronic and thermal Energies= -1911.111189
Sum of electronic and thermal Enthalpies= -1911.110245
Sum of electronic and thermal Free Energies= -1911.182727

W	2.349682	-0.000343	-0.104416
C	3.474351	-0.017045	1.675508
C	1.727885	-1.846186	0.700075
C	1.943422	1.940068	0.608244
C	3.782369	-0.145116	-1.567566
H	3.959845	-0.996339	1.823839
H	2.986062	0.282477	2.613573
H	4.265665	0.730072	1.450297
H	2.620725	-2.486868	0.796068
H	1.019984	-2.302992	-0.010808
H	1.250718	-1.747033	1.687635
H	1.650291	2.507516	-0.293990
H	2.803882	2.421506	1.091693
H	1.087324	1.904561	1.302939
H	3.341677	-0.421531	-2.541996
H	4.505906	-0.929880	-1.269282
H	4.321247	0.815818	-1.676239
Si	-0.967480	0.062844	-0.459370
O	0.661168	0.100389	-0.856982
O	-1.864286	1.044684	-1.417851
O	-1.132381	0.554779	1.113382
O	-1.530785	-1.480601	-0.571790
Si	-3.163621	-1.651947	-0.142546
Si	-2.738993	0.532859	1.668945
Si	-3.518840	1.053612	-1.045886
H	-3.634892	-3.030768	-0.267927
H	-2.849788	0.980903	3.057470
H	-4.289527	1.933212	-1.923270
O	-3.235748	-1.036611	1.408063
O	-3.961945	-0.553435	-1.108294
O	-3.565856	1.472201	0.570123

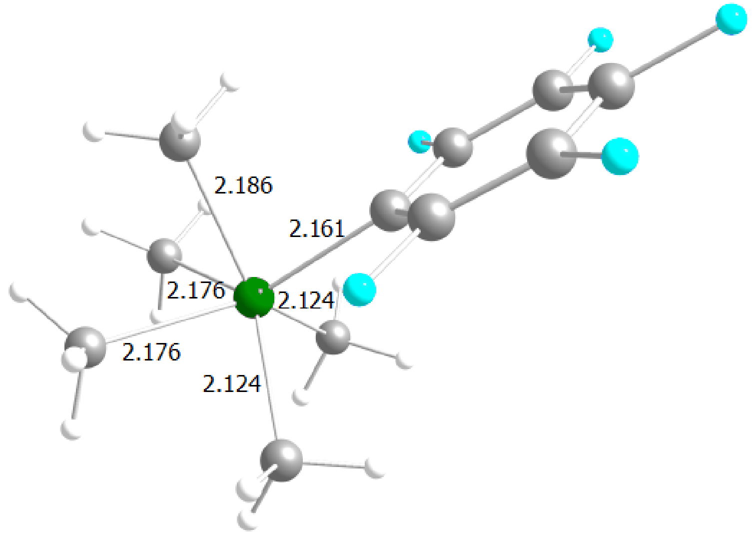
WMe_5—$(C_6F_5)^-$—$MeB(C_6F_5)_2$



Zero-point correction= 0.377940 (Hartree/Particle)
Thermal correction to Energy= 0.420113
Thermal correction to Enthalpy= 0.421058
Thermal correction to Gibbs Free Energy= 0.305209
Sum of electronic and zero-point Energies= -2510.061129
Sum of electronic and thermal Energies= -2510.018956
Sum of electronic and thermal Enthalpies= -2510.018012
Sum of electronic and thermal Free Energies= -2510.133860

B	-0.677239	0.859035	-1.141299
C	0.266840	2.046479	-0.582262
C	-0.055617	3.323491	-1.054691
C	1.386008	2.012935	0.235241
C	0.680201	4.468123	-0.763145
C	2.163623	3.124722	0.551894
C	1.809275	4.368836	0.046547
C	-0.004493	-1.101416	-0.177015
C	-0.707252	-0.983218	1.038234
C	-0.565789	-2.070629	-1.023010
C	-1.789616	-1.760498	1.417028
C	-1.638999	-2.896364	-0.701271
C	-2.262842	-2.727757	0.530408
C	-2.168601	0.807120	-0.542608
C	-2.565654	1.513607	0.600751
C	-3.160094	-0.006406	-1.104317
C	-3.824412	1.382830	1.181339
C	-4.424231	-0.175940	-0.544614
C	-4.761020	0.528991	0.606098
F	-0.108652	-2.238893	-2.266656
F	-2.105098	-3.785784	-1.559067
F	-3.315438	-3.449044	0.844280
F	-2.429479	-1.547931	2.555702
F	-0.429076	0.010239	1.884332
F	1.793431	0.869781	0.831541
F	3.225771	2.999031	1.334653
F	2.525786	5.439189	0.333498
F	0.317877	5.643078	-1.244565
F	-1.135341	3.489940	-1.815102
F	-1.733463	2.344591	1.218464
F	-4.138642	2.064987	2.268973
F	-5.955539	0.390218	1.146992
F	-5.302892	-0.991604	-1.102561
F	-2.925530	-0.714075	-2.207733
C	-0.513783	0.675347	-2.713338
H	0.500444	0.893659	-3.070069
H	-0.833276	-0.289190	-3.117422
H	-1.176984	1.434963	-3.162769
W	2.620807	-1.406167	0.138620
C	1.947246	-1.507039	2.124555
C	4.258104	-2.714630	0.698668
C	2.320989	-3.181931	-0.983414
C	2.465020	-0.419395	-1.756482
C	4.315149	-0.102266	0.215159
H	1.295840	-0.757092	2.572977
H	2.914318	-1.508381	2.663452
H	1.510616	-2.518155	2.237357
H	3.863026	-3.689208	1.028868
H	4.835564	-2.281566	1.529946
H	4.951384	-2.891606	-0.136696
H	1.633445	-3.033985	-1.820005
H	1.837424	-3.863587	-0.256323
H	3.237861	-3.658877	-1.351553
H	3.435521	-0.702087	-2.207369
H	2.392119	0.675084	-1.710034
H	1.652191	-0.802169	-2.378136
H	4.052872	0.906123	-0.130405
H	5.195170	-0.465618	-0.332552
H	4.575167	-0.030579	1.286089

WMe$_5$(C$_6$F$_5$)



Zero-point correction= 0.231947 (Hartree/Particle)
Thermal correction to Energy= 0.253063
Thermal correction to Enthalpy= 0.254007
Thermal correction to Gibbs Free Energy= 0.182788
Sum of electronic and zero-point Energies= -992.491298
Sum of electronic and thermal Energies= -992.470182
Sum of electronic and thermal Enthalpies= -992.469238
Sum of electronic and thermal Free Energies= -992.540458

W	-1.442252	-0.000078	0.085044
C	-2.937885	-1.344837	-0.746140
C	-0.993563	0.000908	-2.054752
C	-2.937716	1.345759	-0.744707
C	-1.600733	-1.514635	1.565002
H	-3.404702	-1.046648	-1.692044
H	-3.727127	-1.503215	0.008442
H	-2.411938	-2.304742	-0.895386
H	-1.856772	0.001030	-2.731697
H	-0.373949	-0.889425	-2.262861
H	-0.374567	0.891936	-2.261791
H	-3.404119	1.048706	-1.691165
H	-2.412524	2.306308	-0.892217
H	-3.727290	1.502157	0.009962
H	-0.772582	-1.271703	2.260729
H	-1.472425	-2.551195	1.226660
H	-2.547430	-1.429822	2.124059
C	0.716434	-0.000232	-0.020540
C	1.449448	-1.182927	-0.036253
C	1.449120	1.182675	-0.036208
C	2.840641	-1.208574	-0.017381
C	2.840293	1.208750	-0.017311
C	3.536280	0.000184	-0.010964
F	0.812578	2.355812	-0.079323
F	3.505505	2.350923	-0.020826
F	4.854635	0.000376	0.001044
F	3.506180	-2.350554	-0.020954
F	0.813312	-2.356269	-0.079435
C	-1.600126	1.513256	1.566432
H	-1.471821	2.550120	1.229046
H	-2.546952	1.427900	2.125206
H	-0.772166	1.269821	2.262182

References

[1] Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J.

W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

[2] a) J. P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 1996, 77, 3865-3868; b) C. Adamo, V. Barone, *J. Chem. Phys.* **1999**, *110*, 6158-6169.

[3] a) S. Grimme, J. Antony, S. Ehrlich, H. Krieg, J. Chem. Phys. **2010**, *132*, 154104-154119. b) S. Grimme, S. Ehrlich, L. Goerigk, *J. Comp. Chem.* **2011**, *32*, 1456-1465.

[4] A. Schaefer, H. Horn, R. Ahlrichs, *J. Chem. Phys*. **1992**, *97*, 2571-2577.

[5] a) U. Haeusermann, M. Dolg, H. Stoll, H. Preuss, *Mol. Phys.* **1993**, *78*, 1211-1224; b) W. Kuechle, M. Dolg, H. Stoll, H. Preuss, *J. Chem. Phys.* **1994**, *100*, 7535-7542; c) Leininger, T.; Nicklass, A.; Stoll, H.; Dolg, M.; Schwerdtfeger, P. *J. Chem. Phys.* **1996**, *105*, 1052-1059.

[6] a) S. Grimme, *Chem. Eur. J.* **2012**, *18*, 9955-9964; b) M. Z. Ertem, L. Gagliardi, C. J. Cramer, *Chem. Sci.* **2012**, *3*, 1293-1299.

[7] F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297-305.

[8] A. V. Marenich, C. J. Cramer, D. G. Truhlar, *J. Phys. Chem. B* **2009**, *113*, 6378-6796.

[9] a) C. A. Urbina-Blanco, A. Poater, T. Lebl, S .Manzini, A. M. Z. Slawin, L. Cavallo, S. P. Nolan, *J. Am. Chem. Soc.* **2013**, *135*, 7073-7079; b) F. P. Rotzinger, *Chem. Rev.* **2005**, *105*, 2003-2037; c) J. Cooper, T. Ziegler, *Inorg. Chem.* **2002**, *41*, 6614-6622; d) P. Margl, *Can. J. Chem.* **2009**, *87*, 891-903; e) X. Solans-Monfort, C. Copéret, O. Eisenstein, *Organometallics* **2012**, *31*, 6812-6822; f) C. Raynaud, J. P. Daudey, F. Jolibois, L. Maron, *J. Phys. Chem. A* **2005**, *110*, 101-105; g) D. Ardura, R. L. Lopez, T. L. Sordo, *J. Phys. Chem. B* **2005**, *109*,

23618-23623; h) B. O. Leung, D. L. Read, D. A. Armstrong, A. Rauk, *J. Phys. Chem. A* **2004**, *108*, 2720-2725.

[10] a) M. García-Melchor, M. C. Pacheco, C. Najera, A. Lledós, G. Ujaque, *ACS Catal.* **2012**, *2*, 135-144; b) S. Manzini, A. Poater, D. J. Nelson, L. Cavallo, S. P. Nolan, *Chem. Sci.* **2014**, *5*, 180-188; c) S. Manzini, A. Poater, D. J. Nelson, L .Cavallo, A. M. Z. Slawin, S. P. Nolan, *Angew. Chem., Int. Ed.* **2014**, *53*, 8995-8999; d) A. Poater, E. Pump, S. V. C. Vummaleti, L. Cavallo, *J. Chem. Theory Comput.* **2014**, *10*, 4442-4448; e) E. Pump, C. Slugovc, L. Cavallo, A. Poater, *Organometallics* **2015**, *34*, 3107-3111; f) N. Riache, A. Dery, E. Callens, A. Poater, M. Samantaray, R. Dey, J. H. Hong, K. Lo, L. Cavallo, J. M. Basset, *Organometallics* **2015**, *34*, 690-695.

[11] R. L. Martin, P. J. Hay, L. R. Pratt, *J. Phys. Chem. A* **1998**, *102*, 3565-3573.