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Communication

Supplementary Materials: Synthesis and Characterization of Cationic Tetramethyl Tantalum(V) Complex

Raju Dey [1,2], Janet C. Mohandas [1], Manoja K. Samantaray [1], Ali Hamieh [1], Santosh Kavitake [1], Yin Chen [1,3], Edy Abou-Hamad [1], Luigi Cavallo [1], Albert Poater [4,*] and Jean-Marie Basset [1,*]

1 King Abdullah University of Science & Technology, KAUST Catalysis Center (KCC), Thuwal 23955-6900, Saudi Arabia; rajudey@nitc.ac.in (R.D.); janet.mohandas@kaust.edu.sa (J.C.M.); manoja.samantaray@kaust.edu.sa (M.K.S.); ali.hamieh@kaust.edu.sa (A.H.); santosh.kavitake@kaust.edu.sa (S.K.); chenyin@iccas.ac.cn (Y.C.); edy.abouhamad@kaust.edu.sa (E.A.-H.); luigi.cavallo@kaust.edu.sa (L.C.)

2 Department of Chemistry, National Institute of Technology Calicut, NIT Campus, Kozhikode 673 601, India

3 College of Chemistry & Chemical Engineering, Central South University, Changsha 410083, China

4 Institut de Química Computacional i Catàlisi and Departament de Química, Universitat de Girona, c/ Mª Aurèlia Capmany 69, 17003 Girona, Catalonia, Spain

* Correspondence: albert.poater@udg.edu (A.P.); jeanmarie.basset@kaust.edu.sa (J.-M.B.); Tel.: +34-97-241-8358 (A.P.)

General Experimental Procedure:

All experiments were carried out by using standard Schlenk and glovebox techniques under an inert argon atmosphere. The syntheses and the treatments of the surface species were carried out using high vacuum lines (< 10^{-5} mbar) and glove-box techniques. Pentane was distilled from a Na/K alloy under argon and dichloromethane from CaH_2. All the solvents were degassed through freeze–pump–thaw cycles. $SiO_{2\text{-}700}$ was prepared from Aerosil silica from Degussa (specific area of 200 m^2/g), which were partly dehydroxylated at 700 °C under high vacuum (< 10^{-5} mbar) for 16 h to give a white solid having a specific surface area of 183 m^2/g and containing 0.5–0.7 OH/nm^2. The elemental analyses were performed at Mikroanalytisches Labor Pascher (Germany) and ACL KAUST.

Liquid State Nuclear Magnetic Resonance (NMR) Spectroscopy:

^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 was 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).

Solid State Nuclear Magnetic Resonance Spectroscopy:

One dimensional ^1H Magic-Angel spinning (MAS) and ^{13}C Cross Polarization (CP)/MAS solid state NMR spectra were recorded on Bruker AVANCE III spectrometers operating at 400 MHz resonance frequencies for ^1H. The 400-MHz experiments employed a conventional double resonance 4 mm CP/MAS probe. In all cases, the samples were packed into rotors under an 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 tetramethylsilane (TMS) and adamantane. For ^{13}C CP/MAS NMR experiments, the following sequence was used: 900 pulse 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 4 s to allow the complete relaxation of the ^{1}H nuclei and the number of scans ranged between 10,000–20,000 for ^{13}C and was 8 for ^{1}H. An exponential apodization function corresponding to a line broadening of 80 Hz was applied prior to Fourier transformation.

Infra-Red Spectroscopy:

IR spectra were recorded on pellets made out of ~30 mg of the sample. The pellet was then placed in a sample holder which can be loaded into an IR Cell made of pyrex glass fitted with CaF_2 windows. The IR cell is designed in such a way that the measurements can be carried out either in vacuum or in controlled atmospheres. Infrared spectra were recorded on a Thermo Scientific Nicolet 6700 FT-IR spectrometer typically accumulating 16 scans for each spectrum with a resolution of 4 cm^{-1}.

Preparation of Pentamethyltantalum, TaMe5:

The molecular precursor $TaMe_5$ was prepared from $TaMe_3Cl_2$ and MeLi[1]. To a cold solution of $TaMe_3Cl_2$ (297 mg, 1 mmol) in pentane (15 mL), at −80 °C, solid MeLi (98.9 mg, 4.5 mmol,) was added and the reaction mixture was stirred for another 1h at this temperature. The reaction mixture was then slowly warmed to −40 °C and stirred at this temperature for another 30 min. After successive filtration, washings with pentane and solvent removal, the slight yellow solid corresponding to $TaMe_5$ was obtained.

^{1}H NMR (CD_2Cl_2, 600 MHz): δ (ppm) 0.9 (s, 15H, TaC**H**$_3$). ^{13}C NMR (CD_2Cl_2, 150 MHz): δ (ppm) 82.4 (s, 5C, Ta**C**H_3). HSQC confirmed the correlation between the ^{1}H and ^{13}C NMR signals. ***Caution!*** This $10e^-$ compound is highly unstable and is prone to violent decomposition.

Preparation of ^{13}C labelled Pentamenthyl Tantalum, Ta(Me*)5:

The labelled ^{13}C molecular precursor of $TaMe_5$ was prepared by a similar strategy, as described for $TaMe_5$ given above, except that the used precursors, $TaMe_3^*Cl_2$ and Me^*Li, were enriched.

Preparation of $[TaMe_4^+ B(C_6F_5)_3Me^-]$:

A cold solution of $B(C_6F_5)_3$ (125 mg, 0.25 mmol) in dichloromethane at −40 °C was added drop wise to the cold solution of pentamethyltantalum (52 mg, 0.2 mmol) in dichloromethane at −40 °C and the mixture was stirred for another 15 min. Color of the solution intensified to dark yellow, indicating the formation of an ionic complex. This $8e^-$ compound is highly unstable and decomposes into black tantalum powder while drying.

^{1}H-NMR (600 MHz) δ (ppm) 0.5 (s, 3H, BC**H**$_3$), 2.6 (s, 12H, TaC**H**$_3$). ^{13}C-NMR (150 MHz) δ (ppm) 10.8 (s, 1C, B**C**H_3), 110.9 (s, 4C, Ta**C**H_3). ***Caution!*** This $8e^-$ compound is highly unstable and is prone to violent decomposition.

Preparation of (≡Si-O-)TaMe4:

In a cold (−70 °C) double-Schlenk tube, $silica_{700}$ (1 g, Aerosil-200 was dehydroxylated at 700 °C for 16 h under 10^{-5} mbar, high vacuum line to generate $silica_{700}$) was added into one compartment, and a cold pentane solution of $TaMe_5$ (0.3 mmol) was added to it from another compartment. The reaction mixture was allowed to stir at −70 °C for 1 h, and −40 °C for another 30 min and allowed to warm up to −20 °C. After filtration and washing with cold pentane for three times, the product was dried on the high-vacuum line for another 1 h to afford a white powder as a product. Elemental analysis gave 4.5% Ta, 1.2% C and 0.32% H.

IR data (cm^{-1}): 3742 (ν, isolated Si-**OH**), 3014, 2981, 2946, 2878 (ν, Ta-**CH**$_3$), 1397 (δ, Ta-**CH**$_3$). ^{1}H solid-state NMR (400 MHz): δ (ppm) 0.9 (Ta-C**H**$_3$); 1.8 (Si-O**H**) ^{13}C CP/MAS solid-state NMR (100 MHz): δ (ppm) 73.0 (Ta-**C**H$_3$). Analysis found: Ta, 4.5; C, 1.2. The C/Ta ratio obtained was 4.0 ± 0.1 (4 was expected).

Reaction between (≡Si-O-)TaMe$_4$ and B(C$_6$F$_5$)$_3$:

A solution of B(C$_6$F$_5$)$_3$ (150 mg, 1.2 equiv) in solvent (dichloromethane, pentane) was reacted with 1.0 g of silica supported (≡Si-O-)TaMe$_4$ at various temperature (−10 °C, 25 °C) for a certain time period (1 h, 6 h). At the end of the reaction, the resulting yellow solid was washed with pentane (3 × 20 mL), dried under dynamic vacuum (<10^{-5} Torr, 1 h) and analyzed by sold state ^{1}H and ^{13}C NMR. ^{1}H NMR (400 MHz): δ (ppm) 1.0 Ta-C**H**$_x$ and 0.0 C**H**$_4$ or Si-C**H**$_3$. ^{13}C CP/MAS solid-state NMR (100 MHz): δ (ppm) 63.0 (Ta-**C**H$_3$) due to the residual carbon of the decomposed complex; 8.9 ppm corresponded to ([**C**H$_3$-B(C$_6$F$_5$)$_3$]$^-$); –4.0 corresponded to (**C**H$_3$-Si).

Liquid State NMR Spectroscopy

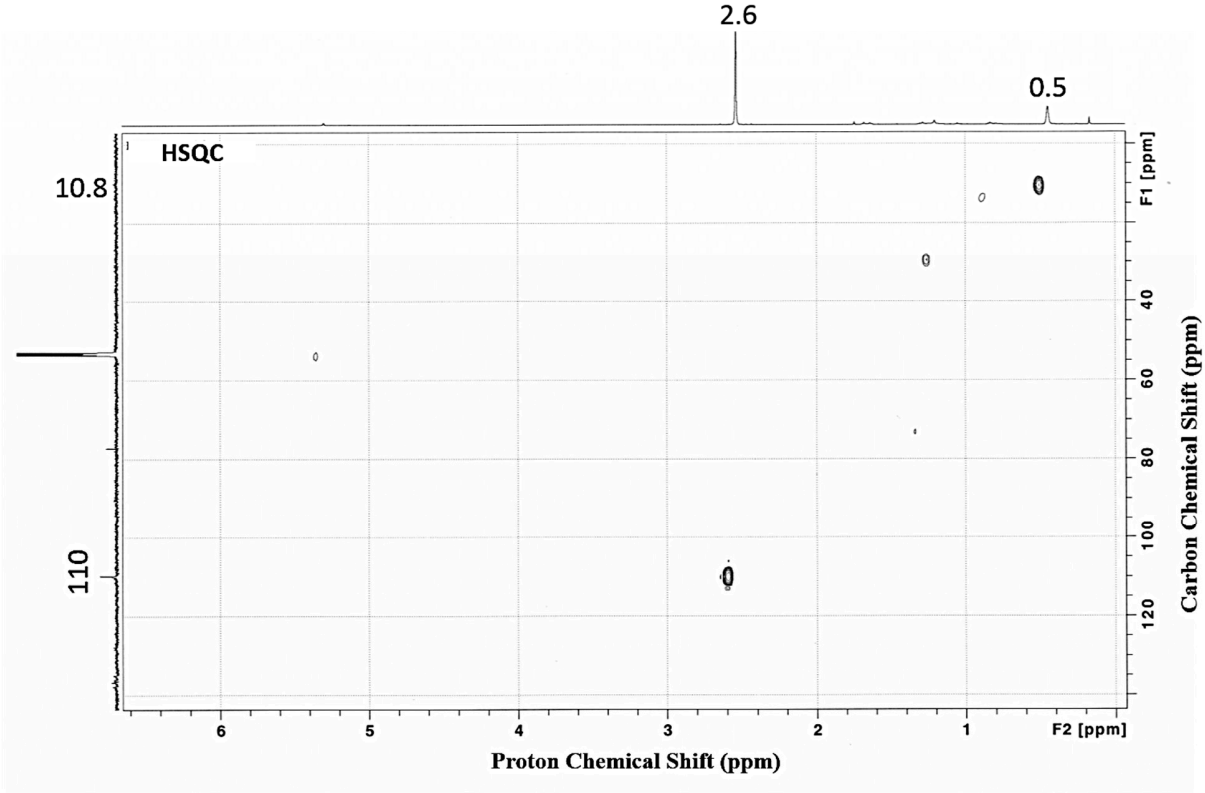


Figure S1. Two-dimensional (2D) liquid-state ^{1}H-^{13}C heteronuclear single quantum correlation (HSQC) NMR spectrum of $[TaMe_4^+ MeB(C_6F_5)_3^-]$ in CD_2Cl_2 recorded at −40 °C.

Solid State NMR Results

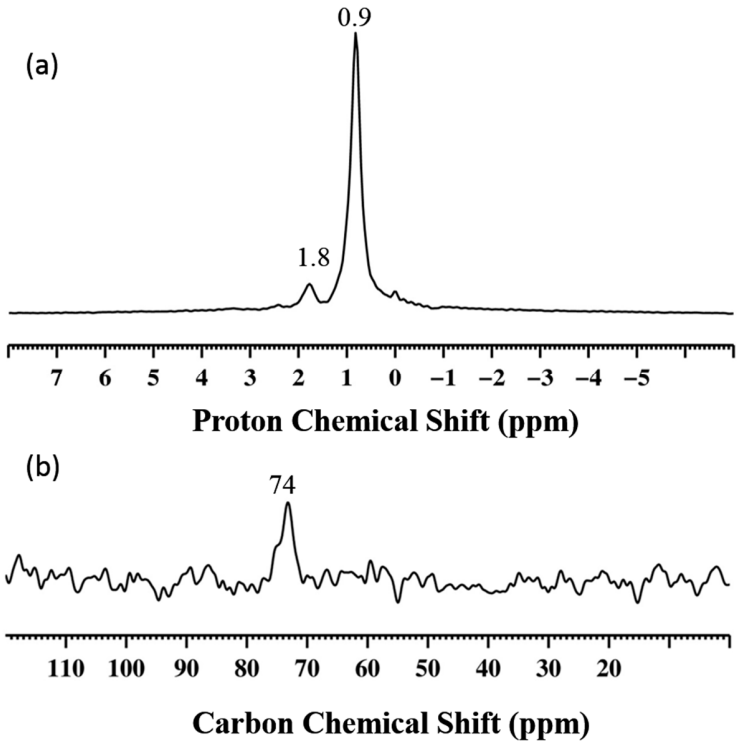


Figure S2. (**a**) One-dimensional (1D) ^{1}H MAS NMR spectrum of (≡Si-O-)TaMe$_4$ acquired at 600 MHz with a 22 kHz MAS frequency, a repetition delay of 5 s, and 8 scans. (**b**) ^{13}C CP MAS NMR spectrum of (≡Si-O-)TaMe$_4$ (acquired at 400 MHz) with a 10 kHz MAS frequency, 10,000 scans, a 4-s repetition delay, and a 2-ms contact time. Exponential line broadening of 80 Hz was applied prior to Fourier transformation. ^{13}C CP MAS spectra were acquired at natural abundance (Reprinted with permission from reference [14]. Copyright 2012 American Chemical Society).

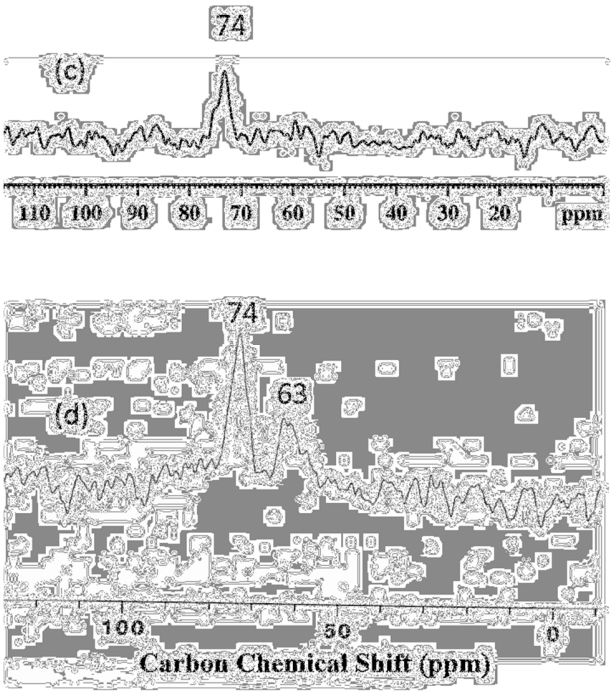


Figure S3. (**a**) One-dimensional (1D) ^{13}C CP MAS NMR spectrum of [(≡Si-O-)TaMe$_4$] (acquired at 400 MHz) with a 10 kHz MAS frequency (Reprinted with permission from reference [14]. Copyright 2012 American Chemical Society). (**b**) ^{13}C CP MAS spectra of [(≡Si-O-)TaMe$_4$] when decomposed on the surface at room temperature during the prolonged NMR measurement. ^{13}C CP MAS spectra were acquired at natural abundance.

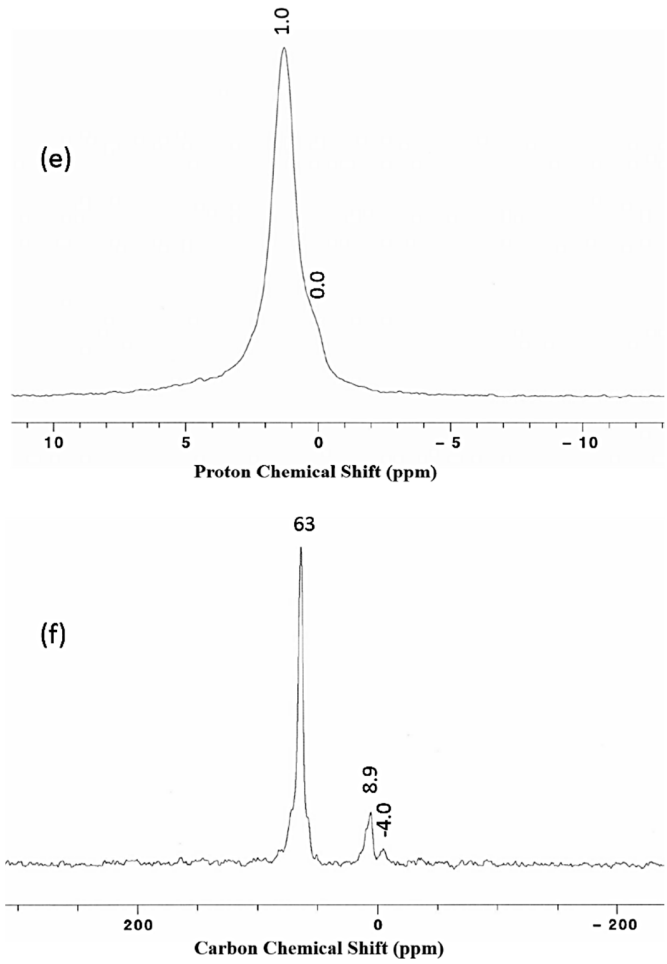


Figure S4. (**a)** One-dimensional (1D) ^{1}H MAS NMR spectrum of [(≡Si-O-)TaMe$_3^+$B(C$_6$F$_5$)$_3$Me$^-$]acquired at 400 MHz with a 22 kHz MAS frequency, a repetition delay of 5 s, and 8 scans (Reprinted with permission from reference [14]. Copyright 2012 American Chemical Society). (**b**) ^{13}C CP MAS NMR spectrum of [(≡Si-O-)TaMe$_3^+$B(C$_6$F$_5$)$_3$Me$^-$].

Computational Details:

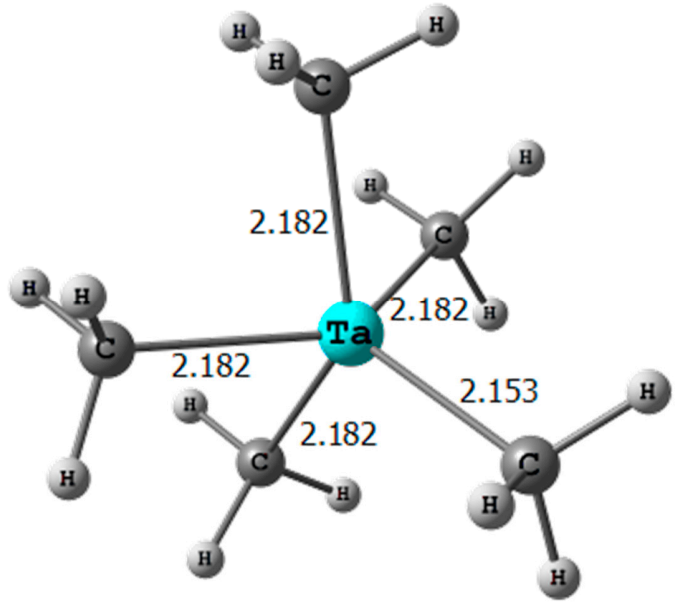
All the Density Functional Theory (DFT) static calculations were performed at the GGA (Generalized Gradient Approximation) level with the Gaussian09 set of programs [2], using the PBE0 function [3,4], corrected by the D3 Grimme pairwise scheme [5,6]. The electronic configuration of the molecular systems was described with the standard split-valence basis set with a polarization (SVP) function of Ahlrichs and co-workers for H, B, C, Si, O, and F (SVP keyword in Gaussian) [7]. For Ta and 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) [8-10]. 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 intrinsic reaction coordinate (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. Zero-point energies and thermal corrections were calculated at the PBE0 level. Single-point energy calculations in solution were performed with the M06 function [11] and the Def2TZVPP basis set [12] for main group atoms and again the same SDD pseudopotential for Ta and W. Solvent effects were included with the polarizable

continuous solvation model (SMD), using dichloromethane as solvent [13]. 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 [14,15] all the thermochemical analysis was performed at P = 1354 atm, as suggested by Martin et al [16] 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).

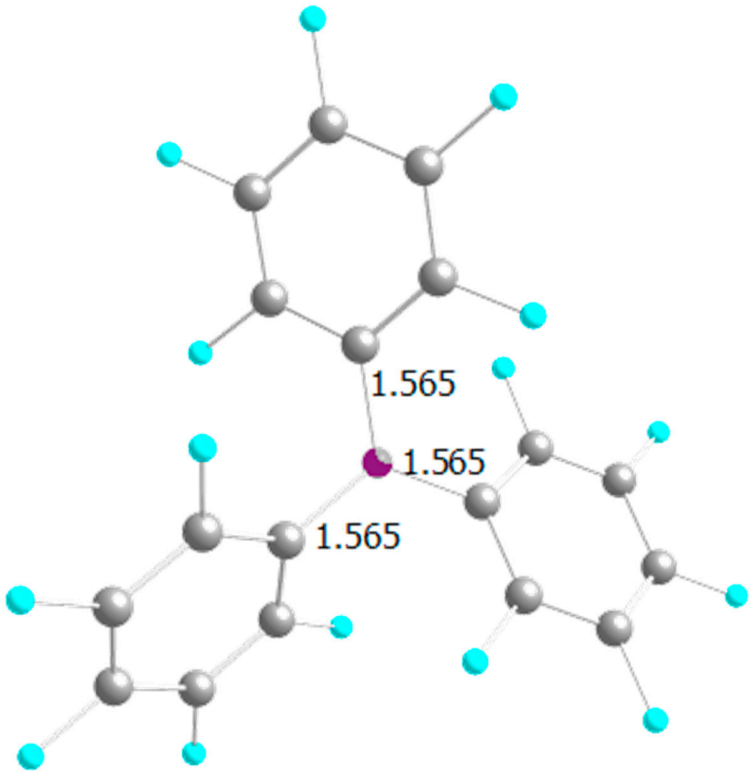
$TaMe_5$



Ta	0.001587	0.001607	0.094858
C	-0.364910	-2.003697	-0.684404
C	-2.005593	0.327657	-0.697535
C	0.071010	0.064858	2.245868
C	1.963150	-0.364899	-0.788666
C	0.324641	1.964238	-0.802906
H	-1.324348	-2.381963	-0.286717
H	0.434124	-2.687682	-0.345839
H	-0.411241	-2.056283	-1.784610
H	-2.686931	-0.446995	-0.300741
H	-2.064854	0.297718	-1.797959
H	-2.382678	1.311512	-0.364655
H	0.945747	0.640009	2.604043
H	0.141611	-0.951008	2.679075
H	-0.834817	0.541572	2.666343
H	2.664683	0.433927	-0.487776
H	1.958647	-0.412999	-1.890126
H	2.361290	-1.324229	-0.410431
H	1.307882	2.359720	-0.490028
H	-0.450945	2.665291	-0.444266
H	0.296170	1.965181	-1.905059

Zero-point correction= 0.174729 (Hartree/Particle)
Thermal correction to Energy= 0.187307
Thermal correction to Enthalpy= 0.188251
Thermal correction to Gibbs Free Energy= 0.136770
Sum of electronic and zero-point Energies= -255.956037
Sum of electronic and thermal Energies= -255.943459
Sum of electronic and thermal Enthalpies= -255.942515
Sum of electronic and thermal Free Energies= -255.993995

$B(C_6F_5)_3$



Zero-point correction= 0.157559 (Hartree/Particle)
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Sum of electronic and thermal Enthalpies= -2204.274250
Sum of electronic and thermal Free Energies= -2204.365465

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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
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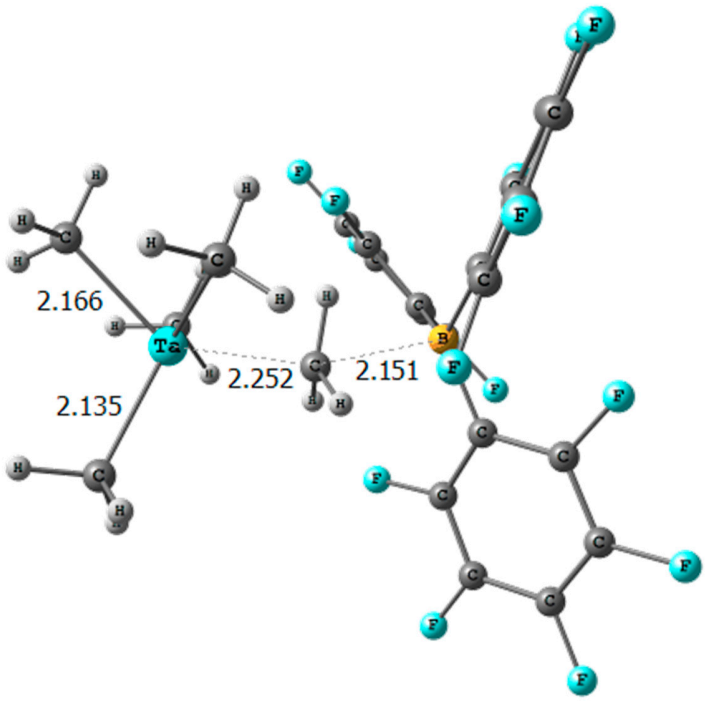
$TaMe_4—CH_3^-—B(C_6F_5)_3$



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C	0.487728	-1.373167	2.037886
C	-1.609712	-2.282038	1.478695
C	0.810260	-2.488500	2.798126
C	-1.337513	-3.412808	2.249177
C	-0.117673	-3.521089	2.908338
C	-2.099128	-0.116352	-0.761793
C	-3.136664	0.806856	-0.923687
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C	-4.112113	0.692422	-1.914423
C	-3.081353	-1.348217	-2.651917
C	-4.083166	-0.389717	-2.786211
C	-0.786288	1.485090	1.034092
C	-0.831824	1.698401	2.413921
C	-0.556779	2.631260	0.268058
C	-0.613854	2.945766	2.999013
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C	-0.350333	4.046892	2.191968
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F	-3.048545	-2.390541	-3.465211
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F	-0.661156	3.087713	4.312134
F	-0.136392	5.231763	2.729535
F	-0.074900	4.925280	0.025491
F	-0.551543	2.558876	-1.067209
Ta	2.945953	-0.103809	-1.518845
C	3.098664	-0.253011	-3.642983
C	4.925541	-0.004428	-0.646543
C	2.833955	1.941234	-0.794781
C	2.916713	-2.029817	-0.510335
C	0.784968	-0.084123	-0.884025
H	2.576256	-1.151640	-4.022170
H	4.158318	-0.327148	-3.954648
H	2.664145	0.631444	-4.145710
H	5.450749	0.893039	-1.019515
H	5.497126	-0.893101	-0.971883
H	4.937518	0.022628	0.454962
H	3.698504	2.494943	-1.203538
H	2.866450	2.031553	0.304168
H	1.916433	2.438539	-1.152954
H	2.064703	-2.641137	-0.857284
H	2.858281	-1.954716	0.587453
H	3.843258	-2.575531	-0.761503
H	0.468915	-1.110466	-1.063574
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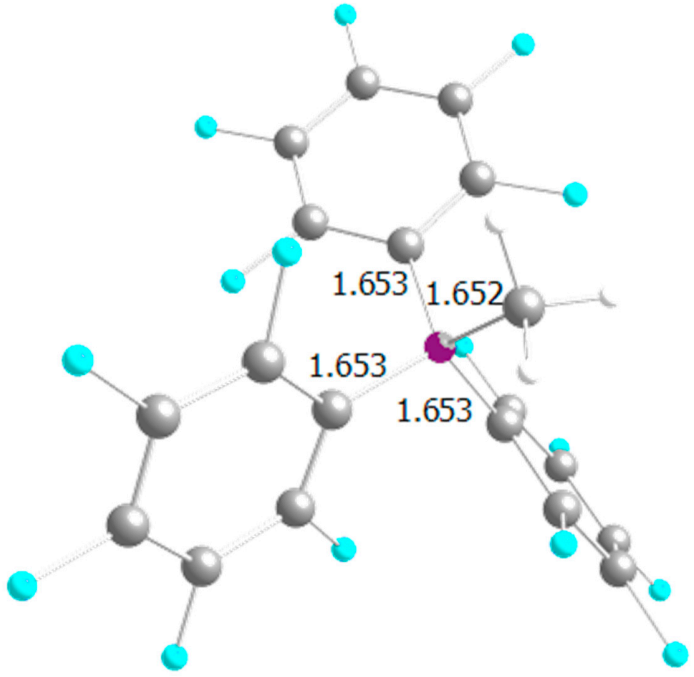
$[CH_3B(C_6F_5)_3]^-$



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C	-0.039349	-3.589599	-0.945799
C	-1.145809	-4.188166	-0.359058
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C	2.630578	-0.231109	0.873877
C	3.128791	1.762199	-0.945397
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F	5.450786	1.429459	-0.676307
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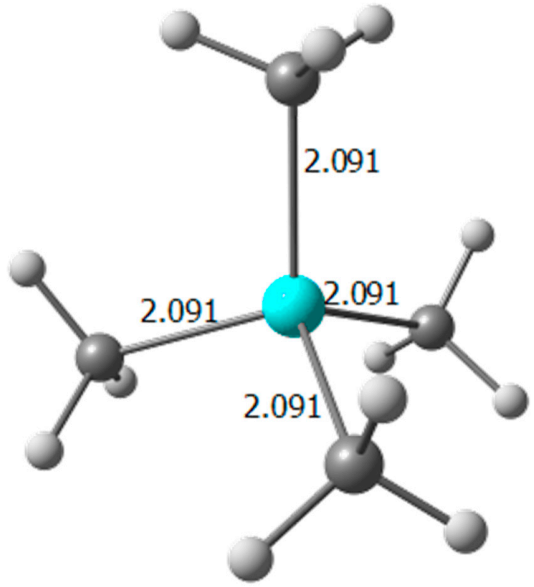
F	0.679471	-4.266796	-1.838872
F	-1.488471	-5.433990	-0.675645
F	-2.973987	-4.014417	1.113472
F	-2.318473	-1.515475	1.723321
F	-2.218614	-0.281026	-1.259558
F	-4.032673	1.542828	-1.842437
F	-3.964315	4.003263	-0.677378
F	-1.995019	4.581353	1.114449
F	-0.156936	2.766418	1.725176
C	0.000652	0.000351	2.495964
H	0.386996	-0.947410	2.900230
H	0.628264	0.808736	2.900430
H	-1.013207	0.139650	2.900489

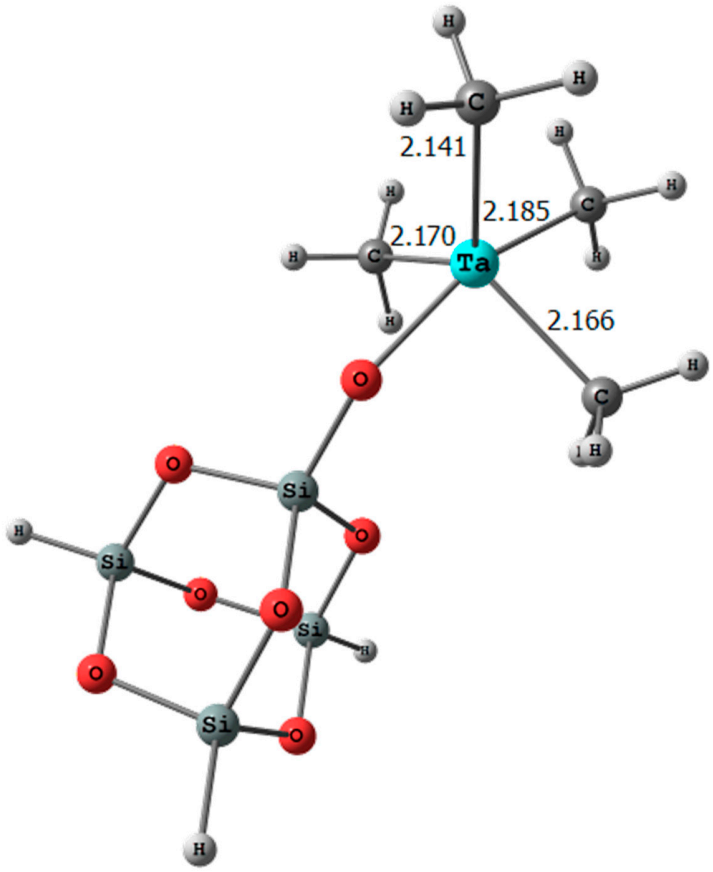
$TaMe_4^+$



Ta	-0.000011	-0.000020	0.000028
C	0.163504	0.519433	-2.019166
C	-0.032804	1.736006	1.165770
C	-1.767652	-1.076152	0.302054
C	1.637012	-1.179125	0.551183
H	0.201560	1.619245	-2.136480
H	-0.704295	0.138433	-2.590634
H	1.084474	0.090658	-2.458213
H	-0.975225	1.800191	1.742400
H	0.045717	2.635800	0.526193
H	0.812871	1.741776	1.879639
H	-1.545908	-2.085966	0.696932
H	-2.322361	-1.188565	-0.648994
H	-2.421858	-0.555112	1.026857
H	1.299775	-2.169991	0.910726
H	2.212363	-0.692362	1.361632
H	2.313306	-1.333628	-0.311144

Zero-point correction= 0.137583 (Hartree/Particle)
Thermal correction to Energy= 0.149072
Thermal correction to Enthalpy= 0.150016
Thermal correction to Gibbs Free Energy= 0.100114
Sum of electronic and zero-point Energies= -215.938538
Sum of electronic and thermal Energies= -215.927049
Sum of electronic and thermal Enthalpies= -215.926104
Sum of electronic and thermal Free Energies= -215.976007

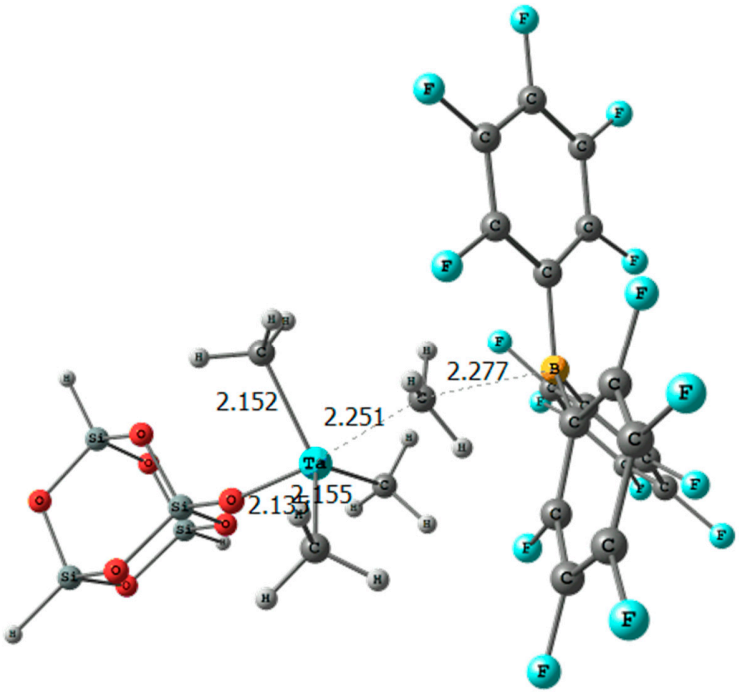
(≡SiO$_2$-)TaMe$_4$



C	-3.932762	-0.446164	-1.432058
C	-2.045925	1.715896	-1.204033
C	-3.757562	0.329889	1.750036
C	-1.796531	-2.005192	-0.328247
H	-4.635790	0.403552	-1.524513
H	-4.516949	-1.330876	-1.115671
H	-3.535170	-0.655815	-2.438430
H	-2.949129	2.135808	-1.672283
H	-1.353563	1.397520	-2.004459
H	-1.539685	2.504539	-0.619069
H	-3.204824	0.597598	2.667882
H	-4.339482	-0.587969	1.955534
H	-4.473631	1.143853	1.530951
H	-1.169153	-2.375862	0.501558
H	-1.175101	-1.999896	-1.242429
H	-2.633449	-2.702300	-0.488227
Si	0.968862	0.160021	0.399747
O	-0.601424	0.295833	0.748416
O	1.874373	1.487959	0.841260
O	1.241066	-0.044732	-1.238792
O	1.698155	-1.147989	1.136494
Si	3.320231	-1.386580	0.817147
Si	2.831996	-0.205266	-1.722737
Si	3.508990	1.433264	0.500936
H	3.876860	-2.554412	1.508280
H	2.977312	-0.377510	-3.172216
H	4.224358	2.641306	0.925210
O	3.443253	-1.491387	-0.847136
O	4.078700	0.043590	1.235411
O	3.619677	1.150588	-1.143346
Ta	-2.438458	0.024971	0.091561

Zero-point correction= 0.206285 (Hartree/Particle)
Thermal correction to Energy= 0.227105
Thermal correction to Enthalpy= 0.228050
Thermal correction to Gibbs Free Energy= 0.156142
Sum of electronic and zero-point Energies= -1901.340526
Sum of electronic and thermal Energies= -1901.319706
Sum of electronic and thermal Enthalpies= -1901.318762
Sum of electronic and thermal Free Energies= -1901.390670

(≡SiO_2-)WMe_4—CH_3^-—$B(C_6F_5)_3$

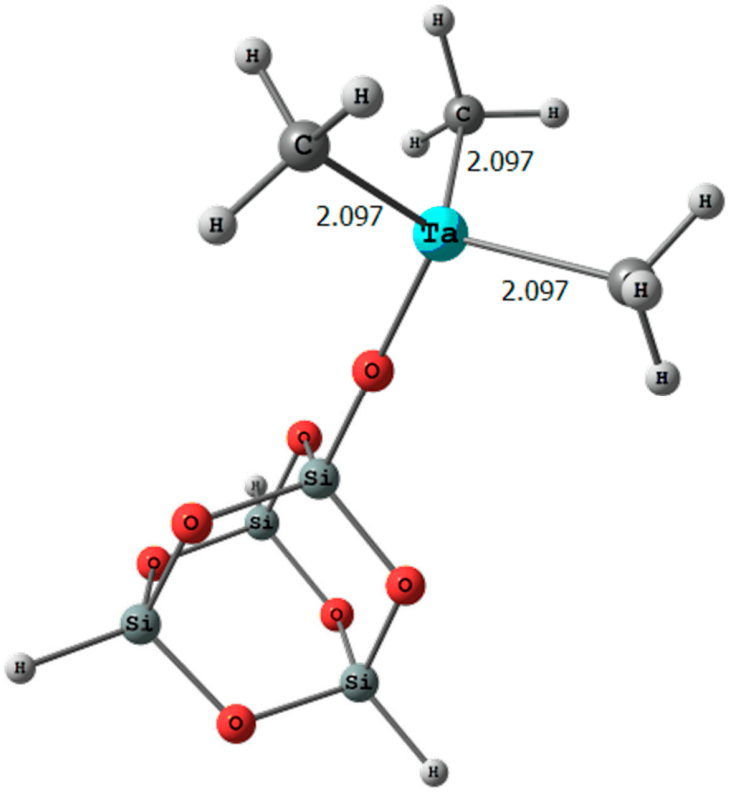


Zero-point correction= 0.365862 (Hartree/Particle)
Thermal correction to Energy= 0.415012
Thermal correction to Enthalpy= 0.415956
Thermal correction to Gibbs Free Energy= 0.280204
Sum of electronic and zero-point Energies= -4105.654907
Sum of electronic and thermal Energies= -4105.605758
Sum of electronic and thermal Enthalpies= -4105.604813
Sum of electronic and thermal Free Energies= -4105.740565

Ta	-1.361976	0.683235	-0.409982
C	-0.825574	2.749446	-0.428398
C	-1.353706	-0.372999	1.468160
C	-1.445208	-0.373821	-2.282065
H	-0.116662	2.991166	0.382300
H	-1.723657	3.379924	-0.310064
H	-0.349291	3.004015	-1.393693
H	-0.758361	0.209468	2.197005
H	-0.892373	-1.370824	1.379118
H	-2.377094	-0.484398	1.861696
H	-2.401963	-0.185084	-2.796005
H	-1.372144	-1.458740	-2.079917
H	-0.611308	-0.098316	-2.949115
Si	-4.845283	0.339729	-0.273150
O	-3.298042	0.814438	-0.371289
O	-5.926041	1.600084	-0.349003
O	-5.161895	-0.461343	1.153885
O	-5.269180	-0.712431	-1.493043
Si	-6.845317	-1.278660	-1.469236
Si	-6.730494	-1.009692	1.364318
Si	-7.547610	1.194944	-0.244531
H	-7.141115	-2.194638	-2.574947
H	-6.929932	-1.698686	2.642745
H	-8.433857	2.360189	-0.319361
O	-7.045080	-1.975036	0.036774
O	-7.809386	0.086550	-1.467600
O	-7.701715	0.338291	1.181952
B	2.986317	-0.180779	0.134065
C	3.425900	1.355785	0.037496
C	2.769274	2.356231	0.760267
C	4.471768	1.806967	-0.772198
C	3.053254	3.709803	0.645474
C	4.804639	3.155379	-0.903357
C	4.087687	4.114172	-0.195463
C	3.435594	-1.172573	-1.034800
C	4.041000	-2.407571	-0.783016
C	3.258649	-0.864575	-2.388659
C	4.410524	-3.294545	-1.793823
C	3.602964	-1.723336	-3.424511
C	4.187371	-2.951655	-3.122439
C	2.788110	-0.798004	1.599221
C	3.409639	-0.268685	2.732994
C	1.962507	-1.900861	1.836032
C	3.189807	-0.758966	4.019629
C	1.701026	-2.408263	3.102080
C	2.324994	-1.832129	4.206220
F	2.735712	0.308693	-2.750568
F	3.394659	-1.382380	-4.684830
F	4.530219	-3.778102	-4.090232
F	4.977629	-4.450603	-1.497190
F	4.312853	-2.798869	0.456233
F	5.218605	0.955796	-1.463411
F	5.799426	3.526028	-1.689362
F	4.385830	5.392309	-0.314349
F	2.359064	4.604988	1.328544
F	1.791020	2.035624	1.616616

	F	4.259679	0.746873	2.633546
	F	3.798750	-0.214880	5.058474
	F	2.099621	-2.303043	5.416518
	F	0.875894	-3.428922	3.262630
	F	1.361333	-2.523355	0.819959
	C	0.808078	0.089661	-0.471409
	H	1.224959	0.684920	-1.288569
	H	0.843251	-0.991029	-0.620775
	H	1.032315	0.438677	0.543118

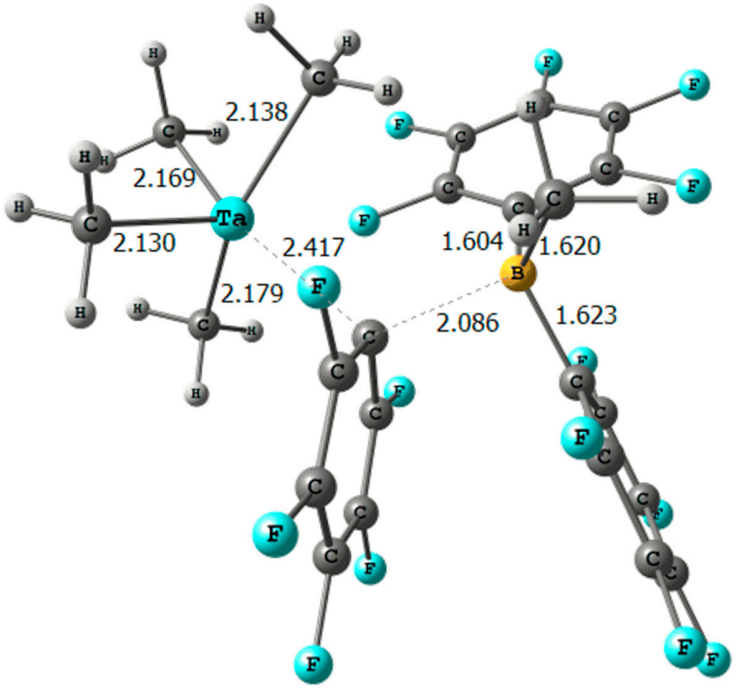
(≡SiO_2-)$TaMe_3^+$



C	3.257810	1.230643	1.551932
C	3.260057	-1.958481	0.290329
C	3.261053	0.729650	-1.840106
H	4.116260	0.748919	2.060654
H	2.475962	1.437445	2.304472
H	3.601753	2.197926	1.135874
H	4.103633	-2.164740	-0.397735
H	2.473446	-2.714101	0.115981
H	3.626157	-2.073724	1.329485
H	2.476631	1.264047	-2.405069
H	3.623484	-0.111640	-2.462868
H	4.107693	1.424478	-1.672154
Si	-0.941657	-0.000043	-0.000836
O	0.731477	-0.000141	-0.000535
O	-1.506482	0.686714	-1.385175
O	-1.505109	0.855545	1.286593
O	-1.505936	-1.542686	0.096491
Si	-3.198883	-1.654070	0.104737
Si	-3.198088	0.917674	1.380523
Si	-3.199609	0.736462	-1.484503
H	-3.668693	-3.036480	0.192253
H	-3.666137	1.684820	2.534655
H	-3.669705	1.352262	-2.725163
O	-3.666821	-0.683072	1.377749
O	-3.668506	-0.851050	-1.279836
O	-3.667584	1.534364	-0.096362
Ta	2.569493	-0.000244	-0.000186

Zero-point correction= 0.169204 (Hartree/Particle)
Thermal correction to Energy= 0.188239
Thermal correction to Enthalpy= 0.189183
Thermal correction to Gibbs Free Energy= 0.118878
Sum of electronic and zero-point Energies= -1861.317057
Sum of electronic and thermal Energies= -1861.298022
Sum of electronic and thermal Enthalpies= -1861.297078
Sum of electronic and thermal Free Energies= -1861.367383

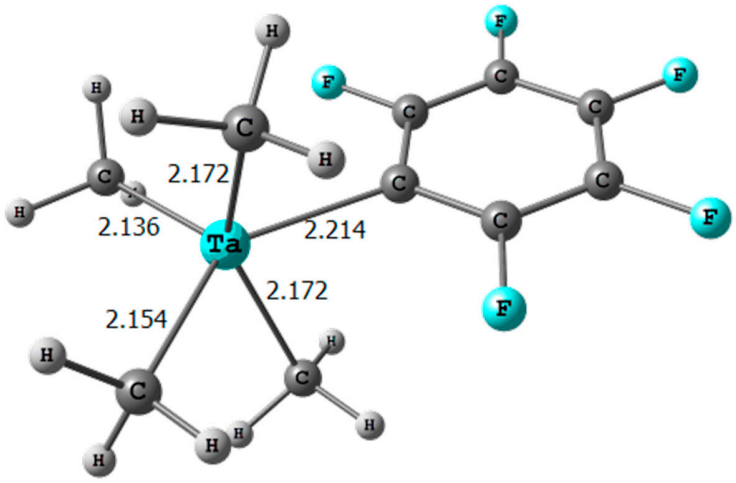
$TaMe_4—(C_6F_5)^-—MeB(C_6F_5)_2$



Zero-point correction= 0.335593 (Hartree/Particle)
Thermal correction to Energy= 0.377614
Thermal correction to Enthalpy= 0.378558
Thermal correction to Gibbs Free Energy= 0.260855
Sum of electronic and zero-point Energies= -2460.259480
Sum of electronic and thermal Energies= -2460.217458
Sum of electronic and thermal Enthalpies= -2460.216514
Sum of electronic and thermal Free Energies= -2460.334218

B	0.427335	0.797983	1.056321
C	-0.552498	1.959176	0.494781
C	-0.334393	3.234734	1.026200
C	-1.618544	1.889279	-0.390921
C	-1.117569	4.345189	0.727787
C	-2.442698	2.964643	-0.713693
C	-2.190057	4.208928	-0.150485
C	0.009411	-0.998597	0.081557
C	0.688676	-0.889704	-1.148685
C	0.420769	-2.091281	0.864111
C	1.706709	-1.744941	-1.543091
C	1.413426	-2.994847	0.516946
C	2.069358	-2.799104	-0.700145
C	1.970178	0.898613	0.564363
C	2.407174	1.732360	-0.471307
C	2.969491	0.106468	1.141242
C	3.727838	1.770850	-0.916597
C	4.295848	0.106481	0.718313
C	4.679782	0.951515	-0.318675
F	-0.232719	-2.312906	2.011876
F	1.744962	-4.007292	1.293006
F	3.022278	-3.622134	-1.063402
F	2.336508	-1.585920	-2.691322
F	0.408447	0.098887	-1.975778
F	-1.944298	0.739862	-1.016927
F	-3.459058	2.800460	-1.547559
F	-2.954263	5.245375	-0.440933
F	-0.852826	5.522592	1.266349
F	0.689975	3.435428	1.854026
F	1.565376	2.535826	-1.111474
F	4.081585	2.578765	-1.900801
F	5.932383	0.973133	-0.731123
F	5.187864	-0.683423	1.293103
F	2.682791	-0.742663	2.130513
C	0.251238	0.587768	2.637162
H	-0.756992	0.827678	3.001669
H	0.539961	-0.392906	3.027359
H	0.922227	1.321082	3.114282
Ta	-2.318885	-1.642895	0.011584
C	-1.921969	-1.901710	-2.115264
C	-2.595227	-3.626048	0.739162
C	-2.970554	-0.226870	1.474682
C	-4.315227	-1.279032	-0.753469
H	-1.724436	-1.013360	-2.730363
H	-2.760637	-2.455403	-2.566887
H	-1.037010	-2.568177	-2.162330
H	-2.811369	-3.681439	1.819856
H	-1.704257	-4.249234	0.535813
H	-3.443500	-4.080738	0.194269
H	-3.651397	-0.867984	2.072904
H	-3.497820	0.699964	1.213339
H	-2.102777	0.011948	2.111193
H	-4.343167	-0.318300	-1.293204
H	-5.041800	-1.227431	0.075213
H	-4.633087	-2.071381	-1.450166

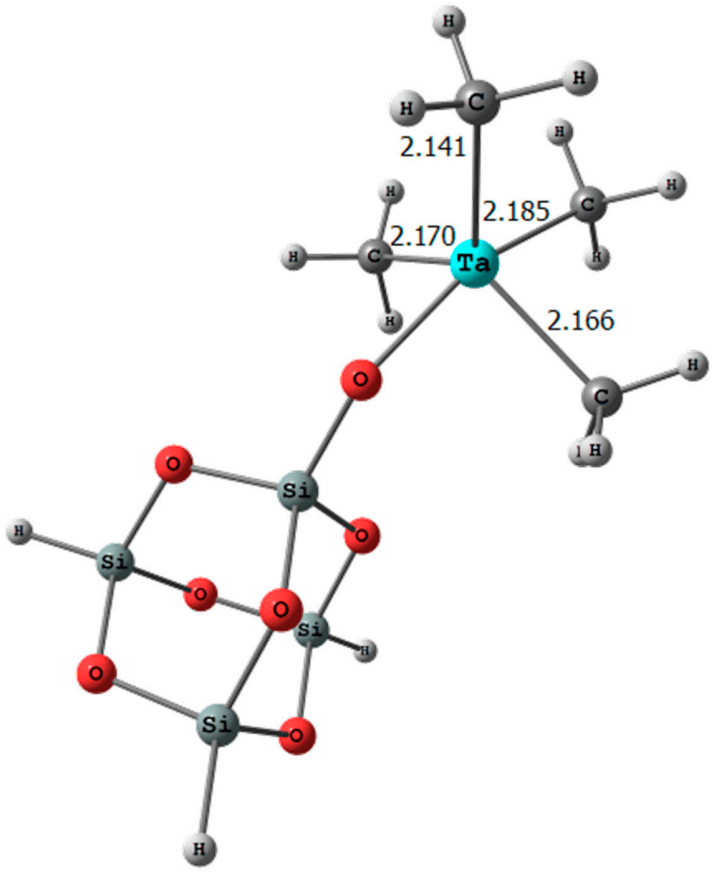
$TaMe_4(C_6F_5)$



Zero-point correction= 0.190071 (Hartree/Particle)
Thermal correction to Energy= 0.210790
Thermal correction to Enthalpy= 0.211734
Thermal correction to Gibbs Free Energy= 0.140642
Sum of electronic and zero-point Energies= -942.670581
Sum of electronic and thermal Energies= -942.649862
Sum of electronic and thermal Enthalpies= -942.648918
Sum of electronic and thermal Free Energies= -942.720010

Ta	-1.598017	0.077558	-0.000025
C	-3.071635	-1.492997	0.000283
C	-1.196598	-0.579137	2.031349
C	-2.541521	1.994245	-0.000131
H	-2.600954	-2.490041	0.001195
H	-3.713189	-1.411775	-0.894875
H	-3.713694	-1.410476	0.894981
H	-2.158883	-0.584824	2.577696
H	-0.539360	0.170645	2.510709
H	-0.721246	-1.565637	2.143342
H	-2.255127	2.581824	-0.892043
H	-2.255926	2.581540	0.892232
H	-3.643264	1.887465	-0.000607
C	0.614506	-0.007699	-0.000021
C	1.337246	1.173934	0.000006
C	1.352035	-1.183986	-0.000051
C	2.729076	1.220470	0.000009
C	2.743115	-1.198123	-0.000031
C	3.431680	0.017017	0.000016
F	0.715492	-2.360332	-0.000047
F	3.421838	-2.333975	-0.000041
F	4.752563	0.023697	0.000052
F	3.383989	2.370352	0.000045
F	0.667176	2.341785	-0.000008
C	-1.196720	-0.579326	-2.031292
H	-0.721494	-1.565913	-2.143175
H	-2.158935	-0.584979	-2.577758
H	-0.539313	0.170289	-2.510692

(≡SiO$_2$-)TaMe$_4$



C	-3.932762	-0.446164	-1.432058
C	-2.045925	1.715896	-1.204033
C	-3.757562	0.329889	1.750036
C	-1.796531	-2.005192	-0.328247
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O	1.874373	1.487959	0.841260
O	1.241066	-0.044732	-1.238792
O	1.698155	-1.147989	1.136494
Si	3.320231	-1.386580	0.817147
Si	2.831996	-0.205266	-1.722737
Si	3.508990	1.433264	0.500936
H	3.876860	-2.554412	1.508280
H	2.977312	-0.377510	-3.172216
H	4.224358	2.641306	0.925210
O	3.443253	-1.491387	-0.847136
O	4.078700	0.043590	1.235411
O	3.619677	1.150588	-1.143346
Ta	-2.438458	0.024971	0.091561

Zero-point correction= 0.206285 (Hartree/Particle)
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Sum of electronic and thermal Enthalpies= -1901.318762
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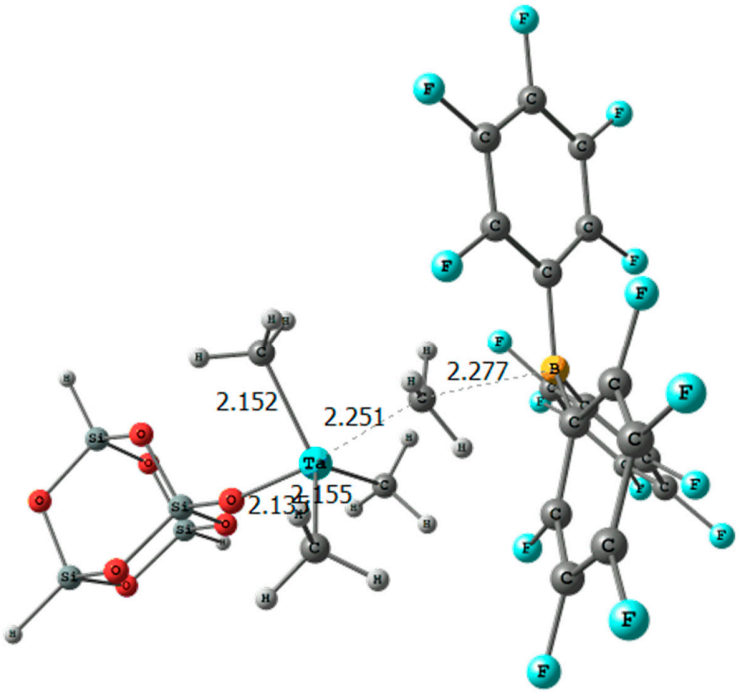
(≡SiO_2-)WMe_4—CH_3^-—$B(C_6F_5)_3$



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Thermal correction to Enthalpy= 0.415956
Thermal correction to Gibbs Free Energy= 0.280204
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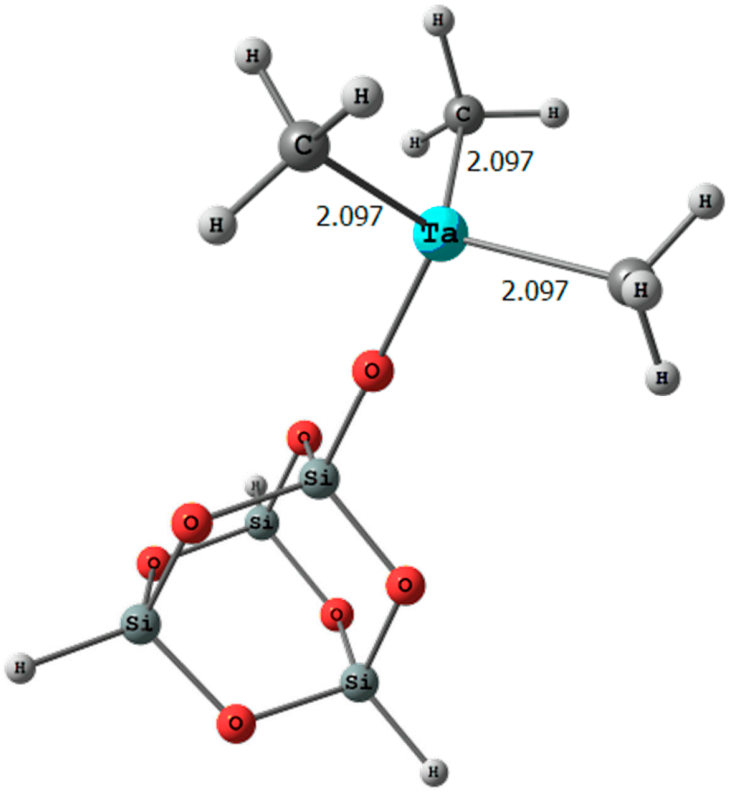
Sum of electronic and thermal Energies= -4105.605758
Sum of electronic and thermal Enthalpies= -4105.604813
Sum of electronic and thermal Free Energies= -4105.740565

Ta	-1.361976	0.683235	-0.409982
C	-0.825574	2.749446	-0.428398
C	-1.353706	-0.372999	1.468160
C	-1.445208	-0.373821	-2.282065
H	-0.116662	2.991166	0.382300
H	-1.723657	3.379924	-0.310064
H	-0.349291	3.004015	-1.393693
H	-0.758361	0.209468	2.197005
H	-0.892373	-1.370824	1.379118
H	-2.377094	-0.484398	1.861696
H	-2.401963	-0.185084	-2.796005
H	-1.372144	-1.458740	-2.079917
H	-0.611308	-0.098316	-2.949115
Si	-4.845283	0.339729	-0.273150
O	-3.298042	0.814438	-0.371289
O	-5.926041	1.600084	-0.349003
O	-5.161895	-0.461343	1.153885
O	-5.269180	-0.712431	-1.493043
Si	-6.845317	-1.278660	-1.469236
Si	-6.730494	-1.009692	1.364318
Si	-7.547610	1.194944	-0.244531
H	-7.141115	-2.194638	-2.574947
H	-6.929932	-1.698686	2.642745
H	-8.433857	2.360189	-0.319361
O	-7.045080	-1.975036	0.036774
O	-7.809386	0.086550	-1.467600
O	-7.701715	0.338291	1.181952
B	2.986317	-0.180779	0.134065
C	3.425900	1.355785	0.037496
C	2.769274	2.356231	0.760267
C	4.471768	1.806967	-0.772198
C	3.053254	3.709803	0.645474
C	4.804639	3.155379	-0.903357
C	4.087687	4.114172	-0.195463
C	3.435594	-1.172573	-1.034800
C	4.041000	-2.407571	-0.783016
C	3.258649	-0.864575	-2.388659
C	4.410524	-3.294545	-1.793823
C	3.602964	-1.723336	-3.424511
C	4.187371	-2.951655	-3.122439
C	2.788110	-0.798004	1.599221
C	3.409639	-0.268685	2.732994
C	1.962507	-1.900861	1.836032
C	3.189807	-0.758966	4.019629
C	1.701026	-2.408263	3.102080
C	2.324994	-1.832129	4.206220
F	2.735712	0.308693	-2.750568
F	3.394659	-1.382380	-4.684830
F	4.530219	-3.778102	-4.090232
F	4.977629	-4.450603	-1.497190
F	4.312853	-2.798869	0.456233
F	5.218605	0.955796	-1.463411
F	5.799426	3.526028	-1.689362
F	4.385830	5.392309	-0.314349
F	2.359064	4.604988	1.328544
F	1.791020	2.035624	1.616616

	F	4.259679	0.746873	2.633546
	F	3.798750	-0.214880	5.058474
	F	2.099621	-2.303043	5.416518
	F	0.875894	-3.428922	3.262630
	F	1.361333	-2.523355	0.819959
	C	0.808078	0.089661	-0.471409
	H	1.224959	0.684920	-1.288569
	H	0.843251	-0.991029	-0.620775
	H	1.032315	0.438677	0.543118

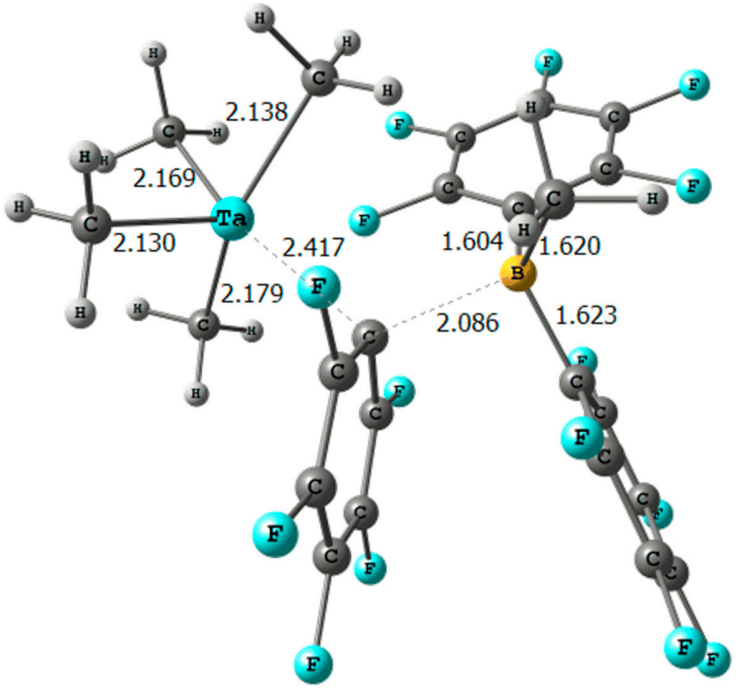
(≡SiO_2-)$TaMe_3^+$



C	3.257810	1.230643	1.551932
C	3.260057	-1.958481	0.290329
C	3.261053	0.729650	-1.840106
H	4.116260	0.748919	2.060654
H	2.475962	1.437445	2.304472
H	3.601753	2.197926	1.135874
H	4.103633	-2.164740	-0.397735
H	2.473446	-2.714101	0.115981
H	3.626157	-2.073724	1.329485
H	2.476631	1.264047	-2.405069
H	3.623484	-0.111640	-2.462868
H	4.107693	1.424478	-1.672154
Si	-0.941657	-0.000043	-0.000836
O	0.731477	-0.000141	-0.000535
O	-1.506482	0.686714	-1.385175
O	-1.505109	0.855545	1.286593
O	-1.505936	-1.542686	0.096491
Si	-3.198883	-1.654070	0.104737
Si	-3.198088	0.917674	1.380523
Si	-3.199609	0.736462	-1.484503
H	-3.668693	-3.036480	0.192253
H	-3.666137	1.684820	2.534655
H	-3.669705	1.352262	-2.725163
O	-3.666821	-0.683072	1.377749
O	-3.668506	-0.851050	-1.279836
O	-3.667584	1.534364	-0.096362
Ta	2.569493	-0.000244	-0.000186

Zero-point correction= 0.169204 (Hartree/Particle)
Thermal correction to Energy= 0.188239
Thermal correction to Enthalpy= 0.189183
Thermal correction to Gibbs Free Energy= 0.118878
Sum of electronic and zero-point Energies= -1861.317057
Sum of electronic and thermal Energies= -1861.298022
Sum of electronic and thermal Enthalpies= -1861.297078
Sum of electronic and thermal Free Energies= -1861.367383

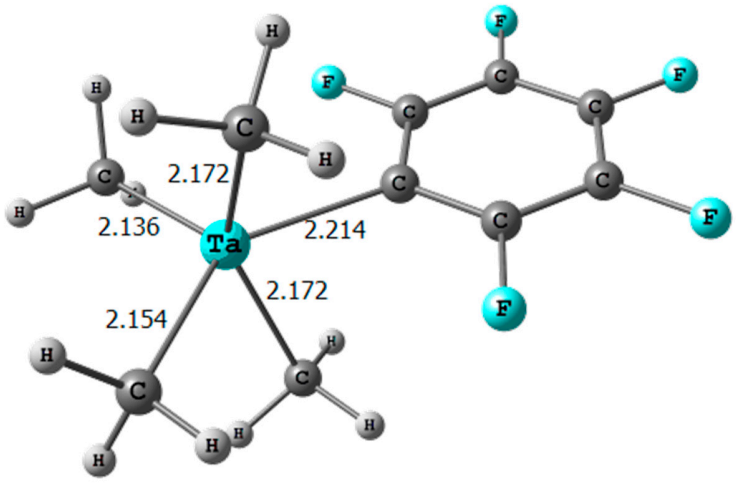
$TaMe_4—(C_6F_5)^-—MeB(C_6F_5)_2$



Zero-point correction= 0.335593 (Hartree/Particle)
Thermal correction to Energy= 0.377614
Thermal correction to Enthalpy= 0.378558
Thermal correction to Gibbs Free Energy= 0.260855
Sum of electronic and zero-point Energies= -2460.259480
Sum of electronic and thermal Energies= -2460.217458
Sum of electronic and thermal Enthalpies= -2460.216514
Sum of electronic and thermal Free Energies= -2460.334218

B	0.427335	0.797983	1.056321
C	-0.552498	1.959176	0.494781
C	-0.334393	3.234734	1.026200
C	-1.618544	1.889279	-0.390921
C	-1.117569	4.345189	0.727787
C	-2.442698	2.964643	-0.713693
C	-2.190057	4.208928	-0.150485
C	0.009411	-0.998597	0.081557
C	0.688676	-0.889704	-1.148685
C	0.420769	-2.091281	0.864111
C	1.706709	-1.744941	-1.543091
C	1.413426	-2.994847	0.516946
C	2.069358	-2.799104	-0.700145
C	1.970178	0.898613	0.564363
C	2.407174	1.732360	-0.471307
C	2.969491	0.106468	1.141242
C	3.727838	1.770850	-0.916597
C	4.295848	0.106481	0.718313
C	4.679782	0.951515	-0.318675
F	-0.232719	-2.312906	2.011876
F	1.744962	-4.007292	1.293006
F	3.022278	-3.622134	-1.063402
F	2.336508	-1.585920	-2.691322
F	0.408447	0.098887	-1.975778
F	-1.944298	0.739862	-1.016927
F	-3.459058	2.800460	-1.547559
F	-2.954263	5.245375	-0.440933
F	-0.852826	5.522592	1.266349
F	0.689975	3.435428	1.854026
F	1.565376	2.535826	-1.111474
F	4.081585	2.578765	-1.900801
F	5.932383	0.973133	-0.731123
F	5.187864	-0.683423	1.293103
F	2.682791	-0.742663	2.130513
C	0.251238	0.587768	2.637162
H	-0.756992	0.827678	3.001669
H	0.539961	-0.392906	3.027359
H	0.922227	1.321082	3.114282
Ta	-2.318885	-1.642895	0.011584
C	-1.921969	-1.901710	-2.115264
C	-2.595227	-3.626048	0.739162
C	-2.970554	-0.226870	1.474682
C	-4.315227	-1.279032	-0.753469
H	-1.724436	-1.013360	-2.730363
H	-2.760637	-2.455403	-2.566887
H	-1.037010	-2.568177	-2.162330
H	-2.811369	-3.681439	1.819856
H	-1.704257	-4.249234	0.535813
H	-3.443500	-4.080738	0.194269
H	-3.651397	-0.867984	2.072904
H	-3.497820	0.699964	1.213339
H	-2.102777	0.011948	2.111193
H	-4.343167	-0.318300	-1.293204
H	-5.041800	-1.227431	0.075213
H	-4.633087	-2.071381	-1.450166

$TaMe_4(C_6F_5)$



Zero-point correction= 0.190071 (Hartree/Particle)
Thermal correction to Energy= 0.210790
Thermal correction to Enthalpy= 0.211734
Thermal correction to Gibbs Free Energy= 0.140642
Sum of electronic and zero-point Energies= -942.670581
Sum of electronic and thermal Energies= -942.649862
Sum of electronic and thermal Enthalpies= -942.648918
Sum of electronic and thermal Free Energies= -942.720010

Ta	-1.598017	0.077558	-0.000025
C	-3.071635	-1.492997	0.000283
C	-1.196598	-0.579137	2.031349
C	-2.541521	1.994245	-0.000131
H	-2.600954	-2.490041	0.001195
H	-3.713189	-1.411775	-0.894875
H	-3.713694	-1.410476	0.894981
H	-2.158883	-0.584824	2.577696
H	-0.539360	0.170645	2.510709
H	-0.721246	-1.565637	2.143342
H	-2.255127	2.581824	-0.892043
H	-2.255926	2.581540	0.892232
H	-3.643264	1.887465	-0.000607
C	0.614506	-0.007699	-0.000021
C	1.337246	1.173934	0.000006
C	1.352035	-1.183986	-0.000051
C	2.729076	1.220470	0.000009
C	2.743115	-1.198123	-0.000031
C	3.431680	0.017017	0.000016
F	0.715492	-2.360332	-0.000047
F	3.421838	-2.333975	-0.000041
F	4.752563	0.023697	0.000052
F	3.383989	2.370352	0.000045
F	0.667176	2.341785	-0.000008
C	-1.196720	-0.579326	-2.031292
H	-0.721494	-1.565913	-2.143175
H	-2.158935	-0.584979	-2.577758
H	-0.539313	0.170289	-2.510692

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