

Supporting Information

Selective Activation of the C–H Bond in Methane by Single Platinum Atomic Anions

*Gaoxiang Liu, Zhaoguo Zhu, Sandra M. Ciborowski, Isuru R. Ariyaratna, Evangelos Miliordos, and Kit H. Bowen**

anie_201903252_sm_miscellaneous_information.pdf

Experimental Method

Anion photoelectron spectroscopy is conducted by crossing a beam of mass-selected negative ions with a fixed-frequency photon beam and energy-analyzing the resultant photodetached electrons. The photodetachment process is governed by the energy-conserving relationship: $h\nu = \text{EBE} + \text{EKE}$, where $h\nu$ is the photon energy, EBE is the electron binding energy, and EKE is the electron kinetic energy. Our apparatus consists of a laser vaporization cluster anion source with an attached ligation cell, a time-of-flight mass spectrometer, a Nd:YAG photodetachment laser (operating at 355 nm), and a magnetic bottle electron energy analyzer with a resolution is ~ 35 meV at 1 eV EKE.¹ Photoelectron spectra were calibrated against the well-known atomic transitions of atomic Cu^- .²

The interaction between Pt^- and methane (CH_4 , CD_4) was studied using a laser vaporization-reaction cell arrangement.³ Atomic platinum anions were generated by laser vaporization of a pure platinum foil wrapped around an aluminum rod. The resultant plasma was cooled with helium gas delivered by a pulsed valve, having a backing pressure of 80 psig. The resulting platinum anions then traveled through a ligation cell (4-mm diameter, 5-cm length), where it encountered CH_4 or CD_4 . The methane was introduced into the ligation cell by a second pulsed valve, backed by 15 psig of CH_4 or CD_4 . The resulting $[\text{PtCH}_4]^-$ and $[\text{Pt}(\text{CD}_4)]^-$ anionic clusters were then mass-analyzed and mass-selected by the time-of-flight mass spectrometer and their photoelectron spectra measured.

Computational Methods

Density functional theory (DFT) calculations The ORCA computational chemistry software package was used.⁴ All calculations were carried out with the PBE0 functional^{5,6} with the D3 dispersion correction⁷ and the RJCOSX approximation⁸. The Ahlrichs Def2 basis sets, Def2-TZVPP were used for geometry optimization.⁹ The Stuttgart effective core potential, SDD¹⁰ and the ECP basis set, Def2-QZVPP|Def2-QZVPP/J were used for the platinum atoms. Frequency calculations were performed to verify that no imaginary frequencies existed and all optimized structures were minima, and the transition states had one imaginary frequency connecting the correct intermediates.

CCSD(T) and MRCI+Q calculations To get more accurate energetics of the different isomers and the transition states connecting them, we performed single point CCSD(T) calculations using the DFT optimized geometries. We used the DFT frequencies to calculate the zero-point energy of each structure, which is then added to the CCSD(T) energies. The optimal geometries for the $\text{Pt}(\text{CH}_4)$ and HPtCH_3^-

structures were refined at the MRCI+Q level of theory and found in excellent agreement with the DFT ones. Using these MRCI+Q geometries, we calculated the CCSD(T) electron affinity and MRCI+Q vertical excitation energies of Pt(CH₄) and HPtCH₃. The CASSCF active space consists of the full valence space except for the three orbitals corresponding to the three σ_{CH} bonds of the CH₃ moiety. All valence electrons are correlated at the MRCI level.

In all of our calculations the aug-cc-pVQZ basis set is used for carbon and hydrogen centers. The 60 inner 1s² through 4d¹⁰ electrons of platinum were replaced by the relativistic Stuttgart pseudopotentials and the rest electrons were treated with the aug-cc-pwCVQZ-PP basis set.¹¹ To include the correlation of the sub-valence electrons, all explicit electrons of platinum are correlated. The final VDE value for an electronic state S of HPtCH₃ is obtained as (X is the ground state of HPtCH₃):

$$\text{VDE}(S) = E(X) - E(X^-) + T(S),$$

where:

$E(X)$... CCSD(T) energy of the ground state of HPtCH₃

$E(X^-)$... CCSD(T) energy of the ground state of HPtCH₃⁻

$T(S)$... MRCI+Q excitation energy for state S of HPtCH₃ at the geometry of HPtCH₃⁻

All calculations were done with MOLPRO 2015.1.¹²

Results

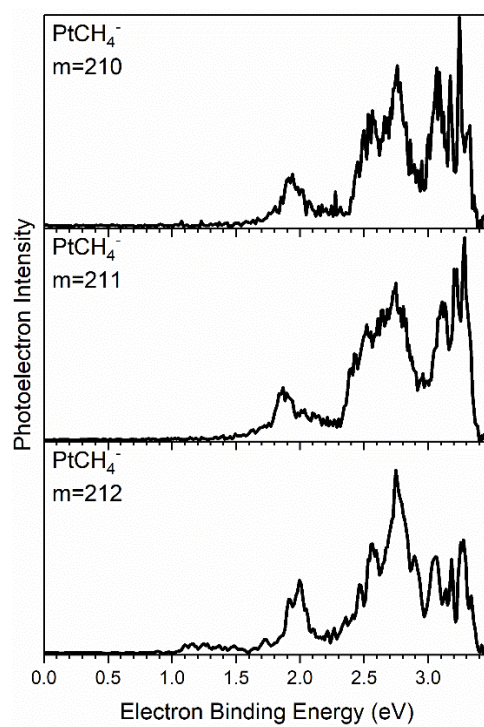


Figure S1. Photoelectron spectra of different isotopes of $[\text{PtCH}_4]^-$ taken with 355 nm (3.496 eV) photon.

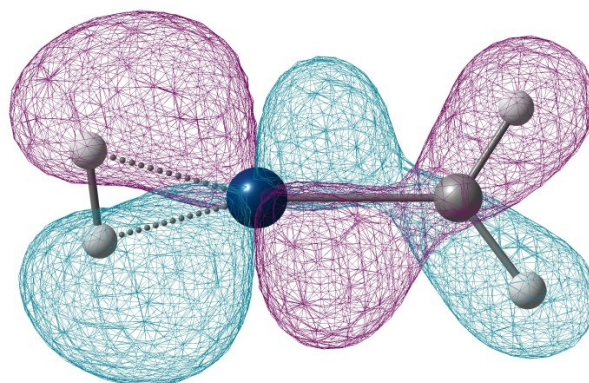


Figure S2. Molecular orbital of $(\text{H}_2)\text{-Pt-CH}_2^-$ that shows back-donation from Pt-carbene moiety to the antibonding σ^* orbital of H_2 .

Table S1. Relative energies (eV) of [PtCD₄]⁻ complexes at CCSD(T) level.

[Pt(CD ₄)] ⁻ structure	Energy
Pt ⁻ + CD ₄	0.000
1	-0.085
TS1/2	0.370
2	-0.667
TS2/3	0.179
3	0.061
TS3/4	0.045
4	-0.007
D ₂ + PtCD ₂ ⁻	0.963
TS3/5	0.969
5	0.970

Cartesian coordinates (Å) and harmonic vibrational frequencies (cm⁻¹) for all intermediates and transition states. The frequencies of [PtCD₄]⁻ are provided in *italic* below the frequencies of [PtCH₄]⁻.

1, Pt⁻(CH₄)

C 3.560159 -0.000040 0.000024
H 3.924486 -0.010254 -1.028578
H 3.927077 -0.884619 0.523166
H 2.464719 -0.001246 0.000775
H 3.924296 0.896486 0.504477
Pt -0.456430 -0.000002 0.000000

67.1 137.2 137.5 1284.3 1337.2 1337.4 1543.5 1543.6 2980.0 3095.9 3132.5 3132.7
60.5 97.4 97.7 970.3 1010.2 1010.3 1091.9 1091.9 2113.3 2289.0 2318.3 2318.5

2, H-Pt-CH₃⁻

C -1.838433 0.067074 -0.000090
Pt 0.208349 -0.019727 -0.000008
H -2.239137 0.562315 -0.893791
H -2.237645 0.566465 0.892024
H -2.206881 -0.974453 0.002840
H 1.463070 0.981901 0.000083

196.9 418.2 498.0 665.8 676.0 1114.0 1409.0 1434.0 1948.1 2934.9 3015.5 3043.3
140.1 297.7 439.2 496.9 518.8 872.0 1024.6 1042.8 1382.4 2105.9 2221.9 2252.4

3, H₂-Pt-CH₂⁻

C	-1.806053	0.025243	0.000178
Pt	0.169447	-0.018137	-0.000134
H	-2.449058	0.032964	-0.894355
H	-2.447519	0.020881	0.895852
H	1.803244	-0.198912	0.000337
H	0.712754	1.408307	0.007545

212.3	275.1	459.8	504.8	585.5	748.1	788.0	1380.1	1916.9	2356.6	2964.6	3011.7
150.5	197.9	327.7	384.2	505.4	571.6	625.3	1035.2	1360.2	1671.9	2147.2	2231.5

4, (H₂)-Pt-CH₂⁻

C	-1.811540	-0.000028	-0.000012
Pt	0.157914	-0.000027	-0.000002
H	-2.439906	-0.892942	-0.100222
H	-2.438102	0.894218	0.100388
H	1.715141	-0.453866	0.197285
H	1.714831	0.454837	-0.197258

249.5	331.9	374.8	516.7	563.6	637.2	949.3	1358.8	2079.4	2257.7	3019.2	3074.8
176.5	239.5	268.0	441.7	455.1	498.9	703.9	1023.6	1473.5	1600.2	2188.1	2278.9

5, H₃-Pt-CH⁻

C	1.696718	0.000109	0.000006
Pt	-0.126567	0.000025	-0.000002
H	-0.666045	1.513521	0.000050
H	2.790305	0.000160	0.000011
H	-0.662591	-1.514390	0.000050
H	-1.769751	-0.001886	0.000025

66.6	94.2	440.7	556.9	584.4	798.9	808.3	887.0	1997.4	2009.9	2154.2	3103.2
49.8	67.8	318.3	397.2	429.6	580.3	696.3	760.9	1420.9	1428.3	1525.0	2295.4

H₄-Pt-C⁻

C	1.649613	-0.000136	0.000029
Pt	-0.089660	-0.000009	0.000000
H	-1.065207	-0.000491	-1.321763
H	-0.385834	1.596921	-0.000937
H	-0.387555	-1.596708	0.000949
H	-1.065592	0.001788	1.321546

109.1	246.7	495.1	627.3	683.6	704.0	779.6	957.6	1812.5	1912.1	1918.1	2193.0
83.7	185.7	350.6	446.6	487.1	503.1	551.4	952.1	1289.5	1362.4	1364.3	1551.7

Pt-CH₂⁻

C	-1.654511	0.000001	-0.000113
Pt	0.184358	0.000000	0.000002
H	-2.226425	-0.932673	0.000259
H	-2.226442	0.932662	0.000259

150.0	718.5	736.1	1328.0	3019.8	3105.9	4404.9
117.3	540.6	659.8	1031.9	2180.0	2311.0	3115.9

TS1/2

Pt	0.248718	-0.003092	-0.000000
C	-1.927680	-0.036960	-0.000007
H	-0.987776	0.975490	0.000039
H	-2.075622	-0.634663	0.902727
H	-2.694604	0.755979	0.000513
H	-2.075955	-0.633836	-0.903230

-586.4	71.7	485.9	822.9	920.9	1186.0	1428.9	1434.6	2177.7	2943.9	3045.3	3112.0
-449.1	50.9	410.8	610.7	706.3	893.8	1036.2	1042.0	1546.8	2118.6	2236.4	2308.6

TS2/3

C	-1.746798	-0.098545	0.000060
Pt	0.174648	-0.002783	-0.000000
H	-2.362125	-0.061797	0.909116

H -2.362050 -0.063162 -0.909103
H -0.201068 1.488782 -0.000685
H 1.783496 -0.555506 0.000332

-358.0 235.4 290.5 499.9 645.6 740.1 746.2 1356.2 1755.9 2282.3 2987.3 3054.1
-255.8 167.1 212.1 355.5 558.6 567.4 610.5 1027.0 1245.4 1619.5 2160.8 2267.0

TS3/4

C 1.842032 0.026242 0.022241
Pt -0.167221 -0.009208 -0.006895
H 2.487782 0.822105 -0.374406
H 2.477604 -0.791055 0.395193
H -1.255737 0.896543 0.595766
H -1.718596 -0.366809 -0.212200

-242.7 305.0 391.4 490.7 518.9 692.0 711.0 1369.2 2061.6 2326.7 2984.9 3037.5
-176.5 218.0 279.5 356.8 458.2 534.2 561.5 1024.4 1462.7 1650.4 2162.9 2249.8

TS3/5

C 1.689527 -0.152819 -0.000077
Pt -0.133917 -0.004816 0.000003
H 0.411401 1.514519 0.000107
H 2.721914 0.208520 0.000203
H -1.257879 -1.184955 0.000094
H -1.567107 0.754467 -0.000215

-201.0 147.4 346.9 586.4 611.4 752.3 803.9 885.6 1934.5 2056.6 2157.0 3099.4
-146.2 110.6 250.3 420.9 444.4 541.1 685.3 762.1 1375.5 1460.4 1527.1 2290.3

References

1. X. Zhang, G. Liu, G. Ganteför, K.H. Bowen, A.N. Alexandrova, *J. Phys. Chem. Lett.* **2014**, *5*, 1596-1601.
2. J. Ho, K.M. Ervin, W.C Lineberger, *J. Chem. Phys.* **1990**, *93*, 6987-7002.
3. G. Liu, S. Ciborowski, K. Bowen, *J. Phys. Chem. A* **2017**, *121*, 5817-5822.
4. F. Neese, *WIREs Comput. Mol. Sci.* **2012**, *2*, 73-78.
5. J. P. Perdew, M. Ernzerhof, K. Burke, *J. Chem. Phys.* **1996**, *105*, 9982-9985.
6. J.P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, *77*, 3865-3868.
7. S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* **2010**, *132*, 154104.
8. F. Neese, F. Wennmohs, A. Hansen, U. Becker, *Chem. Phys.* **2008**, *356*, 98-109.
9. F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297-3305.
10. D. Andrae, U. Häußermann, M. Dolg, H. Stoll, H. Preuß, *Theor. Chim. Acta* **1990**, *77*, 123-141.
11. K. A. Peterson, D. Figgen, M. Dolg and H. Stoll, *J. Chem. Phys.*, **2007**, *126*, 124101.
12. H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, M. Schütz, et al., MOLPRO, version 2015.1, a package of ab initio programs, see <http://www.molpro.net> (Accessed: 1/17/2019).