Electronic Supplementary Information

Theoretical Quest for the Titanium–Substituted Hydrocarbons

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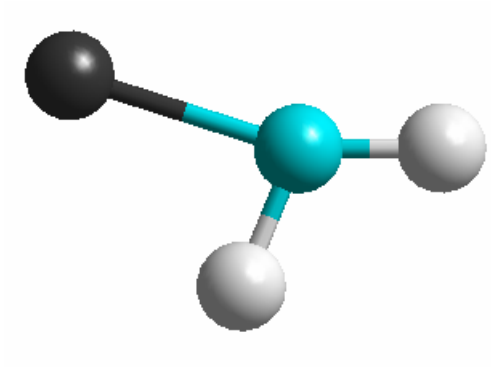
1. **Molecular formula and multiplicity, energy, chosen optimized geometric parameters, Mulliken charges, dipole moment, energy of frontier orbitals, the HOMO/LUMO gap, and harmonic frequencies for molecules studied. Isomers are listed in the order of increasing electronic energy; isomers with imaginary frequencies are listed at the end of each series (only energy and imaginary frequencies are given). C – blue, Ti – black, H – white balls.**

Monomers

$TiCH_2$

(i) $^3TiCH_2$, E = –888.592362435 au



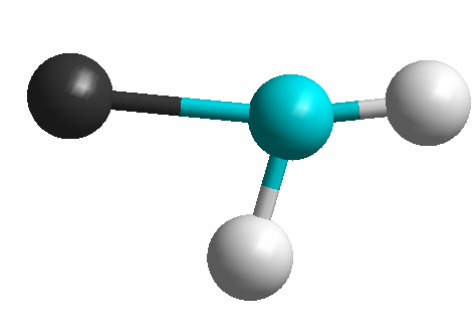
R(Ti–C) = 1.814 Å, R(C–H) = 1.085 Å, 1.126 Å, R(Ti–H) = 2.053 Å, α(TiCH) = 85.1°, 162.0°.

q(Ti) = +0.498 e, q(C) = –0.674 e, q(H_C) = +0.055 e, +0.0121 e, μ_{DIP} = 3.1 D.

$E_{SOMO,\alpha}$ (A') = –0.189 au, $E_{SOMO+1,\alpha}$ (A') = –0.169 au, ΔE = 0.020 au.

Harmonic frequencies (cm^{-1}): ν1 (A') = 436, ν2 (A'') = 457, ν3 (A') = 787, ν4 (A') = 1330, ν5 (A') = 2762, ν6 (A') = 3184.

(ii) $^1TiCH_2$, E = –888.575128306 au



R(Ti–C) = 1.747 Å, R(C–H) = 1.086 Å, 1.149 Å, R(Ti–H) = 1.906 Å, α(TiCH) = 168.6°, 112.0°.

q(Ti) = +0.303 e, q(C) = –0.315 e, q(H_C) = +0.085 e, –0.073 e, μ_{DIP} = 1.8 D.

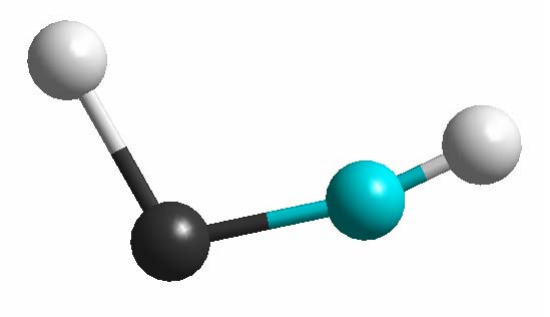
E_{HOMO} = –0.173 au, E_{LUMO} = –0.100 au, ΔE_{HL} = 0.073 au.

Harmonic frequencies (cm^{-1}): ν1 (A'') = 598, ν2 (A') = 634, ν3 (A'') = 871, ν4 (A'') = 1415, ν5 (A'') = 2534, ν6 (A'') = 3184.

(iii) ^{1}HTiCH, bent acetylene-like (cis), E = –888.562309250 au

R(Ti–C) = 1.689 Å, R(Ti–H) = 1.770 Å, R(C–H) = 1.093 Å, α(HTiC) = 166.4°, α(TiCH) = 107.8°.

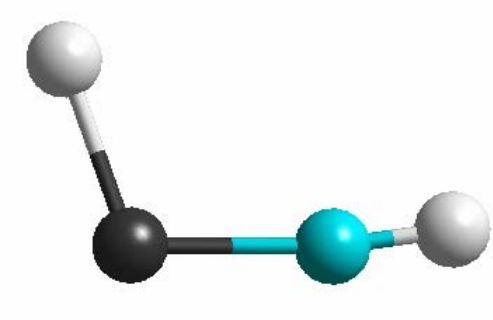
q(Ti) = +1.175 e, q(C) = –0.820 e, q(H_{Ti}) = –0.438 e, q(H_C) = +0.082 e, μ_{DIP} = 5.2 D.



E_{HOMO} (A') = –0.199 au, E_{LUMO} (A') = –0.093 au, ΔE_{HL} = 0.106 au.

Harmonic frequencies (cm^{-1}): ν1 (A') = 422, ν2 (A') = 597, ν3 (A'') = 619, ν4 (A') = 987, ν5 (A') = 1553, ν6 (A') = 3109.

(vi) ^{3}HTiCH, bent acetylene-like (cis), E = –888.535691885 au



R(Ti–C) = 1.820 Å, R(Ti–H) = 1.750 Å, R(C–H) = 1.092 Å, α(HTiC) = 109.1°, α(TiCH) = 171.7°.

q(Ti) = +0.785 e, q(C) = –0.587 e, q(H_{Ti}) = –0.309 e, q(H_C) = +0.112 e, μ_{DIP} = 4.4 D.

$E_{SOMO,\alpha}$ (A'') = –0.210 au, $E_{SOMO+1,\alpha}$ (A') = –0.183 au, ΔE_{HL} = 0.027 au.

Harmonic frequencies (cm^{-1}): ν1 (A') = 338, ν2 (A') = 483, ν3 (A'') = 531, ν4 (A') = 841, ν5 (A') = 1552, ν6 (A') = 3134.

(v) $TiCH_2$, (H_2CO–like), E = –888.570137523 au

Harmonic frequencies (cm^{-1}): one img ν1 (B2) = –245.

(vi) Linear acetylene-like, HTiCH, E = –888.540431756 au

Harmonic frequencies (cm^{-1}): two img ν1 (π) = –383, ν2 (π) = –383.

(vii) H_2TiC (H_2CO–like), E = –888.441167298 au

Harmonic frequencies (cm^{-1}): one img ν1 (B2) = –659.

(viii) Bent acetylene-like, trans form

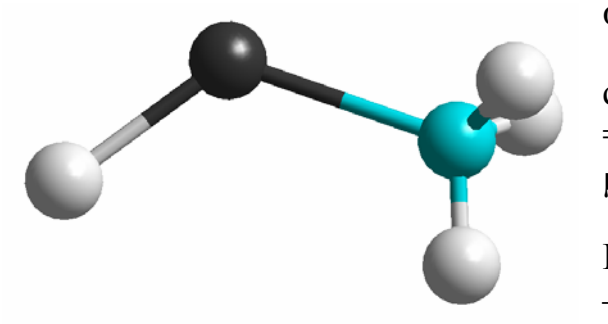
Converges to bent acetylene, cis form.

(ix) TiHHC (two H atoms symmetrically bridging Ti and C)

Converges to (v).

$TiCH_4$

(i) $^3HTiCH_3$, E = –889.845591089 au



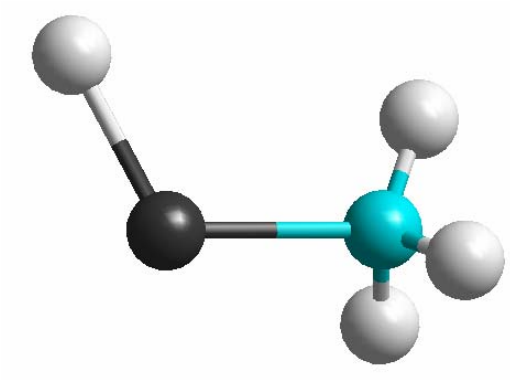
R(Ti–C) = 2.106 Å, R(Ti–H) = 1.762 Å, R(C–H) = 1.096, 1.100 x2 Å, α(HTiC) = 123.7°.

q(Ti) = +0.649 e, q(C) = –0.645 e, $q(H_{Ti})$ = –0.387 e, $q(H_C)$ = 0.113 x2, 0.157 e, μ_{DIP} = 2.7 D.

$E_{SOMO,\alpha}$ (A) = –0.204 au, $E_{SOMO+1,\alpha}$ (A) = –0.185 au, ΔE = 0.019 au.

Harmonic frequencies – all of A symmetry (cm^{-1}): 149, 297, 387, 453, 562, 1151, 1418, 1424, 1558, 2965, 3029, 3064.

(ii) $^1HTiCH_3$, E = –889.810868406 au



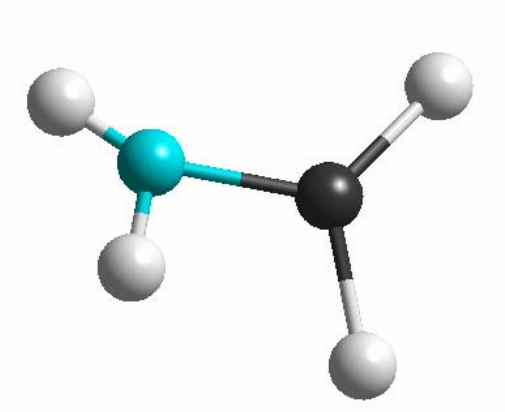
R(Ti–C) = 2.033 Å, R(Ti–H) = 1.697 Å, R(C–H) = 1.093, 1.100, 1.101 Å, α(HTiC) = 112.9°.

q(Ti) = +0.101 e, q(C) = –0.395 e, $q(H_{Ti})$ = –0.196 e, $q(H_C)$ = 0.128, 0.129, 0.233 e, μ_{DIP} = 2.1 D.

E_{HOMO} (A) = –0.168 au, E_{LUMO} (A) = –0.091 au, ΔE_{HL} = 0.077 au.

Harmonic frequencies – all of A symmetry (cm^{-1}): 198, 267, 372, 471, 585, 1116, 1390, 1419, 1669, 2961, 3038, 3104.

(iii) $^1H_2TiCH_2$, non planar, E = –889.808988239 au



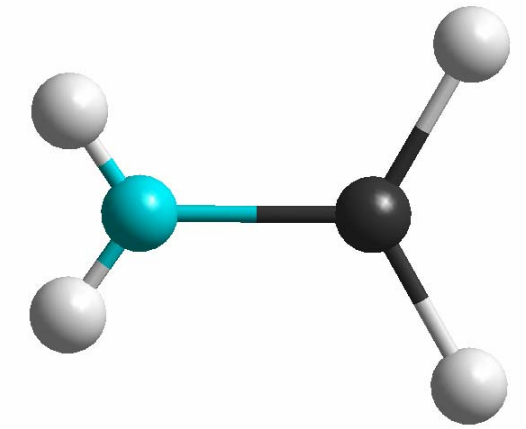
R(Ti–C) = 1.798 Å, R(Ti–H) = 1.732, 1.741 Å, R(C–H) = 1.087, 1.118 Å, α(HTiH) = 111.0°, α(HCH) = 114.6°.

q(Ti) = +1.217 e, q(C) = –0.235 e, $q(H_{Ti})$ = –0.380, –0.394 e, $q(H_C)$ = 0.139, 0.052 e, μ_{DIP} = 1.2 D.

E_{HOMO} (A) = –0.245 au, E_{LUMO} (A) = –0.113 au, ΔE_{HL} = 0.132 au.

Harmonic frequencies – all of A symmetry (cm^{-1}): 94, 317, 481, 537, 668, 693, 835, 1315, 1617, 1662, 2854, 3179.

(iv) $^3H_2TiCH_2$, minor distortions from planarity, E = –889.790990276 au



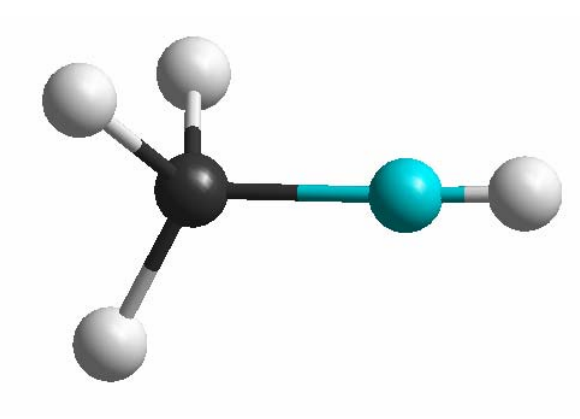
R(Ti–C) = 2.049 Å, R(Ti–H) = 1.738 x2 Å, R(C–H) = 1.095 x2 Å, α(HTiH) = 120.9°, α(HCH) = 110.9°.

$q(Ti) = +0.813$ e, $q(C) = -0.459$ e, $q(H_{Ti}) = -0.318$ e, $q(H_C) = 0.141$ e, $\mu_{DIP} = 1.5$ D.

$E_{SOMO,\alpha}$ (A) = –0.263 au, $E_{SOMO+1,\alpha}$ (A) = –0.224 au, ΔE = 0.039 au.

Harmonic frequencies – all of A symmetry (cm^{-1}): 192, 220, 269, 518, 551, 637, 696, 1346, 1615, 1636, 3038, 3120.

(v) $^1H_3TiCH$, E = –889.683928208 au



R(Ti–C) = 1.975 Å, R(Ti–H) = 1.705, 1.705, 1.683 Å, R(C–H) = 1.092 Å, α(HCTi) = 176.4°.

$q(Ti) = +1.292$ e, $q(C) = -0.388$ e, $q(H_{Ti}) = -0.374, -0.374, -0.348$ e $q(H_C) = 0.193$ e, $\mu_{DIP} = 2.4$ D.

E_{HOMO} (A) = –0.255 au, E_{LUMO} (A) = –0.197 au, $\Delta E_{HL} = 0.058$ au.

Harmonic frequencies – all of A symmetry (cm^{-1}): 134, 292, 389, 458, 573, 625, 668, 736, 1655, 1669, 1737, 3146.

(vi) $^1H_2TiCH_2$, distorted C_2H_4-like, planar, E = –889.808971285 au

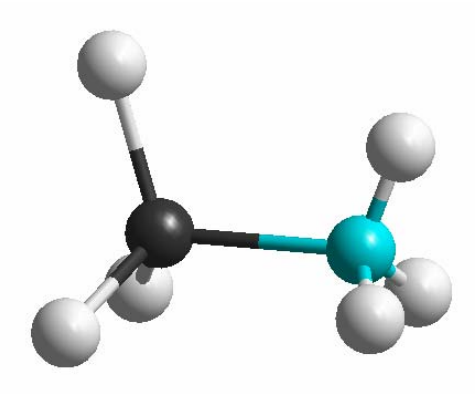
Harmonic frequencies (cm^{-1}): one img ν1 (A'') = –50.

(vii) $^1H_2TiCH_2$, C_2H_4-like, planar, E = –889.808140516 au

Harmonic frequencies (cm^{-1}): one img ν1 (B2) = –659.

$TiCH_6$

(i) $^1H_3TiCH_3$, minor distortions from anticlinic conf., E = –891.0534657115 au



R(Ti–C) = 2.025 Å, R(Ti–H) = 1.697 Å, R(C–H) = 1.097 Å, α(HTiC) = 108.8°, α(HCTi) = 109.1°.

q(Ti) = +1.415 e, q(C) = –0.727 e, $q(H_{Ti})$ = –0.372 e, $q(H_C)$ = 0.142 e, μ_{DIP} = 1.2 D.

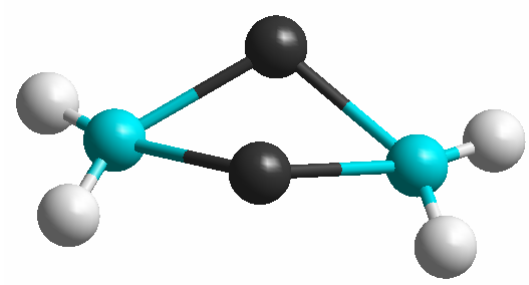
E_{HOMO} (A) = –0.300 au, E_{LUMO} (A) = –0.097 au, ΔE_{HL} = 0.203 au.

Harmonic frequencies (cm^{-1}): 119, 308 x2, 489, 490, 498, 608 x2, 624, 1139, 1401 x2, 1690, 1691, 1743, 2983, 3077, 3078.

Dimers

$(TiCH_2)_2$

(i) ^{1}cyclo-$(TiCH_2)_2$, non-planar Ti_2C_2 core, E = –1777.31612267 au



R(Ti–C) = 2.010, 2.031 Å, R(Ti–Ti) = 2.064 Å, R(C–C) = 3.263 Å, R(C–H) = 1.093, 1.106 Å, α(TiCTi) = 61.4°, α(CTiC) = 106.9°, 108.5°.

q(Ti) = –0.130, +0.115 e, q(C) = –0.262 e, $q(H_C)$ = +0.144, +0.125 e, μ_{DIP} = 1.1 D.

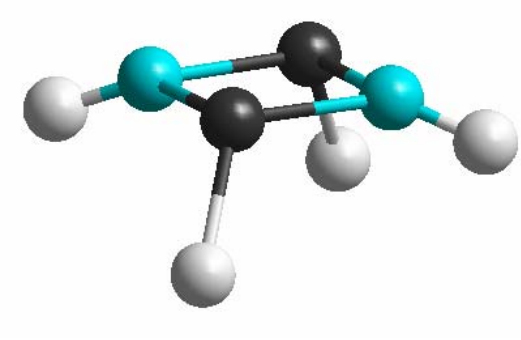
E_{HOMO} (A') = –0.151 au, E_{LUMO} (A') = –0.066 au, ΔE_{HL} = 0.085 au.

Harmonic frequencies (cm^{-1}): ν1 (A') = 163, ν2 (A'') = 168, ν3 (A') = 221, ν4 (A') = 305, ν5 (A'') = 325, ν6 (A') = 456, ν7 (A'') = 500, ν8 (A') = 515, ν9 (A') = 624, ν10 (A'') = 627, ν11 (A') = 681, ν12 (A'') = 689, ν13 (A'') = 1354, ν14 (A') = 1362, ν15 (A') = 2954, ν16 (A'') = 2956, ν17 (A') = 3108, ν18 (A'') = 3109.

(ii) ^{1}cyclo-$(TiHCH)_2$, E = –1777.31026935 au

R(Ti–C) = 1.906 Å, R(Ti–Ti) = 2.773 Å, R(C–C) = 2.616 Å, R(Ti–H) = 1.751 Å, R(C–H) = 1.097 Å, α(TiCTi) = 93.3°, α(C...CH) = 158.8°, α(Ti...TiH) = 127.5°.

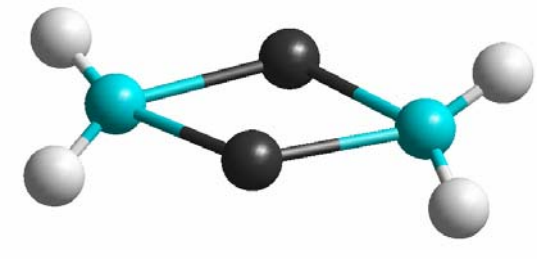
q(Ti) = +1.242 e, q(C) = –0.927 e, q(H_{Ti}) = –0.389 e, q(H_C) = +0.073 e, μ_{DIP} = 5.1 D.



E_{HOMO} (B1) = –0.216 au, E_{LUMO} (A1) = –0.096 au, ΔE_{HL} = 0.120 au.

Harmonic frequencies (cm^{-1}): ν1 (B2) = 170, ν2 (A1) = 187, ν3 (A2) = 304, ν4 (A1) = 311, ν5 (B2) = 342, ν6 (B1) = 356, ν7 (A2) = 387, ν8 (A1) = 390, ν9 (B1) = 474, ν10 (A1) = 520, ν11 (A2) = 589, ν12 (B1) = 737, ν13 (A1) = 741, ν14 (B2) = 763, ν15 (B2) = 1597, ν16 (A1) = 1617, ν17 (B1) = 3071, ν18 (A1) = 3072.

(iii) ^{3}cyclo-$(TiCH_2)_2$, asymmetric, bent core, E = –1777.30562538 au



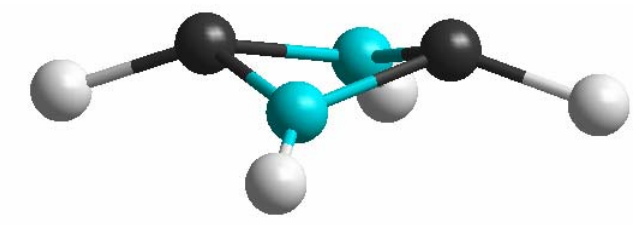
R(Ti–C) = 2.033 x2, 2.06 x2 Å, R(Ti–Ti) = 2.131 Å, R(C–C) = 3.499 Å, R(C–H) = 1.097 x2, 1.105 x2 Å, α(TiCTi) = 62.6°, α(CTiC) = 118.8°, α(HCH) = 107.8°.

q(Ti) = +0.379, =0.227 e, q(C) = –0.586 x2 e, q(H_C) = +0.138 x2, +0.146 x2 e, μ_{DIP} = 0.4 D.

$E_{SOMO,\alpha}$ (A') = –0.165 au, $E_{SOMO+1,\alpha}$ (A') = –0.154 au, ΔE = 0.011 au.

Harmonic frequencies (cm^{-1}): ν1 (A') = 43, ν2 (A'') = 134, ν3 (A') = 182, ν4 (A'') = 208, ν5 (A') = 323, ν6 (A') = 386, ν7 (A'') = 402, ν8 (A') = 445, ν9 (A') = 611, ν10 (A'') = 624, ν11 (A') = 641, ν12 (A'') = 647, ν13 (A'') = 1339, ν14 (A') = 1347, ν15 (A') = 2949, ν16 (A'') = 2050, ν17 (A') = 3054, ν18 (A'') = 3058.

(iv) ^{3}cyclo-$(TiHCH)_2$, umbrella, E = –1777.26184270



R(Ti–C) = 1.960 x4 Å, R(Ti–Ti) = 2.784 Å, R(C–C) = 2.626 Å, R(Ti–H) = 1.756 x2 Å, R(C–H) = 1.096 x2 Å, α(TiCTi) = 93.3°, α(C...CH) = 148.0°, α(Ti...TiH) = 161.2°, α_{dih}(TiCCTi) = 24.6°.

q(Ti) = +0.974 x2 e, q(C) = –0.698 x2 e, q(H_{Ti}) = –0.340 x2 e, q(H_C) = +0.064 x2 e, μ_{DIP} = 2.4 D.

$E_{SOMO,\alpha}$ (B1) = –0.231 au, $E_{SOMO+1,\alpha}$ (A1) = –0.185 au, ΔE = 0.046 au.

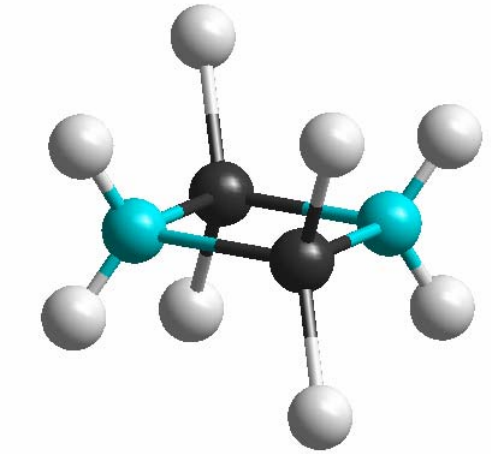
Harmonic frequencies (cm^{-1}): ν1 (A1) = 129, ν2 (A1) = 149, ν3 (B2) = 277, ν4 (A1) = 286, ν5 (B1) = 331, ν6 (A2) = 353, ν7 (A2) = 384, ν8 (B2) = 527, ν9 (B1) = 568, ν10 (A1) = 590, ν11 (A2) = 622, ν12 (B1) = 643, ν13 (A1) = 710, ν14 (B2) = 1005, ν15 (A1) = 1592, ν16 (B2) = 1592, ν17 (B1) = 3080, ν18 (A1) = 3082.

(v) ^{1}cyclo-$(TiCH_2)_2$, planar core, E = –1777.27062075 au

Harmonic frequencies (cm^{-1}): two img ν1 (B3g) = –605, ν2 (B1u) = –232.

$(TiCH_4)_2$

(i) ^{1}cyclo-$(TiH_2CH_2)_2$, C_2, c-C_4H_8-like, E = –1779.76400855 au

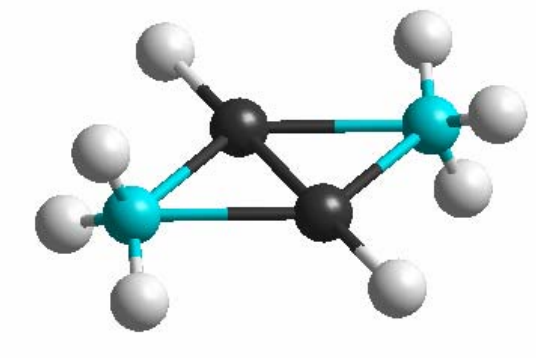


R(Ti–C) = 2.027, 2.028 Å, R(Ti–Ti) = 2.967 Å, R(C–C) = 2.763 Å, R(Ti–H) = 1.830 Å, R(C–H) = 1.102 Å, α(CTiC) = 85.9°, α(TiCTi) = 94.1°, α(C...CH) = 123.9°, α(Ti...TiH) = 121.7°, α(HCH) = 112.2°, α(HTiH) = 116.6°, α_{dih}(TiCTiC) = 0.0°.

q(Ti) = +1.435 e, q(C) = –0.898 e, $q(H_{Ti})$ = –0.375 e, $q(H_C)$ = +0.106 e, μ_{DIP} = 0.0 D.

E_{HOMO} (A) = –0.279 au, E_{LUMO} (A) = –0.109 au, ΔE_{HL} = 0.170 au.

Harmonic frequencies (cm^{-1}): ν1 (A) = 111, ν2 (B) = 184, ν3 (A) = 207, ν4 (B) = 284, ν5 (A) = 297, ν6 (A) = 328, ν7 (A) = 358, ν8 (B) = 414, ν9 (B) = 440, ν10 (A) = 453, ν11 (B) = 475, ν12 (A) = 508, ν13 (B) = 521, ν14 (A) = 542, ν15 (A) = 564, ν16 (B) = 603, ν17 (B) = 649, ν18 (A) = 668, ν19 (B) = 686, ν20 (A) = 689, ν21 (B) = 1256, ν22 (A) = 1268, ν23 (B) = 1667, ν24 (A) = 1674, ν25 (B) = 1689, ν26 (A) = 1711, ν27 (B) = 2967, ν28 (A) = 2968, ν29 (A) = 3051, ν30 (B) = 3052.



(ii) ^{1}cyclo-$(TiHCH_3)_2$, C_i, E = –1779.73441820 au

R(Ti–C) = 2.204, 2.206 Å, R(Ti–Ti) = 1.977 Å, R(C–C) = 3.942 Å, R(Ti–H) = 1.745 Å, R(C–H) = 1.099, 1.101 Å,

α(TiCTi) = 53.3°, α_{dih}(HtiTiH) = 172.6 °.

q(Ti) = +0.294, +0.303 e, q(C) = –0.540 e, q(H_{Ti}) =–0.278 e, q(H_C) = +0.171, +0.174 e, μ_{DIP} = 0.0 D.

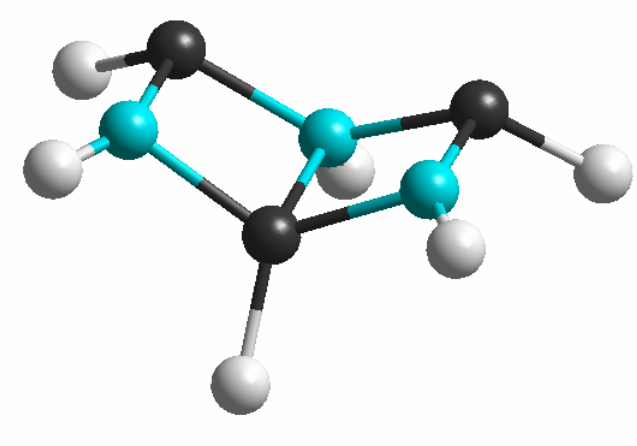
E_{HOMO} (A) = –0.171 au, E_{LUMO} (A) = –0.079 au, ΔE_{HL} = 0.092 au.

Harmonic frequencies – all of A symmetry (cm^{-1}): 56, 61, 111, 158, 245, 271, 344, 442, 456, 479, 483, 514, 564, 602, 608, 637, 1211, 1214, 1407, 1413, 1429, 1433, 1556, 1577, 2956, 2957, 3034, 3037, 3037, 3045.

Trimers

$(TiCH_2)_3$

(i) $^1(TiHCH)_3$ boat, E = –2666.02492797 au

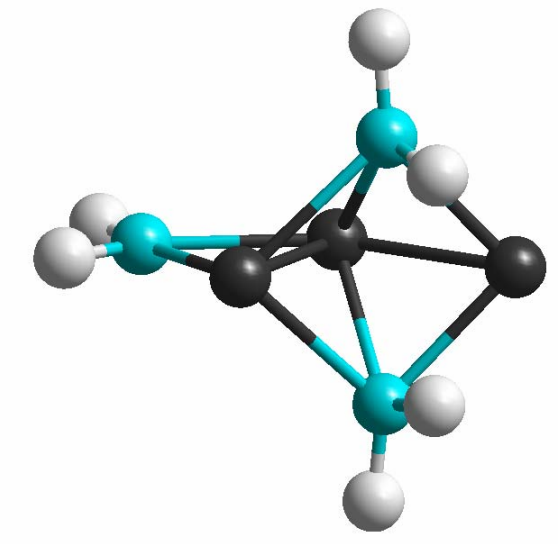


R(Ti–C) = 1.815, 1.816, 2.001, 2.001, 2.020, 2.021, 2.099 Å, R(Ti–Ti) = 2.850 Å, R(C–C) = 2.753 Å, R(Ti–H) = 1.741, 1.743, 1.744 Å, R(C–H) = 1.072, 1.099, 1.099 Å, $\alpha(C_{end}Ti_{mid}C_{end})$ = 125.9°, $\alpha(Ti_{end}C_{mid}Ti_{end})$ = 130.1°, $\alpha(C_{end}Ti_{end}C_{mid})$ = 92.2°, $\alpha(Ti_{end}C_{end}Ti_{mid})$ = 95.8°, $\alpha(C_{mid}Ti_{mid}H)$ = 127.3°, $\alpha(Ti_{mid}C_{mid}H)$ = 128.1°, $\alpha_{dih}(C_{end}Ti_{mid}C_{mid}Ti_{end})$ = 128.7°.

q(Ti) = +0.800, 1.278, 1.278 e, q(C) = –0.880, –0.815, –0.813 e, q(H_{Ti}) = –0.335, –0.351, –0.351 e, q(H_C) = +0.012, +0.088, +0.088 e, μ_{DIP} = 6.5 D.

E_{HOMO} (A) = –0.224 au, E_{LUMO} (A) = –0.113 au, ΔE_{HL} = 0.111 au.

Harmonic frequencies – all of A symmetry (cm^{-1}): 97, 114, 187, 195, 255, 278, 291, 305, 321, 375, 380, 424, 435, 445, 479, 498, 526, 574, 576, 597, 652, 729, 839, 842, 1618, 1620, 1640, 2970, 3055, 3056.



(ii) $^1(TiCH_2)_3$ cluster, E = –2666,02411718 au

R(Ti–C) = 1.945, 2.079, 2.080, 2.158, 2.208, 2.209, 2.213, 2.215 Å, R(Ti–Ti) =

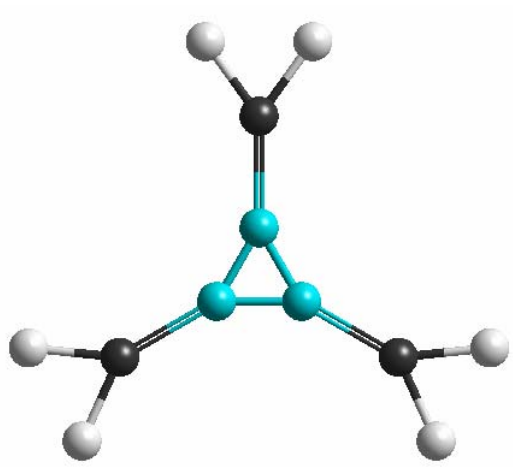
2.205, 2.340 Å, R(C–H) = 1.093, 1.094 x2, 1.119, 1.149x2 Å, α(HCH) = 103.4° x2, 106.8°.

q(Ti) = +1.104, –0.117, –0.289 e, q(C) = –0.400, –0.403, –0.599 e, q(H_C) = +0.036, +0.038, +0.108, +0.154, +0.156, +0.212 e, μ_{DIP} = 0.9 D.

E_{HOMO} (A) = –0.142 au, E_{LUMO} (A) = –0.068 au, ΔE_{HL} = 0.074 au.

Harmonic frequencies – all of A symmetry (cm^{-1}): 110, 172, 192, 249, 271 x2, 306, 362, 407, 454, 456, 515, 526, 573, 639, 641, 676, 677, 693, 789, 802, 1377, 1434, 1438, 2500, 2513, 2819, 3059, 3060, 3101.

(iii) $^1(CTiH_2)_3$ planar triangle C_3 core, E = –2664.39847981 au



R(Ti–C) = 1.921 x3 Å, R(C–C) = 1.460 x3 Å, R(Ti–H) = 1.579 x6 Å, α(HTiH) = 71.5°.

q(Ti) = –2.468 e, q(C) = +0.469 e, q(H_{Ti}) = +1.000 e, μ_{DIP} = 0.0 D.

E_{HOMO} (A'') = –0.149 au, E_{LUMO} (A') = –0.082 au, ΔE_{HL} = 0.067 au.

Harmonic frequencies – all real frequencies of A symmetry (cm^{-1}).

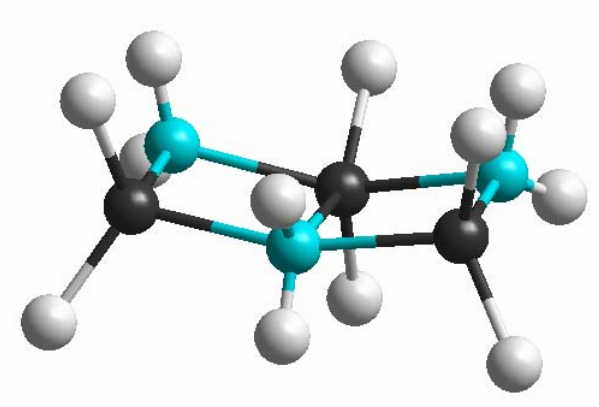
(iv) $^1(TiCH_2)_3$ planar triangle Ti_3 core, E = –2664.91764174 au

Harmonic frequencies – all of A symmetry (cm^{-1}): 6 img.

(v) $^1(TiCH_2)_3$ planar benzene-like, E = –2665.9865878.

Harmonic frequencies (cm^{-1}): three img ν1 (A2) = –167, ν2 (B1) = –166, ν3 (B1) = –156.

(vi) Cyclohexane-like chair structures, not stable.



$(TiCH_4)_3$

(i) $^1(TiH_2CH_2)_3$ boat with nearly planar TiC core, E = –2669.66028806

R(Ti–C) = 1.925 x2, 2.083 x2, 2.130 x2, 2.347 Å, R(Ti–H) = 1.688, 1.706, 1.712 x2, 1.715 x2 Å, R(C–H) = 1.095 x2, 1.111, 1.112 x2, 1.121 Å, $\alpha(C_{end}Ti_{mid}C_{end})$ = 149.1°, $\alpha(Ti_{end}C_{mid}Ti_{end})$ = 163.5°, $\alpha(C_{end}Ti_{end}C_{mid})$ = 93.5°, $\alpha(Ti_{end}C_{end}Ti_{mid})$ = 97.7°, $\alpha(C_{mid}Ti_{mid}H)$ = 112.5, 136.5°, $\alpha(Ti_{mid}C_{mid}H)$ = 118.6, 133.2°, $\alpha_{dih}(C_{end}Ti_{mid}C_{mid}Ti_{end})$ = 159.5°.

q(Ti) = +1.584, 1.580, 1.269 e, q(C) = –0.930, –0.913, –0.909 e, $q(H_{Ti})$ = –0.438, –0.437, –0.364, –0.363, –0.337, –0.311 e, $q(H_C)$ = –0.069, +0.106, +0.131 x2, +0.135 x2 e, μ_{DIP} = 0.5 D.

E_{HOMO} (A) = –0.269 au, E_{LUMO} (A) = –0.119 au, ΔE_{HL} = 0.150 au.

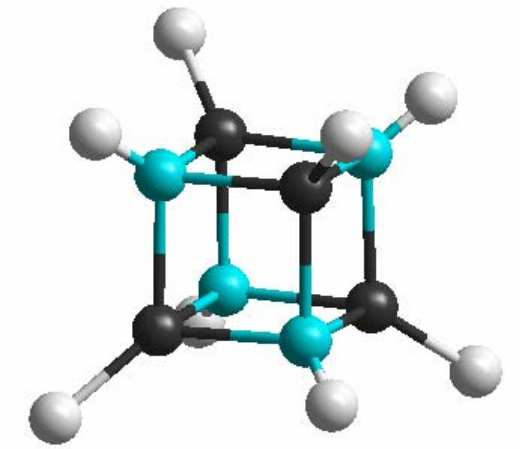
Harmonic frequencies – all of A symmetry (cm^{-1}): 74, 81, 145, 160, 213, 223, 247, 277, 284, 293, 334, 356, 359, 375, 411, 429, 439, 458, 465, 490, 519, 539, 540, 553, 606, 613, 616, 638, 675, 686, 713, 744, 803, 1272, 1273, 1292, 1669, 1673, 1689, 1691, 1703, 1726, 2811, 2905, 2907, 2940, 3094, 3095.

(ii) $^1(TiHCH_3)_3$ cyclic structure with alternating TiH and CH_3 units, as in analogous cyclic dimer, $^1(TiHCH_3)_2$;

not stable.

$(TiCH_2)_4$

$^1(TiHCH)_4$ cube, E = –3554.87080918 au



R(Ti–C) = 2.036 x5, 2.038 x5, 2.039 x2 Å, α(CTiC) = 87.7°, α(TiCTi) = 92.3°, α(HTiC) = 126.8°, α(HCTi) = 123.6°.

q(Ti) = +1.016, +1.020, +1.021, 1.027 e, q(C) = –1.093 x2, –1.096 x2 e, μ_{DIP} = 0.0 D.

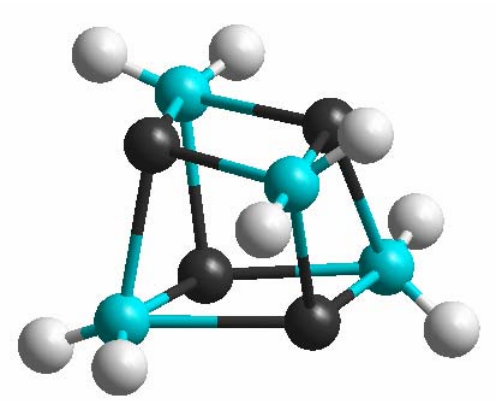
E_{HOMO} (A) = –0.262 au, E_{LUMO} (A) = –0.126 au, ΔE_{HL} = 0.136 au.

Harmonic frequencies – all of A symmetry (cm^{-1}): 233, 233, 305, 306, 307, 307, 307, 309, 328, 329, 396, 396, 397, 397, 398, 399, 404, 447, 448, 454, 455, 458, 549, 550, 550, 637, 653, 653, 654, 655, 657, 687, 688, 689, 1622, 1623, 1625, 1652, 3014, 3015, 3019, 3020.

$^1(TiCH_2)_4$ cube, E = –3554.79034942 au

R(Ti–C) = 2.027 x2, 2.066 x2, 2.172 x2, 2.284 x2, 2.214 x2, 2.512 x2 Å, R(C–H) = 1.094 x2, 1.111 x2, 1.101 x2, 1.106 x2 Å, α(CTiC) = 93.6°, 94.4°, 115.8°, 119.1°, α(HCH) = 106.1°, α_{dih}(TiCCTi) = 3.3°.

q(Ti) = +0.198 x2, +0.216 x2 e, q(C) = –0.602 x2, –0.677 x2 e, q(H) = +0.136 x2, +0.212 x2, +0.232 x2, +0.285 x2 e, μ_{DIP} = 0.5 D.

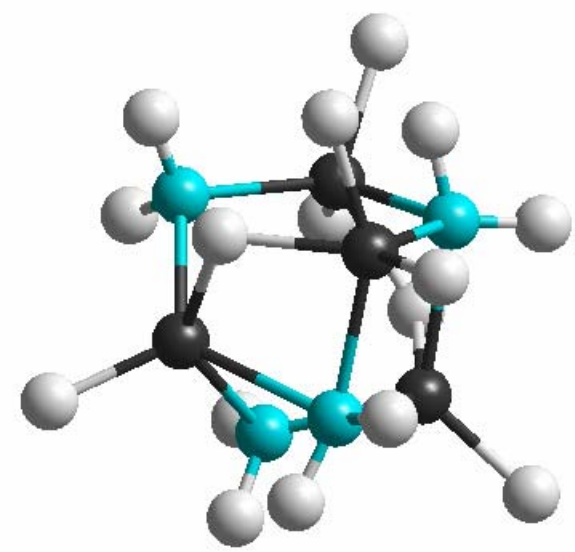


E_{HOMO} (A) = –0.130 au, E_{LUMO} (A) = –0.054 au, ΔE_{HL} = 0.076 au.

Harmonic frequencies – all of A symmetry (cm^{-1}): 130, 144, 172, 175, 196, 207, 221, 238, 264, 275, 300, 339, 346, 394, 396, 443, 450, 451, 458, 480, 494, 540, 561, 573, 610, 620, 646, 660, 667, 687, 1321, 1323, 1358, 1360, 2892, 2894, 2932, 2933, 3023, 3023, 3089, 3089.

$(TiCH_4)_4$

$^1(TiCH_4)_4$ cube, complex polyhedron, E = –3559.58431488 au



R(Ti–C) = 2.020, 2.038, 2.039, 2.068, 2.069, 2.096, 2.168, 2.169, 2.268, 2.280 Å, R(C–H) = 1.092, 1.096 x2, 1.104, 1.107, 1.109, 1.114, 1.121 Å, R(Ti–H) = 1.697, 1.711, 1.712, 1.713 x2, 1.719, 1.791, 1.823, 1.840, 1.846 Å, α(HCH) = 105.0°, 106.7°, 111.0°, 112.3°, α(HTiH) = 91.2°, 100.6°, 106.7°, 106.8°.

q(Ti) = +1.272, 1.310, 1.468, 1.516 e, q(C) = –0.816, –1.013, –1.139, –1.345 e, q(H_{Ti}) = –0.227, –0.230, –0.279, –0.280, –0.369, –0.371, –0.395, –0.433 e, q(H_C) = +0.111, +0.114, +0.139, +0.145, +0.172, +0.188, +0.193, +0.270 e, μ_{DIP} = 1.6 D.

E_{HOMO} (A) = –0.267 au, E_{LUMO} (A) = –0.133 au, ΔE_{HL} = 0.134 au.

Harmonic frequencies – all of A symmetry (cm^{-1}): 76, 108, 155, 174, 186, 208, 229, 245, 259, 289, 303, 311, 319, 347, 359, 368, 383, 393, 395, 406, 426, 438, 450, 475, 477, 496, 515, 534, 550, 558, 561, 570, 591, 595, 617, 634, 641, 652, 669, 686, 713, 759, 807, 828, 1209, 1229, 1271, 1325, 1329,

1440, 1454, 1521, 1650, 1669, 1678, 1690, 1699, 1717, 2786, 2874, 2924, 2946, 2994, 3062, 3080, 3110.

2. Calculated energies and chosen properties of the reaction products.

Monomers

TiH_2

(i) $^3TiH_2$, bent, symmetric E = –850.485694939 au

R(Ti–H) = 1.812 Å, α(HTiH) = 132.3°.

q(Ti) = +0.956 e, $q(H_{Ti})$ = –0.478 e, μ_{DIP} = 3.6 D.

$E_{SOMO,\alpha}$ (A2) = –0.189 au, $E_{SOMO+1,\alpha}$ (A2) = –0.185 au, ΔE = 0.004 au.

Harmonic frequencies (cm^{-1}): ν1 (A1) = 437, ν2 (B2) = 1447, ν3 (A1) = 1495.

(ii) $^1TiH_2$, bent, symmetric E = –850.459774254 au

R(Ti–H) = 1.695 Å, α(HTiH) = 113.5°.

q(Ti) = +0.409 e, $q(H_{Ti})$ = –0.205 e, μ_{DIP} = 2.7 D.

E_{HOMO} (A1) = –0.175 au, E_{LUMO} (A1) = –0.099 au, ΔE_{HL} = 0.176 au.

Harmonic frequencies (cm^{-1}): ν1 (A1) = 582, ν2 (A1) = 1665, ν3 (B2) = 1693.

$^1TiH_4$

(i) T_d, E = –851.700082437 au

R(Ti–H) = 1.685 Å, α(HTiH) = 109.5°.

q(Ti) = +1.415 e, $q(H_{Ti})$ = –0.354 e, μ_{DIP} = 0.0 D.

E_{HOMO} (T2) = –0.321 au, E_{LUMO} (E) = –0.113 au, ΔE_{HL} = 0.208 au.

Harmonic frequencies (cm^{-1}): ν1 (T2) = 540, ν2 (E) = 629, ν3 (T2) = 1718, ν4 (A1) = 1788.

$^1CH_4$

(i) T_d, E = –40.53395627333 au

R(C–H) = 1.091 Å, α(HCH) = 109.5°.

$q(C) = -0.532$ e, $q(H_C) = +0.133$ e, $\mu_{DIP} = 0.0$ D.

E_{HOMO} (T2) = –0.395 au, E_{LUMO} (A1) = –0.006 au, $\Delta E_{HL} = 0.389$ au.

Harmonic frequencies (cm^{-1}): ν1 (T2) = 1340, ν2 (E) = 1559, ν3 (A1) = 3023, ν4 (T2) = 3129.

CH_2

(i) $^3CH_2$, bent, symmetric E = –39.1661174920 au

R(C–H) = 1.080 Å, α(HCH) = 135.3°.

$q(C) = -0.266$ e, $q(H_C) = +0.133$ e, $\mu_{DIP} = 0.7$ D.

$E_{SOMO,\alpha}$ (?) = –0.283 au, $E_{SOMO+1,\alpha}$ (?) = –0.250 au, $\Delta E = 0.033$ au.

Harmonic frequencies (cm^{-1}): ν1 = 1042, ν2 = 3118, ν3 = 3362.

(ii) $^1CH_2$, bent, symmetric E = –39.1467444737 au

R(C–H) = 1.114 Å, α(HCH) = 101.5°.

$q(C) = -0.219$ e, $q(H_C) = +0.109$ e, $\mu_{DIP} = 2.1$ D.

E_{HOMO} (?) = –0.261 au, E_{LUMO} (?) = –0.142 au, $\Delta E_{HL} = 0.119$ au.

Harmonic frequencies (cm^{-1}): ν1 = 1385, ν2 = 2895, ν3 = 2961.

TiC

(i) ^{3}TiC, E = –887.292272584 au

R(Ti–C) = 1.648 Å.

$q(Ti) = +0.395$ e, $q(C) = -0.395$ e, $\mu_{DIP} = 3.3$ D.

$E_{SOMO,\alpha}$ (σ) = –0.237 au, $E_{SOMO+1,\alpha}$ (δ) = –0.085 au, $\Delta E = 0.152$ au.

Harmonic frequencies (cm^{-1}): ν1 (σ) = 1029.

(ii) ^{1}TiC, E = –887.285521272 au

R(Ti–C) = 1.592 Å.

q(Ti) = +0.608 e, q(C) = –0.608 e, μ_{DIP} = 7.1 D.

E_{HOMO} (σ) = –0.154 au, E_{LUMO} (σ) = –0.103 au, ΔE_{HL} = 0.151 au.

Harmonic frequencies (cm^{-1}): ν1 (σ) = 961.

H_2

(i) E = –1.17957151815 au

R(H–H) = 0.744 Å.

q(H) = 0.0 e, μ_{DIP} = 0.0 D.

E_{HOMO} (σg) = –0.434 au, E_{LUMO} (σu) = +0.020 au, ΔE_{HL} = 0.454 au.

Harmonic frequencies (cm^{-1}): ν1 (σg) = 4420.

Ti

(i) ^{3}Ti, E = –849.287930089 au

$E_{SOMO,\alpha}$ (?A) = –0.226 au, $E_{SOMO+1,\alpha}$ (A1g) = –0.180 au, ΔE = 0.046 au.

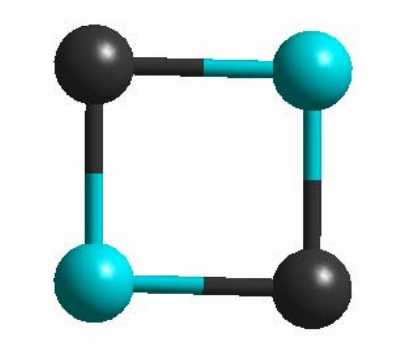
(ii) ^{1}Ti, E = –849.226050066 au

E_{HOMO} (?C) = –0.166 au, E_{LUMO} (?A) = –0.097 au, ΔE = 0.069 au.

Dimers

$(TiC)_2$

(i) $^1(TiC)_2$ dimer planar rhomb, E = –1774.83423089 au



R(Ti–C) = 1.826 Å, R(Ti–Ti) = 2.619 Å, R(C–C) = 2.546 Å.

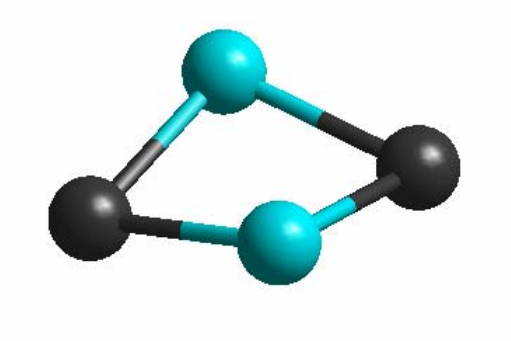
q(Ti) = +0.920 e, q(C) = –0.920 e, μ_{DIP} = 0.0 D.

E_{HOMO} (Bu) = –0.166 au, E_{LUMO} (Ag) = –0.083 au, ΔE_{HL} = 0.083 au.

Harmonic frequencies (cm^{-1}): ν1 (Au) = 217, ν2 (Ag) = 449, ν3 (Ag) = 460, ν4 (Bu) = 742, ν5 (Ag) = 854, ν6 (Bu) = 903.

(ii) $^5(TiC)_2$ rhomboid, E = –1774.80823309 au, not optimized, conv. failure.

(iii) $^3(TiC)_2$ rhomboid, non planar, E = –1774.80750938 au



R(Ti–C) = 1.845 Å, R(Ti–Ti) = 2.671 Å, R(C–C) = 2.450 Å, α(CTiC) = 83.2°.

q(Ti) = +0.620 e, q(C) = –0.620 e, μ_{DIP} = 1.8 D.

$E_{SOMO,\alpha}$ (A) = –0.145 au, $E_{SOMO+1,\alpha}$ (B) = –0.090 au, ΔE = 0.055 au.

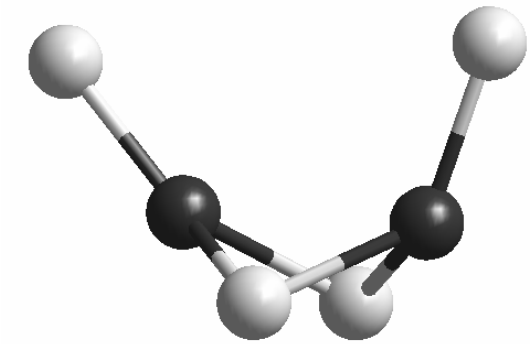
Harmonic frequencies (cm^{-1}): ν1 (A) = 155, ν2 (A) = 393, ν3 (A) = 547, ν4 (B) = 634, ν5 (A) = 806, ν6 (B) = 1303.

(iv) $^3(TiC)_2$ rhomb, planar, E = –1774.80625599 au

Harmonic frequencies (cm^{-1}): ν1 (Au) = –133.

$(TiH_2)_2$

(i) $^3(TiH_2)_2$, $HTiH_2TiH$, asymmetric and nonplanar, E = –1701.07033440 au



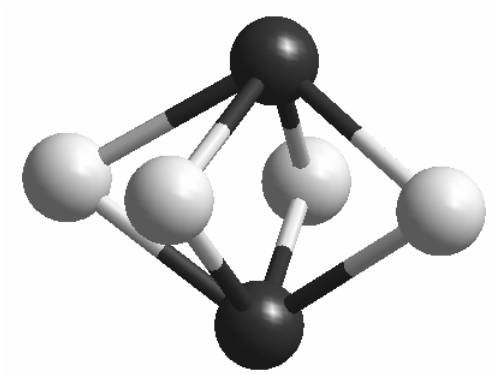
R(Ti–Ti) = 2.385 Å, R(Ti–H) = 1.743, 1.790, 1.863 x2, 1.903 x2 Å, α($TiH_{mid}Ti$) = 78.6°, α($H_{end}Ti\ldots Ti$) = 132.5, 108.3°.

q(Ti) = +0.896, +0.660 e, q(H) = –0.367, –0.394, –0.397 x2 e, μ_{DIP} = 5.0 D.

$E_{SOMO,\alpha}$ (A') = –0.201 au, $E_{SOMO+1,\alpha}$ (A') = –0.187 au, ΔE = 0.014 au.

Harmonic frequencies (cm^{-1}): ν1 (A') = 147, ν2 (A') = 248, ν3 (A'') = 275, ν4 (A') = 299, ν5 (A'') = 440, ν6 (A') = 574, ν7 (A') = 1088, ν8 (A'') = 1091, ν9 (A'') = 1318, ν10 (A') = 1334, ν11 (A') = 1541, ν12 (A') = 1589.

(ii) $^3(TiH_2)_2$, deformed TiH_4Ti, E =–1701.1701.06172690 au



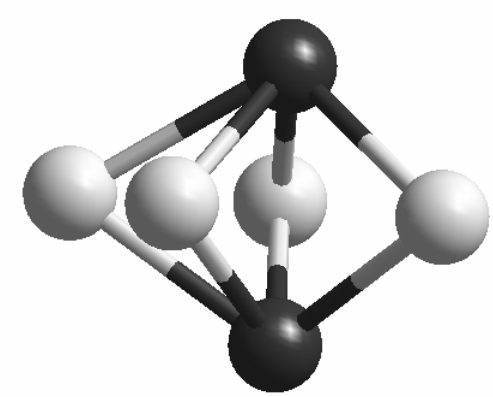
R(Ti–Ti) = 2.005 Å, R(Ti–H) = 1.886 x4, 1.908 x4 Å, α(TiHTi) = 63.4°, 64.2°.

q(Ti) = +0.623 x2 e, q(H) = –0.267 x2, –0.356 x2 e, μ_{DIP} = 1.1 D.

$E_{SOMO,\alpha}$ (A') = –0.135 au, $E_{SOMO+1,\alpha}$ (A') = –0.081 au, ΔE = 0.054 au.

Harmonic frequencies (cm^{-1}): 382 (A''), 423 (A'), 473 (A'), 548 (A''), 662 (A'), 730 (A''), 735 (A''), 858 (A'), 1128 (A'), 1312 (A'), 1314 (A'), 1356 (A').

(iii) $^1(TiH_2)_2$, deformed TiH_4Ti, E =–1701.05717110 au



R(Ti–Ti) = 1.996 Å, R(Ti–H) = 1.857 x4, 1.874 x4 Å, α(TiHTi) = 64.4° x2, 65.0°, α(HHHH) = 0.0°.

q(Ti) = +0.458 x2 e, q(H) = –0.159 x2, –0.299 x2 e, μ_{DIP} = 1.8 D.

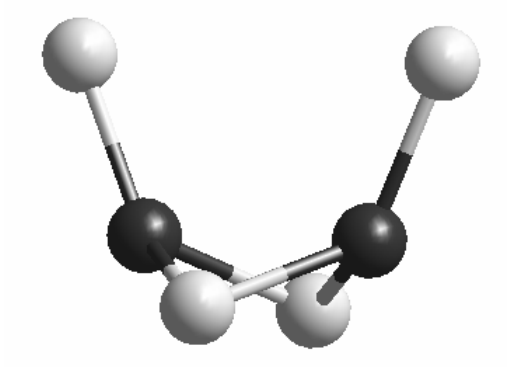
E_{HOMO} (A') = –0.311 au, E_{LUMO} (A'') = –0.073 au, ΔE = 0.238 au.

Harmonic frequencies (cm^{-1}): ν1 (A') = 503, ν2 (A') = 714, ν3 (A') = 732, ν4 (A'') = 753, ν5 (A') = 792, ν6 (A'') = 835, ν7 (A'') = 951, ν8 (A') = 1000, ν9 (A') = 1248, ν10 (A') = 1347, ν11 (A') = 1410, ν12 (A') = 1417.

(iv) $^1(TiH_2)_2$, $HTiH_2TiH$, nonplanar, E = –1701.05569109 au

R(Ti–Ti) = 2.191 Å, R(Ti–H) = 1.739 x2, 1.856 x4 Å, α($TiH_{mid}Ti$) = 72.3°, α($H_{end}Ti\ldots Ti$) = 112.7° x2.

q(Ti) = +0.712 x2 e, q(H) = –0.356 x4 e, μ_{DIP} = 5.9 D.

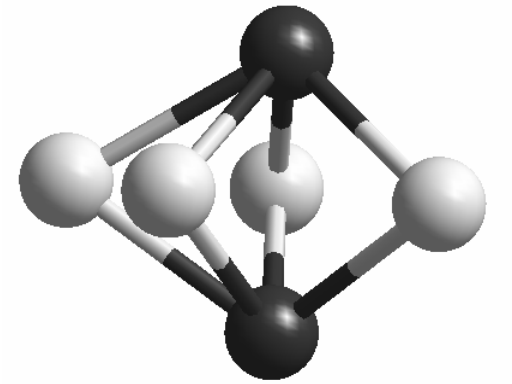


E_{HOMO} (A') = –0.168 au, E_{LUMO} (A'') = –0.088 au, ΔE = 0.080 au.

Harmonic frequencies (cm^{-1}): 254 (A''), 338 (A'), 416 (A''), 437 (A'), 507 (A'), 546 (A'), 1150 (A''), 1189 (A'), 1369 (A''), 1386 (A'), 1586 (A'), 1603 (A').

(v) $^5(TiH_2)_2$, deformed TiH_4Ti, E = –1701.04551810 au

R(Ti–Ti) = 1.952 Å, R(Ti–H) = 1.921 x8 Å, α(TiHTi) = 61.1° x4, α(HHHH) = 0.0°.

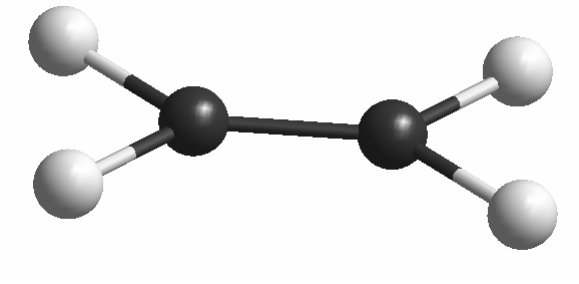


q(Ti) = +0.576 x2 e, q(H) = –0.288 x4 e, μ_{DIP} = 0.0 D.

$E_{SOMO,\alpha}$ (A') = –0.223 au, $E_{SOMO+1,\alpha}$ (A') = –0.165 au, ΔE = 0.058 au.

Harmonic frequencies (cm^{-1}): ν1 (A') = 488, ν2 (A') = 493, ν3 (A'') = 543, ν4 (A'') = 549, ν5 (A') = 660, ν6 (A'') = 673, ν7 (A') = 719, ν8 (A'') = 1110, ν9 (A') = 1284, ν10 (A') = 1297, ν11 (A') = 1354, ν12 (A') = 1378.

(vi) $^1(TiH_2)_2$, ethene-like, symmetric and planar, E = –1700.95658210 au



R(Ti–Ti) = 1.933 Å, R(Ti–H) = 1.703 Å, α(HTiH) = 86.4°.

q(Ti) = +0.698 e, q(H) =–0.349 e, μ_{DIP} = 0.0 D.

E_{HOMO} (Ag) = –0.224 au, E_{LUMO} (B2u) = –0.149 au, ΔE = 0.075 au.

ν1 (B2u) = 191, ν2 (Au) = 349, ν3 (B1u) = 364, ν4 (B3g) = 391, ν5 (B2g) = 402, ν6 (Ag) = 402, ν7 (Ag) = 502, ν8 (B3g) = 528, ν9 (B3g) = 1602, ν10 (B2u) = 1612, ν11 (Ag) = 1662, ν12 (B1u) = 1665.

(vii) $^1(TiH_2)_2$, $HTiH_2TiH$, symmetric and planar, E = –1701.04638383 au

Harmonic frequencies (cm^{-1}): 2 img –101, –47.

(viii) $^3(TiH_2)_2$, $HTiH_2TiH$, symmetric and planar, E = –1701.04578251 au

Harmonic frequencies (cm^{-1}): 3 img –1091, –302, –118.

(ix) $^3(TiH_2)_2$, ethene-like, symmetric and planar, E = –1700.98138265 au

Harmonic frequencies (cm^{-1}): 4 img –432, –314, –288, –211.

(x) $^5(TiH_2)_2$, ethene-like, symmetric and planar, E = –1700.99481455 au

Harmonic frequencies (cm^{-1}): 4 img –510, –349, –282, –257.

Ti_2

(i) $^1Ti_2$, E = –1698,61879618 au

R(Ti–Ti) = 1.865 Å.

E_{HOMO} (A') = –0.201 au, E_{LUMO} (A') = –0.187 au, ΔE = 0.014 au.

Harmonic frequencies (cm^{-1}): ν1 = 629.

(i) $^3Ti_2$, E = –1698,61768288 au

R(Ti–Ti) = 1.840 Å.

E_{HOMO} (A') = –0.201 au, E_{LUMO} (A') = –0.187 au, ΔE = 0.014 au.

Harmonic frequencies (cm^{-1}): ν1 = 586.

$(CH_2)_2$

(i) $^1(CH_2)_2$ ethene, E = –78.6155382199 au

R(C–C) = 1.329 Å, R(C–H) = 1.085 x4 Å, α(HCH) = 121.7°.

q(C) = –0.222 e, q(H) = +0.111 x4 e, μ_{DIP} = 0.0 D.

E_{HOMO} (B3u) = –0.282 au, E_{LUMO} (B2g) = –0.011 au, ΔE = 0.271 au.

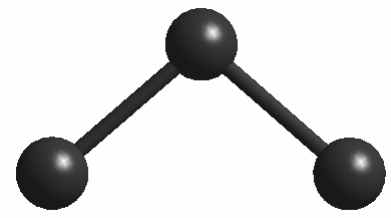
Harmonic frequencies – all of A symmetry (cm^{-1}): 836 (B2u), 975 (B3u), 978 (B2g), 1059 (Au), 1239 (B3g), 1378 (Ag), 1472 (B1u), 1685 (Ag), 3119 (B1u), 3134 (Ag), 3191 (B3g), 3219 (B2u).

Trimers

Ti_3

(i) $^3Ti_3$, E = –2547.95220135 au

R(Ti–Ti) = 1.895 x2, 2.916 Å.



q(Ti) = +0.665, –0.332 x2 e, μ_{DIP} = 0.5 D.

$E_{SOMO,\alpha}$ (A) = –0.153 au, $E_{SOMO+1,\alpha}$ (B) = –0.134 au, ΔE = 0.019 au.

Harmonic frequencies (cm^{-1}): 213, 459, 476.

(ii) $^1Ti_3$, E = –2547.93380049 au

R(Ti–Ti) = 1.832 x2, 2.766 Å.

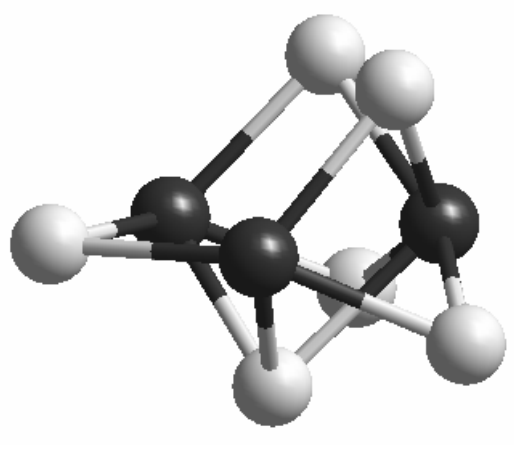
q(Ti) = +1.058, –0.529 x2 e, μ_{DIP} = 0.3 D.

E_{HOMO} (A') = –0.111 au, E_{LUMO} (A') = –0.081 au, ΔE_{HL} = 0.030 au.

Harmonic frequencies (cm^{-1}): 248, 480, 617.

$(TiH_2)_3$

(i) $^3(TiH_2)_3$, triangle with bridging Ti…H_2…Ti, planar Ti_3 core, E = –2551.71629587 au



R(Ti–Ti) = 2.370, 2.376, 2.617 Å, R(Ti–H) = 1.838, 1.874, 1.895, 1.900, 1.901, 1.904, 1.928, 1.935, 1.952, 1.961, 1.963, 1.978, 1.984 Å.

q(Ti) = +0.606, +0.701, _0.790 e, q(H) = –0.234, –0.347, –0.360, –0.381, –0.383, –0.395 e, μ_{DIP} = 1.5 D.

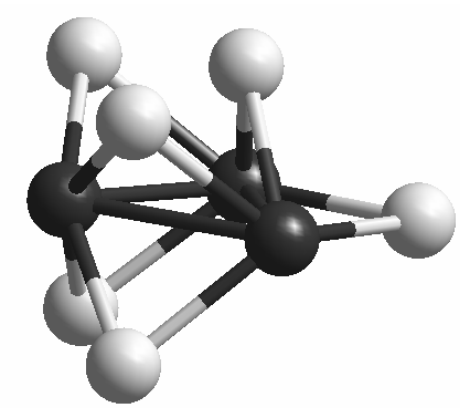
$E_{SOMO,\alpha}$ (A) = –0.161 au, $E_{SOMO+1,\alpha}$ (A) = –0.150 au, ΔE_{HL} = 0.011 au.

Harmonic frequencies – all real frequencies of A symmetry (cm^{-1}): 170, 260, 297, 325, 395, 524, 666, 781, 855, 874, 914, 935, 1002, 1041, 1146, 1157, 1218, 1232, 1275, 1291, 1374.

(ii) $^1(TiH_2)_3$, triangle with bridging Ti…H_2…Ti, planar Ti_3 core, E = –2551.70542580 au

R(Ti–Ti) = 2.223 x2, 2.612 Å, R(Ti–H) = 1.825, 1.843, 1.869, 1.923, 1.935, 1.980 Å.

q(Ti) = +0.699 x2, +0.539 e, q(H) = –0.340 x2, –0.347x2, –0.129, –0.432 e, μ_{DIP} = 1.7 D.

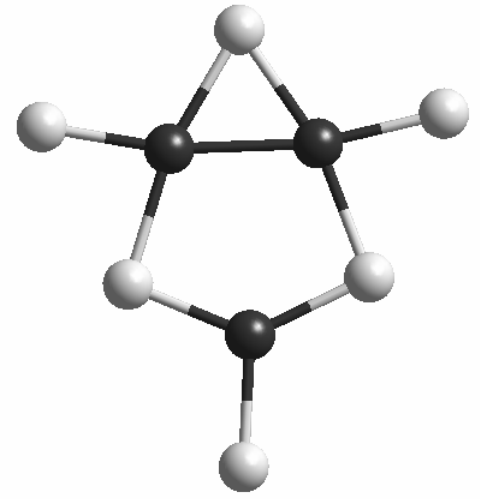


E_{HOMO} (A) = –0.145 au, E_{LUMO} (A) = –0.068 au, ΔE_{HL} = 0.077 au.

Harmonic frequencies – all real frequencies of A symmetry (cm^{-1}): 240, 294, 339, 433, 489, 626, 681, 713, 826, 853, 918, 1020,

1069, 1072, 1167, 1225, 1305, 1342, 1373, 1387, 1411.

(iii) $^3(TiH_2)_3$, triangle with bridging Ti…H…Ti, planar Ti_3 core, E = –2551.61646058 au

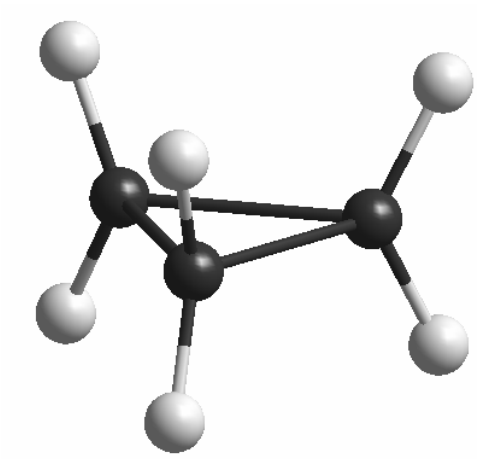


Harmonic frequencies (cm^{-1}): 3 img freq.

(iv) $^1(TiH_2)_3$, triangle with bridging Ti…H…Ti, planar Ti_3 core, E = –2551.59215696 au

Harmonic frequencies (cm^{-1}): 5 img freq.

(v) $^1(TiH_2)_3$, equilateral triangle, planar Ti_3 core, E = –2551.52847568 au



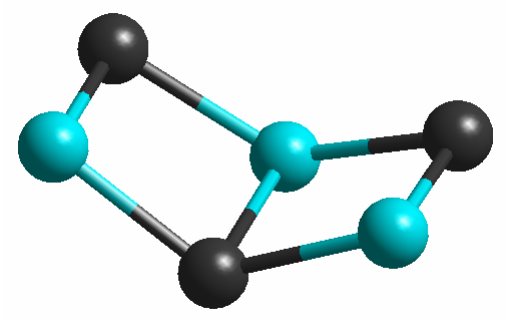
R(Ti–Ti) = 2.898 x3 Å, R(Ti–H) = 1.722 x6 Å.

Harmonic frequencies (cm^{-1}): 1 img – 254.

(vi) $^3(TiH_2)_3$, equilateral triangle, planar Ti_3 core, E = – 2551.537 au, convergence failure

$(TiC)_3$

(i) $^1(TiC)_3$ boat, E = –2662.32730132 au



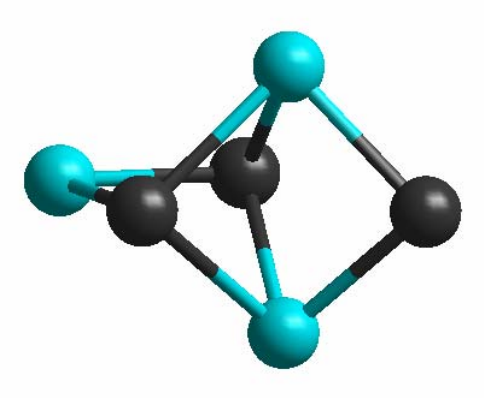
R(Ti–C) = 1.746, 1.993, 1.931, 1.937 Å, $\alpha(C_{end}Ti_{mid}C_{end})$ = 125.3°, $\alpha(Ti_{end}C_{mid}Ti_{end})$ = 129.3°, $\alpha_{dih}(Ti_{end}C_{mid}Ti_{mid}C_{end})$ = 127.8°.

q(Ti) = +0.897, +0.930 x2 e, q(C) = –1.104, –0.826 x2 e, μ_{DIP} = 6.2 D.

E_{HOMO} (A) = –0.163 au, E_{LUMO} (B) = –0.090 au, ΔE = 0.073 au.

Harmonic frequencies – all of A symmetry (cm^{-1}): 117, 143, 230, 344, 407, 422, 556, 557, 728, 751, 901, 934.

(ii) $^3(TiC)_3$ boat, E = –2662.32650257 au



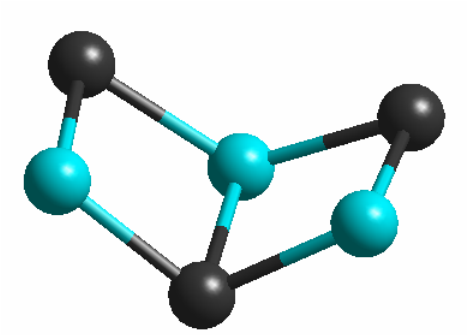
R(Ti–C) = 1.857, 1.858, 1.911 x2, 2.027, 2.028 x2, 2.029 Å, $\alpha(Ti_{mid}C_{end}Ti_{mid})$ = 85.5°, $\alpha(C_{mid}Ti_{end}C_{mid})$ = 83.7°, $\alpha_{dih}(Ti_{end}Ti_{mid}Ti_{mid}C_{end})$ = 0.0°.

q(Ti) = +0.778, +0.777, +0.047 e, q(C) = –0.577 x2, –0.447 e, μ_{DIP} = 3.9 D.

$E_{SOMO,\alpha}$ (A) = –0.181 au, $E_{SOMO+1,\alpha}$ (A) = –0.175 au, ΔE = 0.006 au.

Harmonic frequencies – all of A symmetry (cm^{-1}): 193, 215, 223, 268, 346, 411, 414, 586, 622, 729, 754, 777.

(iii) $^5(TiC)_3$ boat, E = –2662.28084499 au



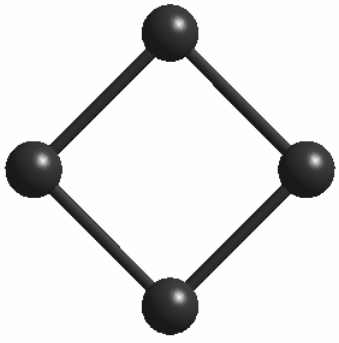
R(Ti–C) = 1.865, 1.880, 1.884, 1.905, 1.911, 1.939, 2.010 Å, $\alpha(C_{end}Ti_{mid}C_{end})$ = 111.1°, $\alpha(Ti_{end}C_{mid}Ti_{end})$ = 120.8°, $\alpha_{dih}(Ti_{end}C_{mid}Ti_{mid}C_{end})$ = 115.3°.

q(Ti) = +1.297, +0.357, +0.355 e, q(C) = –1.020, –0.511, –0.477 e, μ_{DIP} = 4.2 D.

$E_{SOMO,\alpha}$ (A) = –0.191 au, $E_{SOMO+1,\alpha}$ (A) = –0.183 au, ΔE = 0.008 au.

Harmonic frequencies – all of A symmetry (cm^{-1}): 59, 106, 168, 178, 368, 436, 454, 537, 590, 693, 786, 802.

Ti_4



(i) $^3Ti_4$ nearly square, nonplanar E = –3397,25293797 au

R(Ti–Ti) = 2.313 x4 Å, α(TiTiTi) = 86.0°, α_{dih}(TiTiTiTi) = 29.7°.

$E_{SOMO,\alpha}$ (B1) = –0.149 au, $E_{SOMO+1,\alpha}$ (B2) = –0.149 au, ΔE = 0.000 au.

Harmonic frequencies (cm^{-1}): 140, 155, 189, 190, 190, 175.

(ii) $^1Ti_4$ square, E = –3397,21460433 au

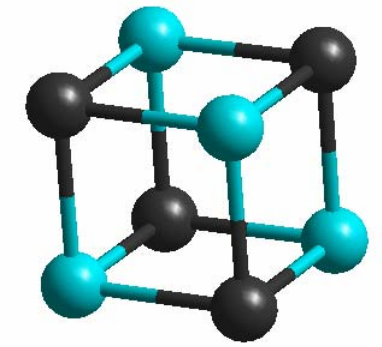
R(Ti–Ti) = 2.285 x4 Å, α(TiTiTi) = 90°.

E_{HOMO} (A1g) = –0.139 au, E_{LUMO} (Eu) = –0.087 au, ΔE = 0.052 au.

Harmonic frequencies (cm^{-1}): 54, 132, 245, 245, 341, 346.

$(TiC)_4$

(i) $^1(TiC)_4$ cube, E = –3550.00199292 au



R(Ti–C) = 1.944-1.945 Å, α(TiCTi) = 90.7°, α(CTiC) = 89.3°.

q(Ti) = +1.099 e, q(C) = –1.099e, μ_{DIP} = 0.0 D.

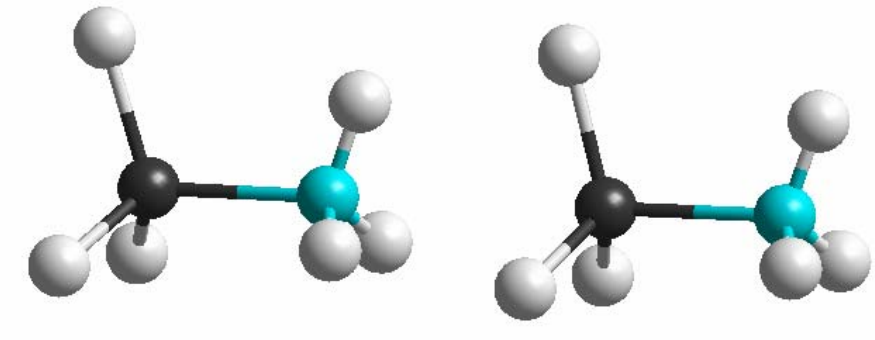
E_{HOMO} (A) = –0.187 au, E_{LUMO} (B) = –0.054 au, ΔE = 0.133 au.

Harmonic frequencies – all of A symmetry (cm^{-1}): 288, 288, 357, 358, 358, 454, 468, 468, 469, 510, 511, 684, 684, 684, 735, 758, 758, 759.

3. Estimate of the dimerization energy for c-$(H_3TiCH_3)_2$ via $CH^+ \cdots {}^-HTi$ interactions.

$^1(H_3TiCH_3)_2$ head-to-tail linear dimer, E = –1782.10964262 au

R(Ti–C) = 2.029, 2.034 Å, R(Ti…C) = 3.152 Å, R(Ti–H) = 1.694 x3, 1.701 x3 Å, R(C–H) = 1.097 x3, 1.098 x3 Å, α(CTi…C) = 180.0°, α(TiC…Ti) = 179.4°.



q(Ti) = +1.394, +1.000 e, q(C) = –0.633, –0.572 e, $q(H_{Ti})$ = –0.358 x3, –0.309 x3 e, $q(H_C)$ = +0.156 x3, +0.115 x3 e, μ_{DIP} = 1.1 D.

E_{HOMO} (A) = –0.293 au, E_{LUMO} (A) = –0.104 au, ΔE = 0.189 au.

Harmonic frequencies – all of A symmetry (cm^{-1}): 35, 40, 46, 51, 77, 103, 104, 157, 335, 339, 366, 367, 484, 498, 498, 515, 516, 519, 606, 606, 607,

644, 645, 645, 1104, 1135, 1400, 1401, 1408, 1410, 1678, 1679, 1699, 1700, 1731, 1749, 2971, 2986, 3076, 3077, 3080, 3081.

E($^1(H_3TiCH_3)_2$) per one $TiCH_6$ unit = – 891.05482131 au;
E($^1(H_3TiCH_3)$) = –891.0534657115 au;
Dimerization energy per one $TiCH_6$ unit = –0.00135 au (–0.04 eV).

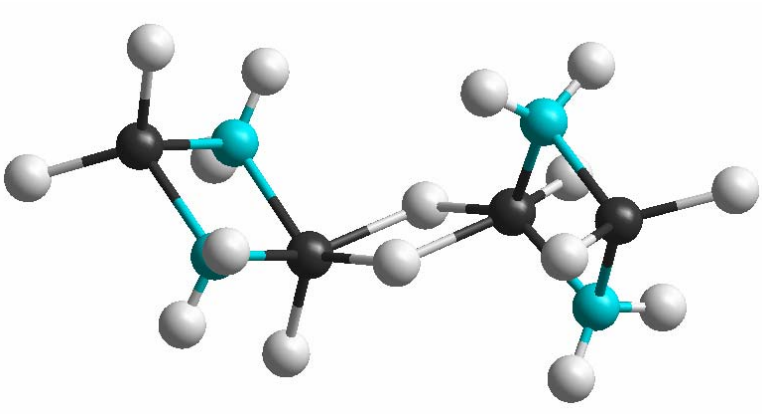
4. Estimate of the dimerization energy for c-$(TiHCH)_2$ (cis) via formation of the Ti…C bonds.

$^1(TiHCH)_4$ cube, E = –3554.87080918 au

E($^1(TiHCH)_4$) per one $TiCH_2$ unit = –888,7177025 au;
E($^1(TiHCH)_2$) per one $TiCH_2$ unit = –888,655135 au;
Dimerization energy per one $TiCH_2$ unit = –0,0625675 au (–1.7 eV).

5. Estimate of the dimerization energy for c-$(TiH_2CH_2)_2$ via $TiH^-…^-HTi$ interactions.

$^1(TiH_2CH_2)_2$ dimer, E = –3559.57334120 au



R(Ti–C) = 2.031, 2.036, 2.017, 2.019, 2.025, 2.029, 2.033, 2.036 Å, $\alpha(H_{bridg}TiH_{bridg})$ = 67.9°, 68.1°, $\alpha_{dih}(TiH_{bridg}H_{bridg}Ti)$ = 179.1°.

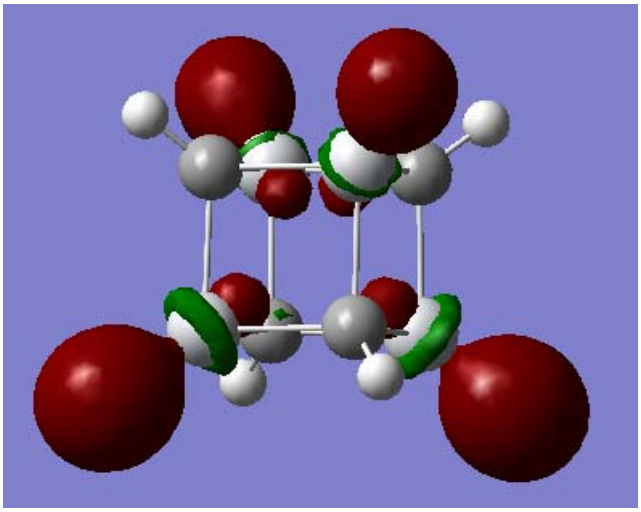
E_{HOMO} (A) = –0.273 au, E_{LUMO} (A) = –0.118 au, ΔE_{HL} = 0.155 au.

Harmonic frequencies – all real frequencies for modes of A symmetry (cm^{-1}): 17, 23, 36 etc.

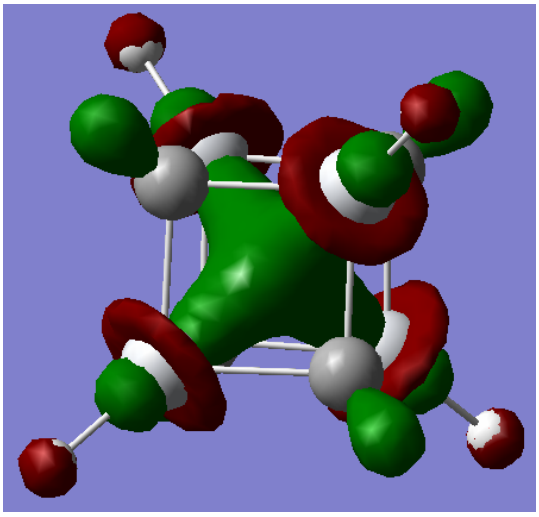
E($^1(TiH_2CH_2)_2$ dimer) per one $TiCH_4$ unit = –889.8933353 au;
E($^1(TiH_2CH_2)_2$) per one $TiCH_2$ unit = –889.882004275 au;
Dimerization energy per one $TiCH_2$ unit = –0.011331025 au (–0.31 eV).

6. Chosen orbitals (particularly the frontier ones) of selected Ti–Substituted Hydrocarbons (TSHs).

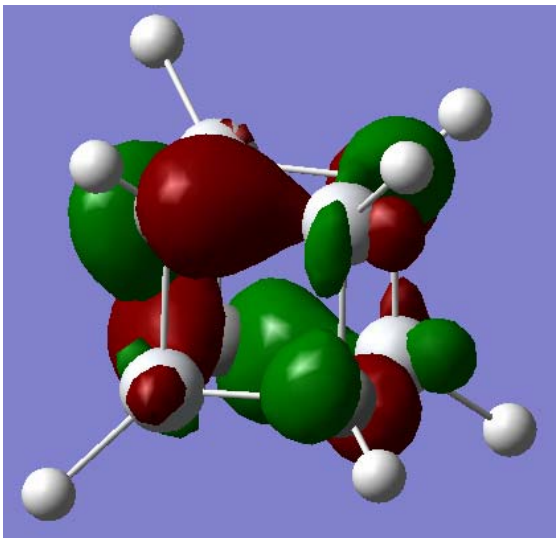
^{1}(TiHCH)$_4$ cube



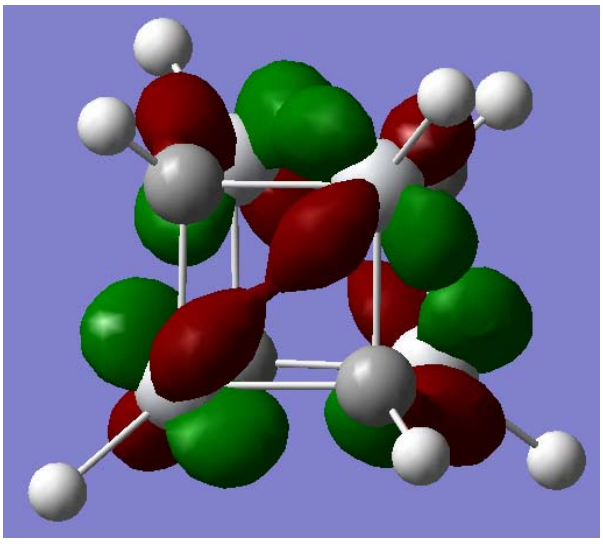
HOMO – the bonding combination of 1s orbitals of H_{Ti} and d(z^2) orbitals of Ti.



LUMO – the slightly bonding combination of d(z^2) orbitals of Ti with smaller contribution from 1s orbitals of H_{Ti} and H_C.

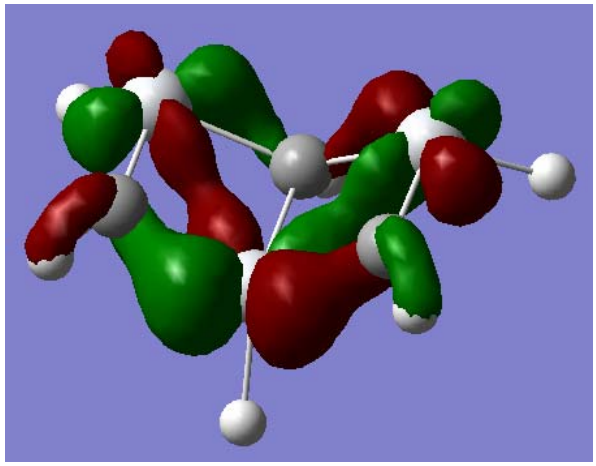


HOMO–2 – the bonding combination of 2p orbitals of C and d orbitals of Ti.

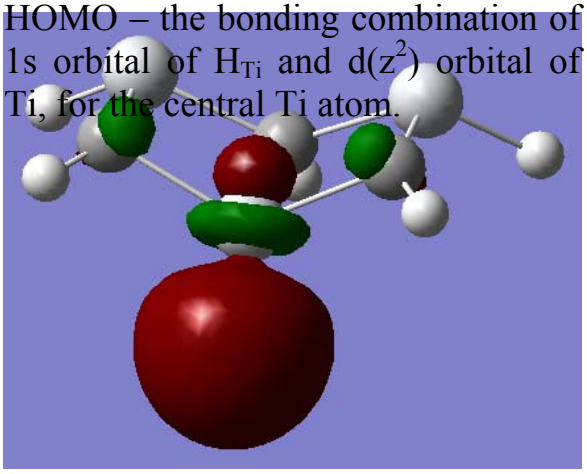


LUMO+1 – the essentially nonbonding combination of d (x^2–y^2) orbitals of Ti.

^{1}(TiHCH)$_3$ trimer, boat

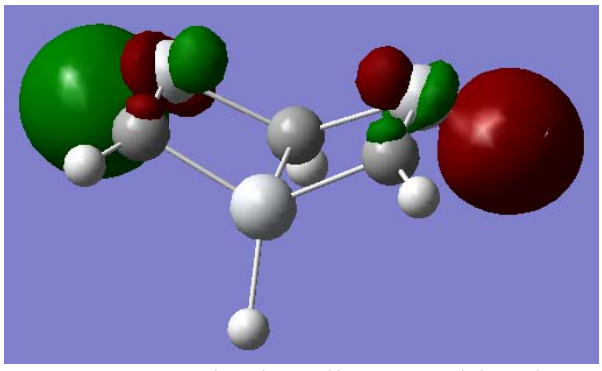


HOMO – the bonding combination of 1s orbital of H_{Ti} and d(z^2) orbital of Ti, for the central Ti atom.

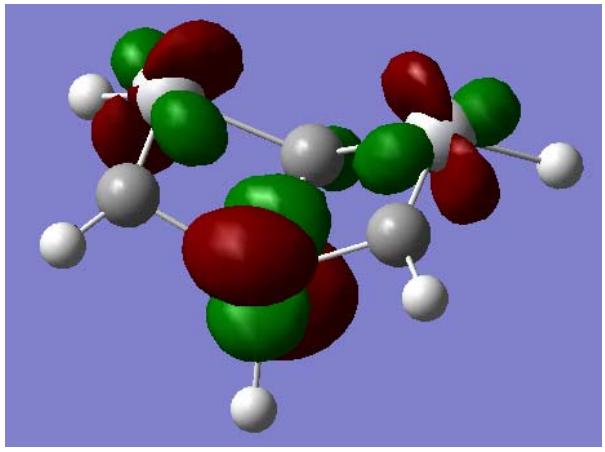


with smaller contribution from orbitals of the CH entities.

LUMO – the slightly bonding combination of d($x^2 - y^2$) orbitals of Ti

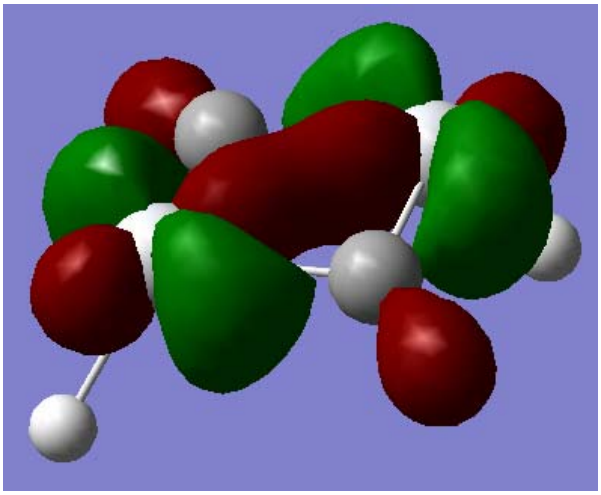


HOMO–1 – the bonding combination of 1s orbital of H_{Ti} and d(z^2) orbital of Ti, for terminal Ti atoms.

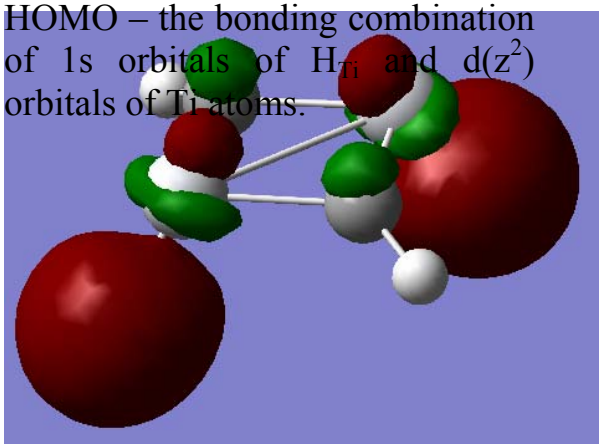


LUMO+1 – the nonbonding combination of d(xy) orbitals of Ti atoms.

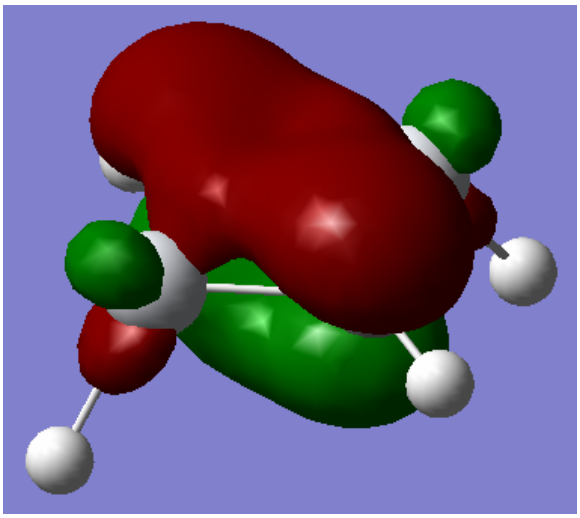
$^1(TiHCH)_2$ dimer, umbrella

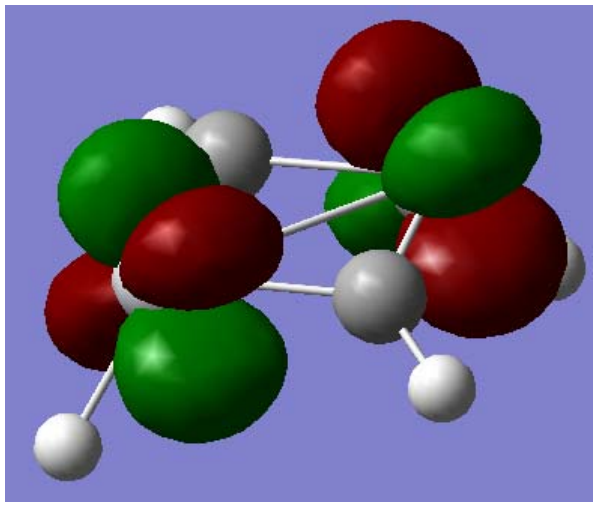


HOMO – the bonding combination of 1s orbitals of H_{Ti} and $d(z^2)$ orbitals of Ti atoms.



LUMO – the weakly bonding combination of $d(x^2–y^2)$ orbitals of Ti atoms, with small contribution from 1s orbitals of H_C atoms.

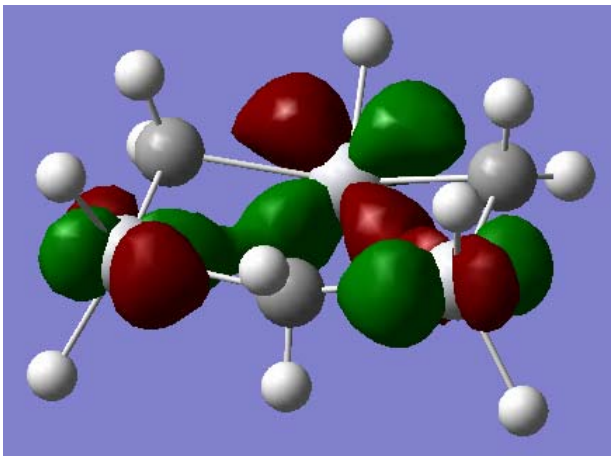


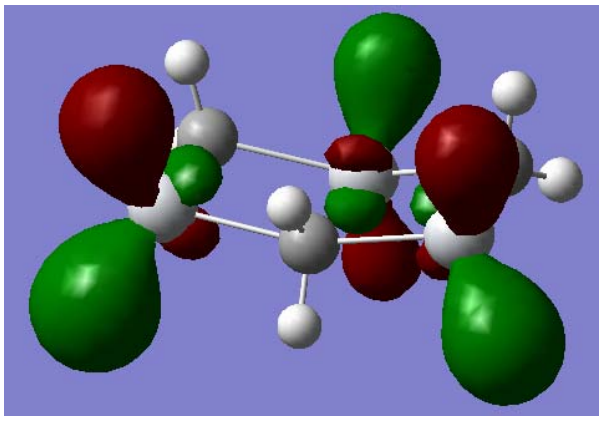


HOMO–3 – the bonding combination of 2p(z) orbitals of C and d(xz) orbitals of Ti atoms.

LUMO+1 – the nonbonding combination of d(yz) orbitals of Ti atoms.

$^1(TiH_2CH_2)_3$ trimer, boat

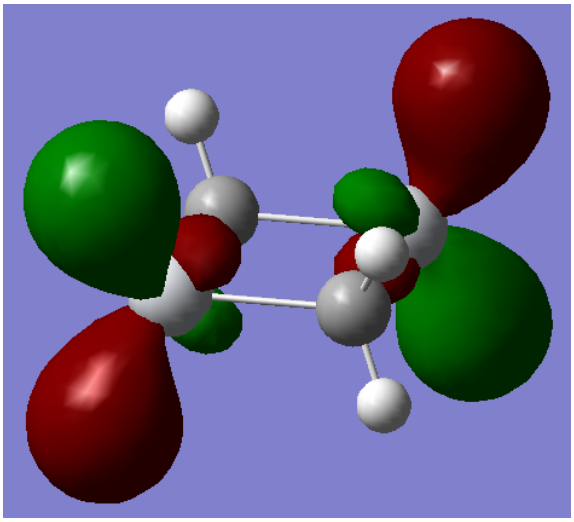




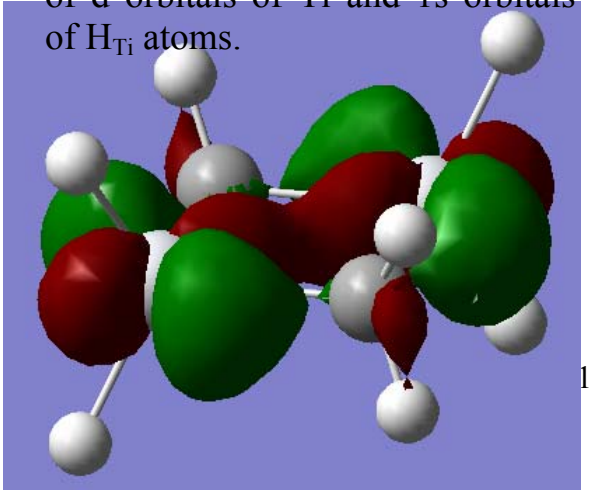
HOMO – the bonding combination of d orbitals of Ti and 1s orbitals of H_{Ti} atoms.

LUMO – the nonbonding combination of d orbitals of Ti atoms.

$^1(TiH_2CH_2)_2$ dimer

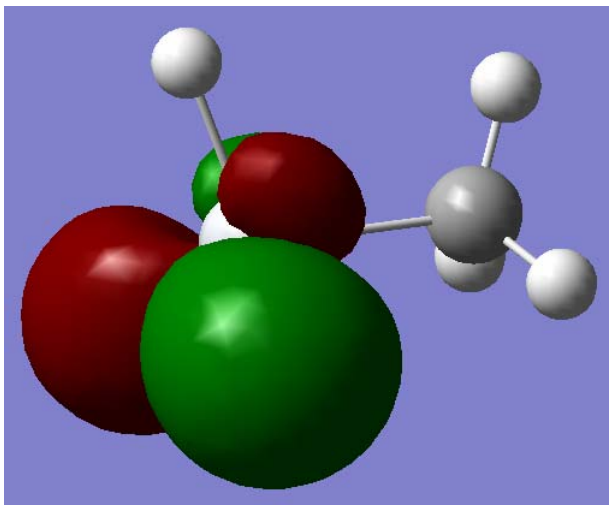


HOMO – the bonding combination of d orbitals of Ti and 1s orbitals of H_{Ti} atoms.

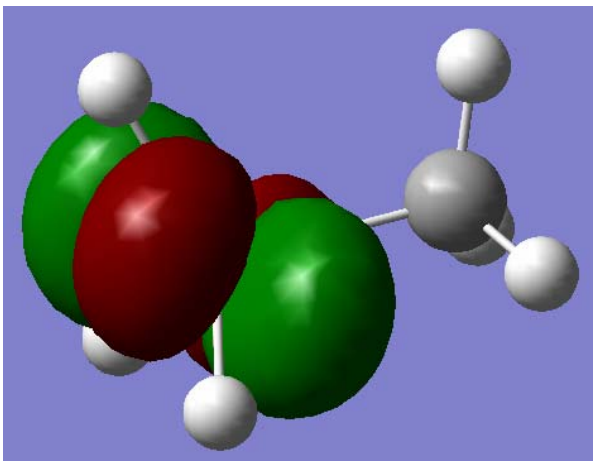


LUMO – the essentially nonbonding combination of d orbitals of Ti atoms.

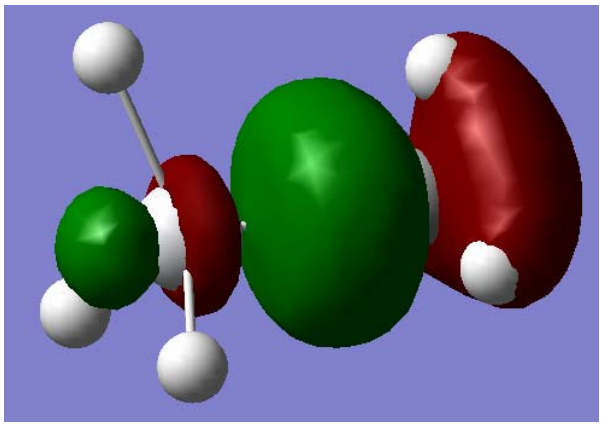
$^1(H_3TiCH_3)$ monomer



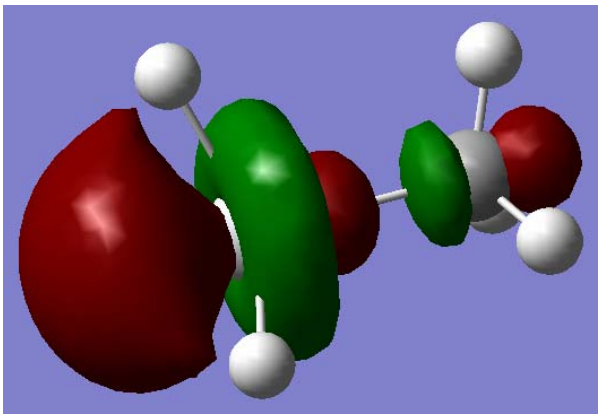
HOMO – the bonding combination of d orbital of Ti and 1s orbitals of two H_{Ti} atoms.



LUMO – the nonbonding d orbital of Ti.



HOMO–3 – the bonding combination of $d(z^2)$ orbital of Ti and p(z) orbital of C atom (σ).



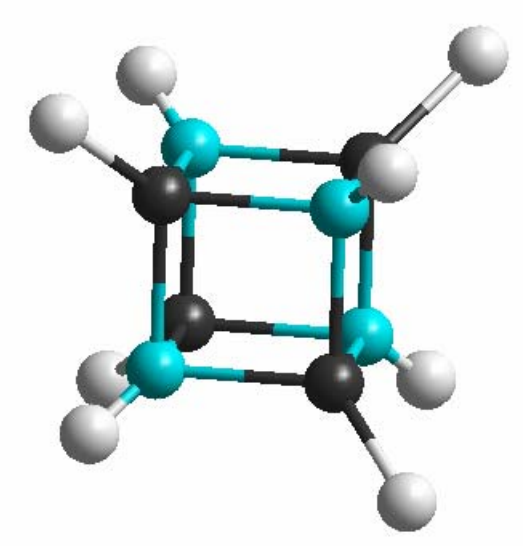
LUMO+2 – the antibonding combination of $d(z^2)$ orbital of Ti and p(z) orbital of C, with Ti-H bonding contribution from 1s orbital of H_{Ti}.

7. Estimate of the vertical and relaxed ionization potential and electron affinity of $(TiHCH)_4$.

$^1(TiHCH)_4$ cube, E = –3554,87080918 au

$^2(TiHCH)_4^{1-}$ cube, non relaxed, E = –3554,94214970 au; E_A^{vert} = –1.94 eV

$^2(TiHCH)_4^{1-}$ cube, relaxed, E = –3554,94800333 au; E_A^{rel} = –2.10 eV



R(Ti–C) = 2.026 x2, 2.013 x2, 2.032 x4, 2.071 x4 Å, R(Ti–H) = 1.697 x2, 1.701 x2 Å, R(C–H) = 1.103 x4 Å.

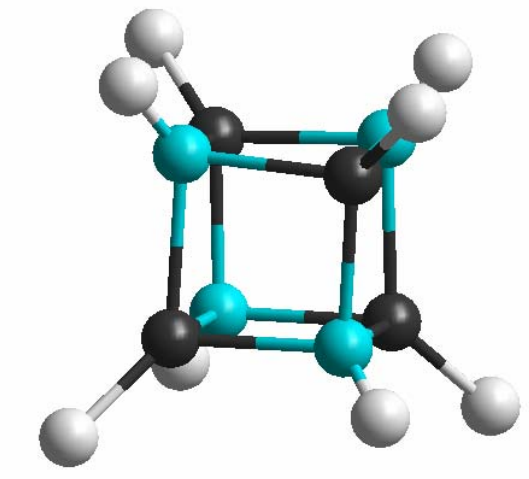
$E_{SOMO,\alpha}$ (A) = –0.029 au, $E_{SOMO+1,\alpha}$ (A) = +0.034 au, ΔE = 0.063 au.

q(Ti) = +1.093 x4 e, q(C) = –1.177, –1.178, –1.180, –1.181 e, $q(H_{Ti})$ = –0.238 x4 e, $q(H_C)$ = +0.075 x4 e, μ_{DIP} = 0.0 D.

Harmonic frequencies – all real frequencies for modes of A symmetry.

$^2(TiHCH)_4^{1+}$ cube, non relaxed, E = –3554,54968800 au; I_P^{vert} = 8.75 eV

$^2(TiHCH)_4^{1+}$ cube, relaxed, E = –3554,55989288 au; I_P^{rel} = 8.47 eV



R(Ti–C) = 2.043 x8, 2.044 x4 Å, R(Ti–H) = 1.807 x 4 Å, R(C–H) = 1.102 x4 Å.

$E_{SOMO,\alpha}$ (A) = –0.431 au, $E_{SOMO+1,\alpha}$ (A) = –0.294 au, ΔE = 0.137 au.

q(Ti) = +0.854 x2, +1.218 x2 e, q(C) = –0.972 x2, –1.154 x2 e, $q(H_{Ti})$ = +0.054 x2, +0.091 x2 e, $q(H_C)$ = +0.189 x2, +0.219 x2 e, μ_{DIP} = 0.6 D.

Harmonic frequencies – all real frequencies for modes of A symmetry.

The values of I_P^{rel}, E_A^{rel}, μ_{EN}, and η of cubic $^1(TiHCH)_4$ tetramer (8.47 eV, 2.10 eV, 5.29 eV, 3.19 eV) are comparable to those for atom of 'noble' Au (9.22 eV 2.3 eV, 5.76 eV and 3.46 eV, respectively), or of NO_2 radical (9.60, 2.27 eV, 5.94 eV, 3.67 eV). This indicates that $^1(TiHCH)_4$ could form moderately stable anions, by analogy to known Au^- and NO_2^-.

8. Estimate of the enthalpies (at T=0 K) of the reactions of H_2 detachment, hydrocarbon elimination, and clustering of various TSHs.

(i) No zero-vibrational corrections have been introduced.

(ii) Paths leading to compounds of (formally) Ti^{1+} or Ti^{3+} have not been considered.

(iii) Lowest energy structures have been taken into calculations.

(iv) All values are per one TiC unit, in eV/molecule.

I. Dehydrogenation.

$TiCH_6 \rightarrow TiCH_4 + H_2$	+0.77 eV
$TiCH_4 \rightarrow TiCH_2 + H_2$	+2.01 eV
$TiCH_2 \rightarrow TiC + H_2$	+3.28 eV
$\frac{1}{2}\,(TiCH_4)_2 \rightarrow \frac{1}{2}\,(TiCH_2)_2 + H_2$	+1.21 eV
$\frac{1}{2}\,(TiCH_2)_2 \rightarrow \frac{1}{2}\,(TiC)_2 + H_2$	+1.67 eV
$\frac{1}{3}\,(TiCH_4)_3 \rightarrow \frac{1}{3}\,(TiCH_2)_3 + H_2$	+0.88 eV
$\frac{1}{3}\,(TiCH_2)_3 \rightarrow \frac{1}{3}\,(TiC)_3 + H_2$	+1.44 eV
$\frac{1}{4}\,(TiCH_4)_4 \rightarrow \frac{1}{4}\,(TiCH_2)_4 + H_2$	–0.33 eV
$\frac{1}{4}\,(TiCH_2)_4 \rightarrow \frac{1}{4}\,(TiC)_4 + H_2$	+0.95 eV

II. Hydrocarbon elimination.

$TiCH_6 \rightarrow TiH_2 + CH_4$	+0.92 eV
$TiCH_6 \rightarrow TiH_4 + \frac{1}{2}\,C_2H_4$	+1.24 eV
$TiCH_4 \rightarrow Ti + CH_4$	+0.65 eV
$TiCH_4 \rightarrow TiH_2 + \frac{1}{2}\,C_2H_4$	+1.42 eV
$TiCH_2 \rightarrow Ti + \frac{1}{2}\,C_2H_4$	–0.09 eV
$\frac{1}{2}\,(TiCH_4)_2 \rightarrow \frac{1}{2}\,Ti_2 + CH_4$	+2.11 eV
$\frac{1}{2}\,(TiCH_4)_2 \rightarrow \frac{1}{2}\,(TiH_2)_2 + \frac{1}{2}\,C_2H_4$	+1.06 eV

$\frac{1}{2}$ $(TiCH_2)_2$ -> $\frac{1}{2}$ Ti_2 + $\frac{1}{2}$ C_2H_4 +1.11 eV

$\frac{1}{3}$ $(TiCH_4)_3$ -> $\frac{1}{3}$ Ti_3 + CH_4 +0.96 eV

$\frac{1}{3}$ $(TiCH_4)_3$ -> $\frac{1}{3}$ $(TiH_2)_3$ + $\frac{1}{2}$ C_2H_4 +0.19 eV

$\frac{1}{4}$ $(TiCH_4)_4$ -> $\frac{1}{4}$ Ti_4 + CH_4 +1.33 eV

$\frac{1}{3}$ $(TiCH_2)_3$ -> $\frac{1}{3}$ Ti_3 + $\frac{1}{2}$ C_2H_4 +1.36 eV

$\frac{1}{4}$ $(TiCH_2)_4$ -> $\frac{1}{4}$ Ti_4 + $\frac{1}{2}$ C_2H_4 +2.64 eV

III. Clustering.

$TiCH_4$ -> $\frac{1}{2}$ $(TiCH_4)_2$ –0.99 eV

$\frac{1}{2}$ $(TiCH_4)_2$ -> $\frac{1}{3}$ $(TiCH_4)_3$ –0.13 eV

$\frac{1}{3}$ $(TiCH_4)_3$ -> $\frac{1}{4}$ $(TiCH_4)_4$ +0.05 eV

$TiCH_2$ -> $\frac{1}{2}$ $(TiCH_2)_2$ –1.79 eV

$\frac{1}{2}$ $(TiCH_2)_2$ -> $\frac{1}{3}$ $(TiCH_2)_3$ –0.46 eV

$\frac{1}{3}$ $(TiCH_2)_3$ -> $\frac{1}{4}$ $(TiCH_2)_4$ –1.16 eV

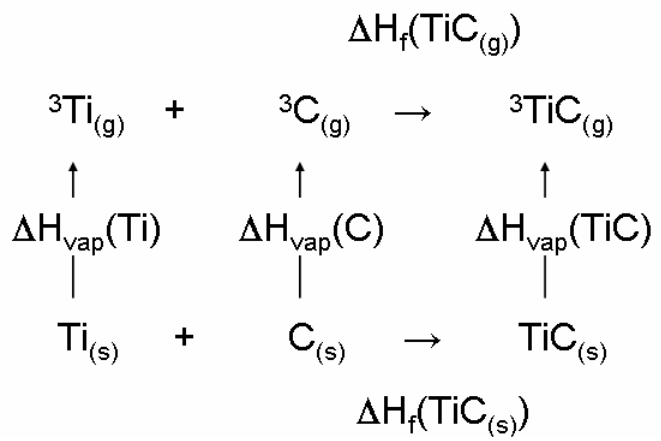
TiC -> $\frac{1}{2}$ $(TiC)_2$ –3.40 eV

$\frac{1}{2}$ $(TiC)_2$ -> $\frac{1}{3}$ $(TiC)_3$ –0.69 eV

$\frac{1}{3}$ $(TiC)_3$ -> $\frac{1}{4}$ $(TiC)_4$ –1.58 eV

9. Estimate of the vaporization enthalpy of solid TiC.

From the Born–Haber cycle (graph below) one can write:



$\Delta H_{vap}(TiC) = \Delta H_{vap}(Ti) + \Delta H_{vap}(C) + \Delta H_f(TiC_{(g)}) - \Delta H_f(TiC_{(s)})$.

If we use experimental values (knovel database) of $\Delta H_{vap}(Ti)$ = +4.94 eV, $\Delta H_{vap}(C)$ = +7.43 eV, $\Delta H_f(TiC_{(s)})$ = −1.91 eV, and theoretical value of $\Delta H_f(TiC_{(g)})$ = −4.01 eV (this work), the impressively large value of $\Delta H_{vap}(TiC)$ = +6.45 eV is obtained. The experimental value of T_{boil} of TiC is about 3140 ^oC. If the value of $\Delta H_f(TiC_{(g)})$ = −3.08 eV (Ref.17a) is used, somewhat smaller $\Delta H_{vap}(TiC)$ = +5.52 eV is obtained.

10. Calculation of the minimum values of the thermal decomposition temperature for chosen TSHs.

Approximate minimum values of the thermal decomposition temperature, T_{dec}, for the process of H_2 elimination from TSHs

$TiCH_{2x} \rightarrow TiCH_{2x-2} + H_2$,

can be obtained from the condition of the thermodynamic stability:

$\Delta G_{dec} = \Delta H_{dec} + T_{dec}\, \Delta S_{dec} = 0$.

If $TiCH_{2x}$ and $TiCH_{2x-2}$ are solids, then the entropy of the decomposition reaction is approximately equal to the entropy of gaseous H_2 (=130.68 J mol^{-1} K^{-1}). Thus:

$T_{dec} \geq \Delta H_{dec} / S(H_2)$, where ΔH_{dec} is per 1 mole of TiC units.

The values of T_{dec} determined using this method are listed below for selected TSHs.

TSH	**T_{dec} /K**
$Ti_4C_4H_8$	701
$Ti_3C_3H_{12}$	649
$TiCH_6$	568

Obviously, these values are overestimated if (a) gradual H_2 evolution occurs and (b) simultaneous clustering of the TiC takes place.

11. H_2 absorption path for ^{3}TiC and ^{1}TiC.

Figure A1 shows the electronic energy of the $H_2/^3TiC$ and $H_2/^1TiC$ systems during geometry optimization, *vs.* step number. **Figures A2** and **A3** show the

concomitant changes of the TiC and HH distances for $H_2/^3TiC$ and $H_2/^1TiC$, respectively.

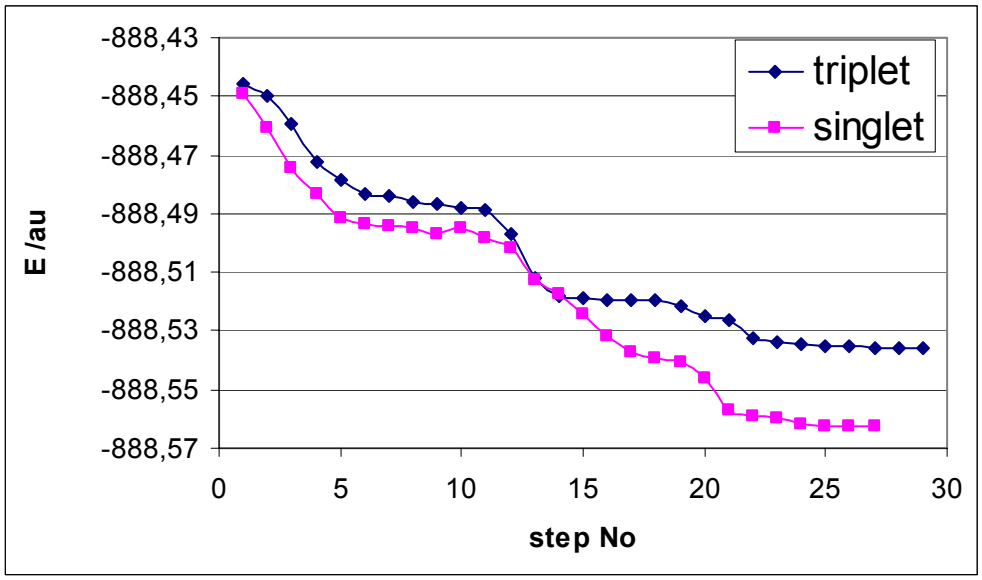


Figure A1.

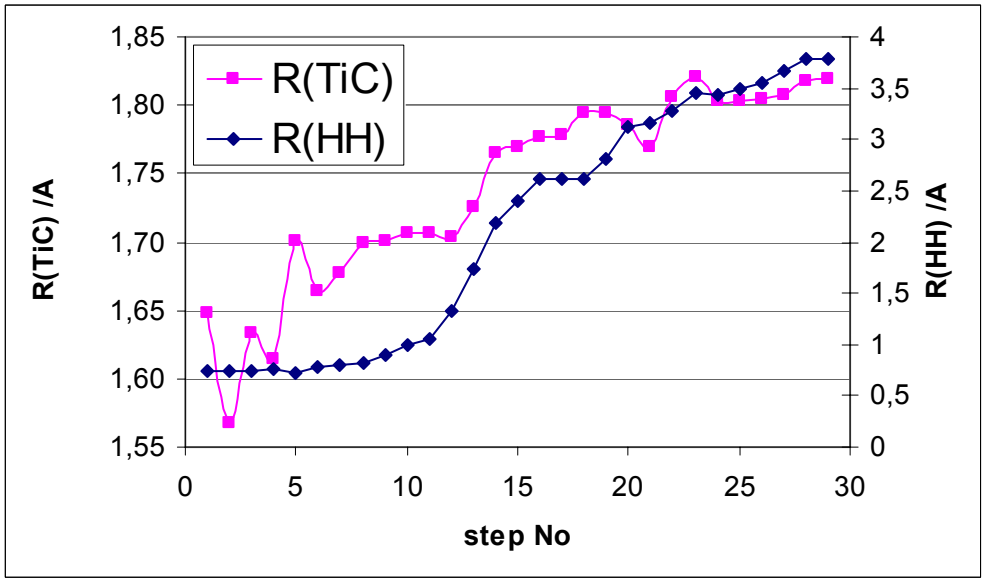


Figure A2. ^3TiC

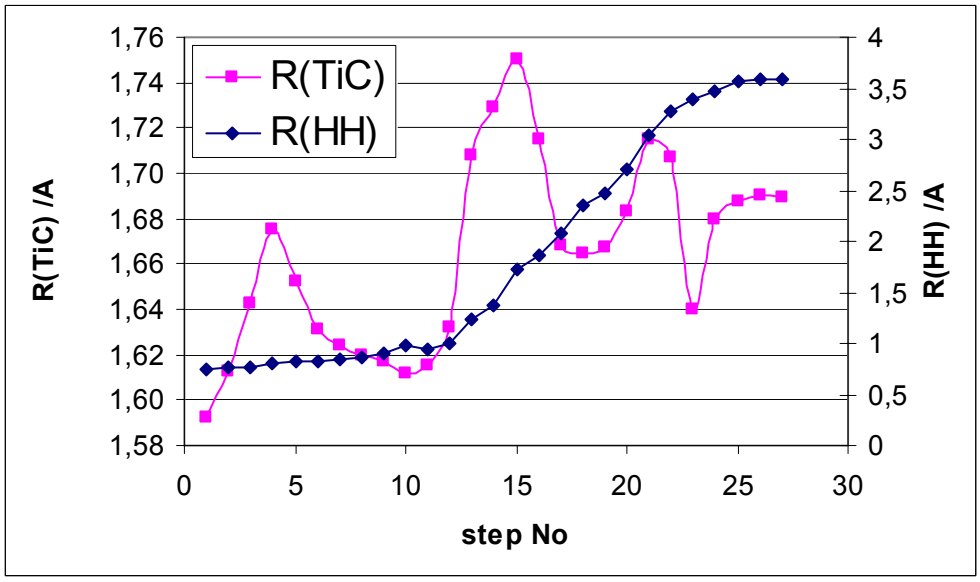
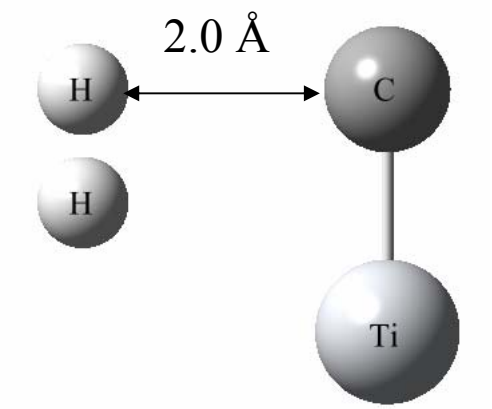


Figure A3. ^1TiC

Starting geometry for both optimizations corresponds to set of coplanar and paralel TiC and H_2 molecules at their equilibrium bond lengths, as in a schematic picture below.



Advanced calculations show that TiC molecule has triplet ground state, but the singlet state is only 0.05–0.07 eV above the ground state. (a) C. W. Bauschlicher, P. E. M. Siegbahn, *Chem. Phys. Lett.*, 1984, **104**, 331; (b) M. D. Hack, R. G. A. R. Maclagan, G. E. Scuseria, M. S. Gordon, *J. Chem. Phys.*, 1996, **104**, 6628. Our calculations reproduce qualitatively this feature. ^{3}TiC could easily be excited thermally to ^{1}TiC at 298 K.

Figure **A4** shows the schematic diagram of the H_2 absorption path for ^{3}TiC + H_2 and ^{1}TiC + H_2 reactions.

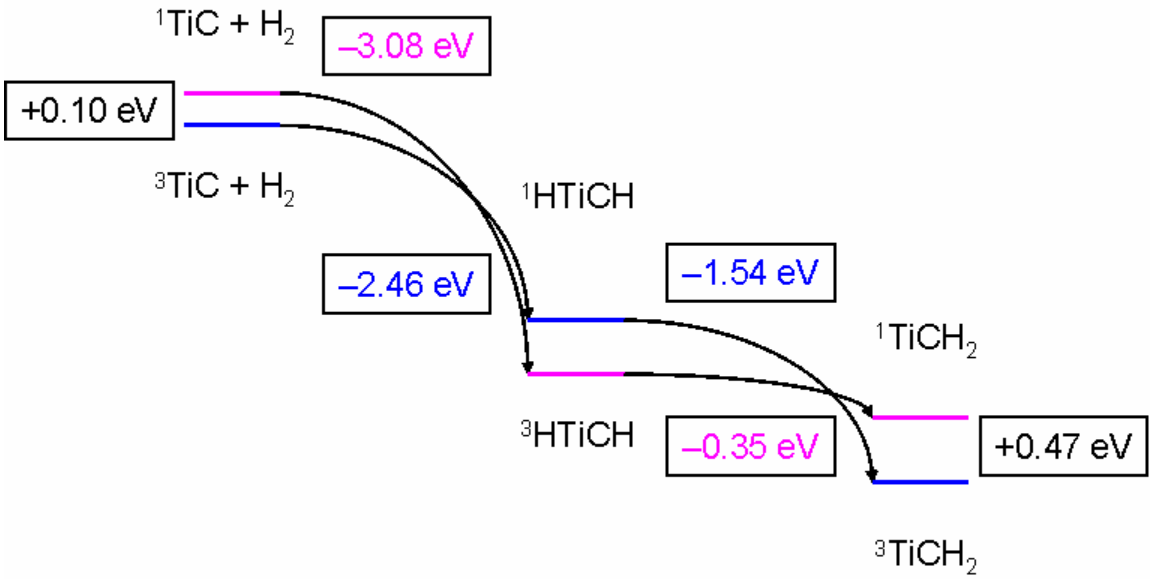


Fig. A4

It turns out that H_2 molecule easily reacts with ^{3}TiC and ^{1}TiC while initially producing the high-energy isomers (acetylene-like cis-HTiCH forms, bent on C and on Ti) of $^3TiCH_2$ and $^1TiCH_2$, respectively. Remarkably, reaction shows no apparent energy barrier at this stage (regardless of multiplicity of TiC species), despite necessity of an endothermic heterolytic splitting of H_2 molecule. At the second stage of reaction, H transfer occurs between Ti and C, thus yielding the most stable isomers of the products. We have not computed the isomerization pathway for this step, but it is supposed to be connected with an energy barrier which determines the kinetics of the overall process.

Larger $(TiCH_{2n})_m$ clusters (n=1,2; m=3,4) show preference for the $H^{\delta-}$ Ti…$CH^{\delta+}$ form; now isomerization to Ti…CH_2 form leads to energy increase. We anticipate that H_2 attachment reactions could occur for these clusters with little or no energy barrier, similar to the first stage of reaction for ^{1}TiC and ^{3}TiC.

12. H_2 absorption for $^1Ti_4C_4$. Reaction path for $^1Ti_4C_4H_6 + H_2$.

E ($^1Ti_4C_4$) = 3550.002 au

Δ=0.837 au (endothermic)

E ($^1Ti_4C_4H_2$) = 3550.839 au

Δ=1.602 au (egzothermic)

E ($^1Ti_4C_4H_4$)* = 3552.441 au

$E(H_2)$ = 1.1796 au

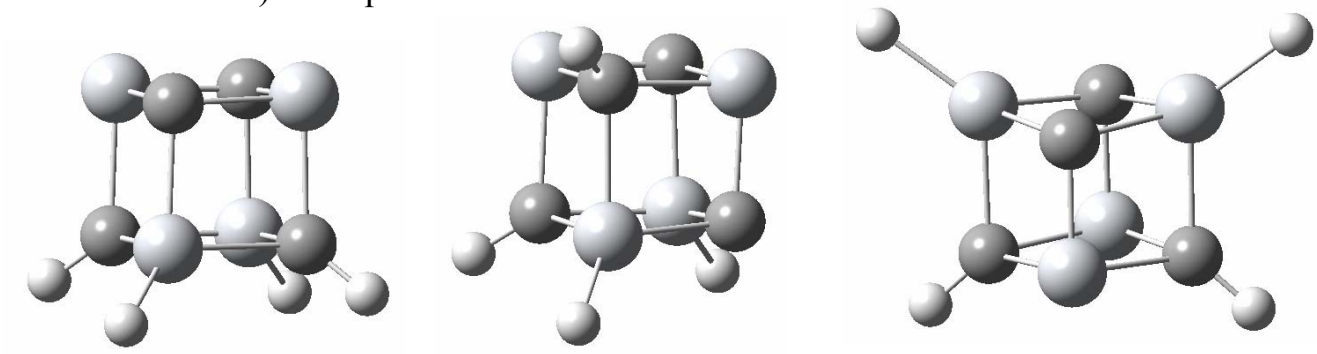
E ($^1Ti_4C_4H_6$) = 3553.654 au

Δ=1.213 au (egzothermic)

E ($^1Ti_4C_4H_8$) = 3554.871 au

Δ=1.217 au (egzothermic)

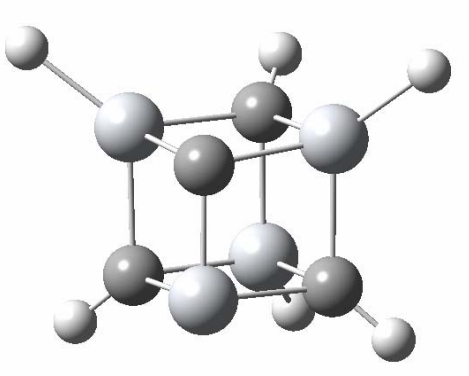
* for isomer a) – see pictures below



a) E=3552.441 au b) E=3552.432 au c) E=3552.425 au

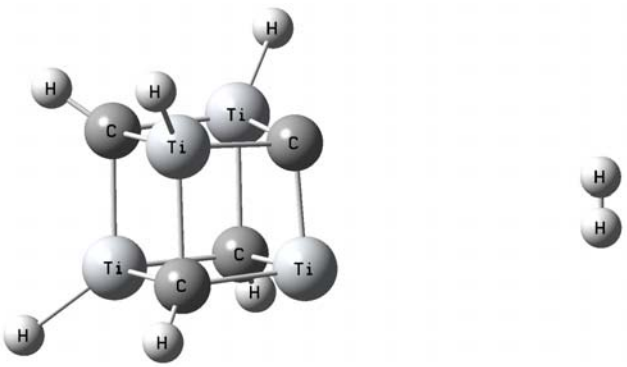
Three isomers of $^1Ti_4C_4H_4$ (top) and $^1Ti_4C_4H_6$ (bottom).

E = 3553.654 au



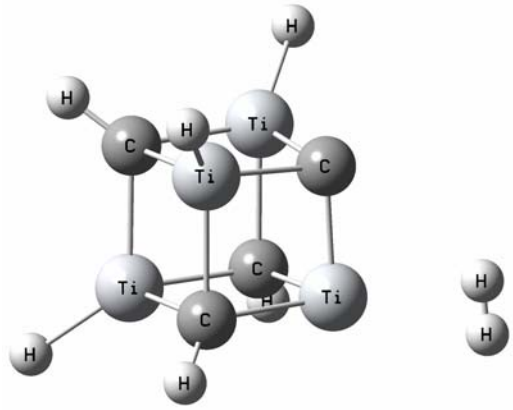
No imaginary vibrational frequencies have been detected for computed energy minima found for $Ti_4C_4H_2$, three isomers of $Ti_4C_4H_4$, and $Ti_4C_4H_6$.

We have then studied the H_2 absorption path for partially hydrogenated $Ti_4C_4H_6$ cluster (substrates, **S**); here $Ti_4C_4H_8$ is the thermodynamically stable reaction product (**P**). It turns out that reaction path is complicated; reaction proceeds *without any barrier* from substrates to the dihydrogen complex **H_2C**, and subsequently through transition state **TS** (with the corresponding barrier of 0.33 eV = 7.6 kcal/mole), to the product.

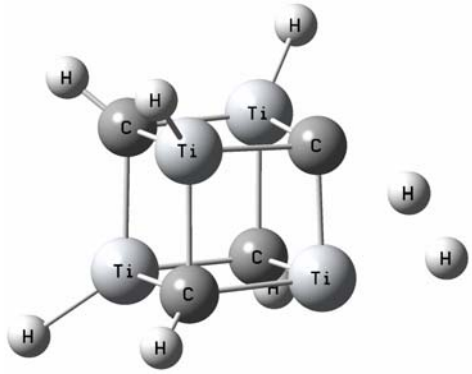


Starting geometry of substrates, **S**, corresponds to set of $Ti_4C_4H_6$ and H_2 molecules at their equilibrium geometries, and at rather large mutual separation > 4.5 Å (as in picture on the left): R(HH) = 0.744 Å; R(TiH) = 4.601-4.783 Å; R(CH) = 4.678-4.789 Å; R(TiC) = 1.857 Å.

The dihydrogen complex, **H_2C**, has the following structure: R(HH) = 0.763 Å; R(TiH) = 2.168, 2.241 Å; R(CH) = 2.682, 3.217 Å; R(TiC) = 1.857 Å; $\alpha(H^1CTi)$ = 53.4°; $\alpha(H^2TiC)$ = 103.0°; $\alpha(H^1CTiH^2)$ = 0.0°. No img freq have been detected.



TS has the following geometry: R(HH) = 1.047 Å; R(TiH) = 1.818, 1.881 Å; R(CH) = 1.478, 2.415 Å; R(TiC) = 1.879 Å; $\alpha(H^1CTi)$ = 64.3°; $\alpha(H^2TiC)$ = 70.9°; $\alpha(H^1CTiH^2)$ = 0.0°. One img freq has been detected, ν_1 = –1225.6 cm^{-1}.



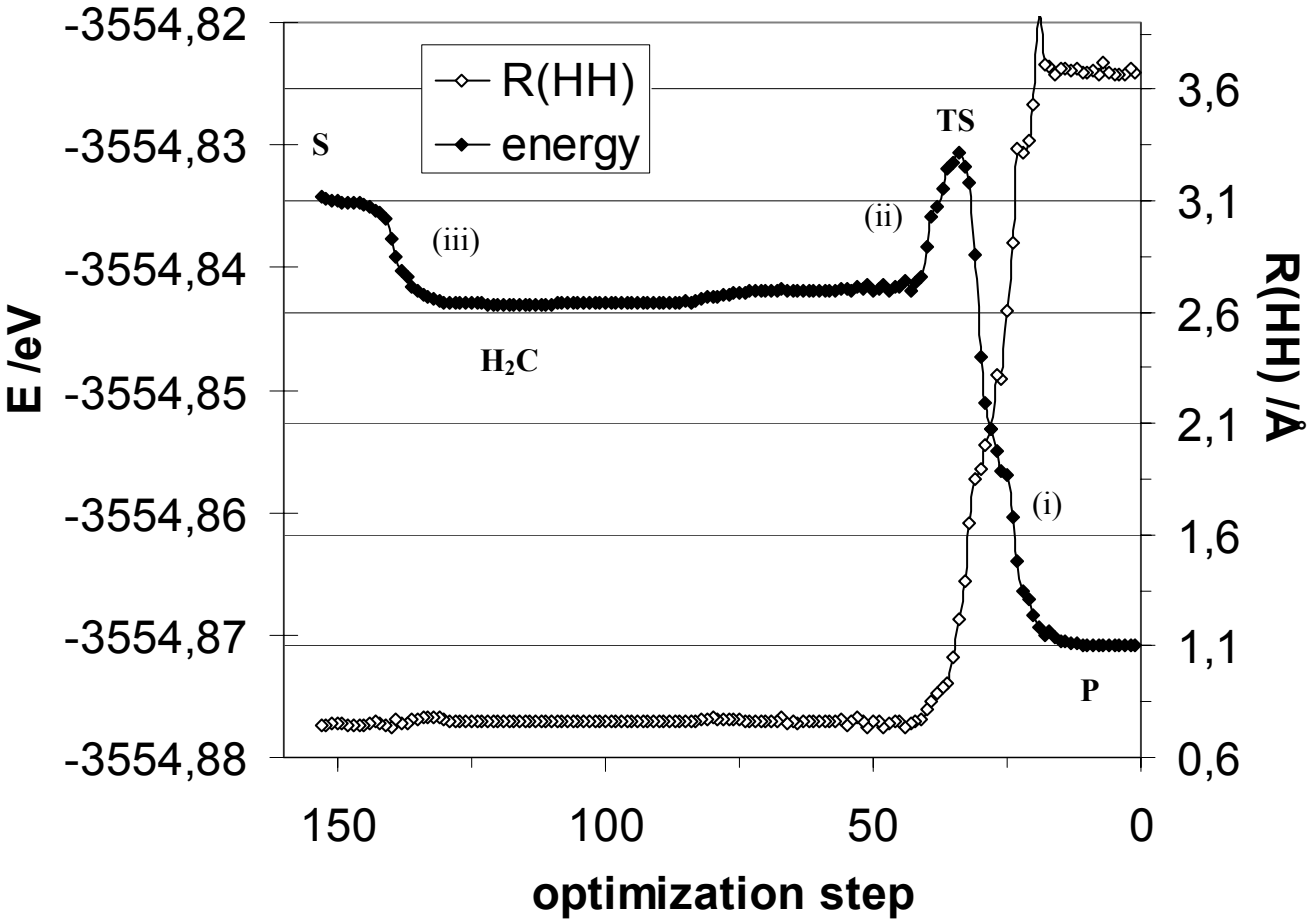
One can anticipate that there might exist another transition state, **TS'**, leading *directly* from **S** to **P**, with geometry rather similar to that of **TS**, and of absolute energy somewhat higher than that of **TS**; **TS'** should yield only *minor energy barrier* (slightly larger than 0.1 eV); unfortunately, we have failed to detect it on the complex PES of the reaction.

Subsequently, three independent optimizations were performed: (i) one has begun at the TS and proceeded towards the reactants; (ii) another started at TS, too, and proceeded towards the product (both optimizations have been initiated from genuine TS very slightly distorted along the normal coordinate which

shown imaginary frequency in our calculations). The last optimization (iii) started at substrates and proceeded towards the dihydrogen complex, H_2C.

Results of these three optimizations are shown together in a common picture. **Figure A5** shows the electronic energy of the $H_2/^1Ti_4C_4H_6$ system during optimizations, *vs.* step number, and the concomitant changes of the HH distance.

Figure A5. Reaction (optimization) path for $^1Ti_4C_4H_6$ & H_2. See text for definition of abreviations.



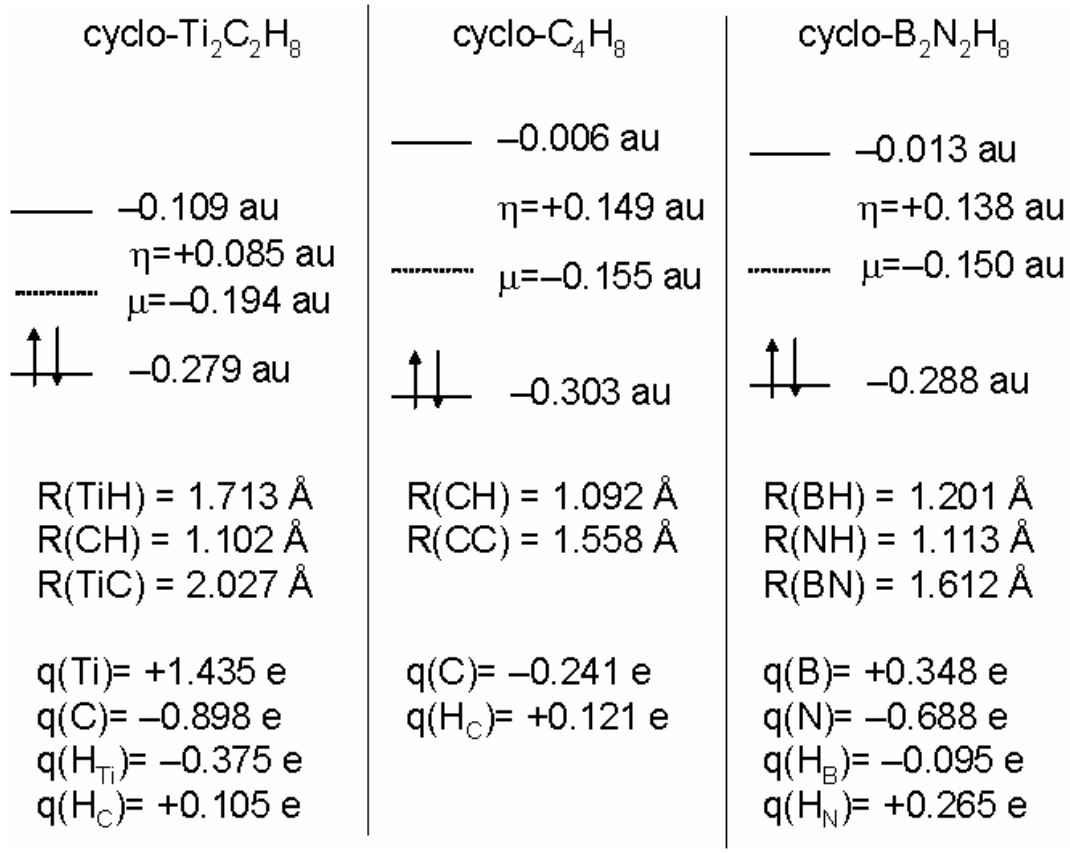
The kinetically stable H_2C intermediate state corresponds to the complex of H_2 with $Ti_4C_4H_6$; here H_2 is attached at the Ti corner, and the HH bond is only slightly elongated (0.763 Å). As the energy barrier from H_2C to product is small, only at low temperatures would the reaction get stuck at the kinetic intermediate (H_2C).

Fig.3 shown in the paper is identical with Fig.A5, except that many points of the flat parts of the PES (corresponding to very small geometry changes) have been removed for clarity in the former. The optimization path, rather than process taking place along intrinsic reaction coordinate, is calculated here

(note: DFT underestimates energy bariers). Still, effective barrier is thought to be very small due to immense zero-vibrational energy of C–H and Ti–H oscillators (> 0.5 eV per pair of H atoms).

13. Electronegativity perturbations for cyclo-C_4H_8.

Scheme below shows the consequences of two different electronegativity perturbations (ENPs) on cyclo-C_4H_8 for energy of frontier orbitals, Mulliken electronegativity (μ), Pearson hardenss (η), chosen bond lengths (R) and Mulliken charges on atoms (q).



Both ENPs result in elongation of the element–H bonds, in they increased ionicity, and in decrease of Pearson hardness of a molecule. It can be seen that the ENP leading to $Ti_2C_2H_8$ has much more pronounced consequences for the electronic structure, molecular geometry, and concomitant molecular parameters, than the electronegativity perturbation leading to $B_2N_2H_8$. This occurs despite the fact, that electronegativity differences of (Ti, C) and (B, N) are nearly identical.