Theoretical quest for the titanium-substituted hydrocarbons†

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Using theoretical calculations we predict a novel family of compounds, which might serve for hydrogen storage, and for chemical vapour deposition of titanium carbide coatings.

The electronegativity perturbation (ENP)[1] has significant consequences for the thermodynamic and kinetic stability of substituted hydrocarbons. The increase of thermodynamic stability of a molecule upon ENP may be giant, as for borazine, $B_3N_3H_{6(l)}$ (ΔG_f^0 = −392.7 kJ mol^{-1}) as compared to $C_6H_{6(l)}$ (ΔG_f^0 = +124.5 kJ mol^{-1}).[2] But another effect – an inter- or intramolecular proton–hydride interaction[3] – simultaneously decreases the thermal stability of the substituted compounds. In consequence the "perturbed" compounds often solidify easily (due to electrostatic stabilization of the crystal lattice, nearly absent for hydrocarbons), and they decompose with H_2 evolution at much lower temperatures than their carbon analogues. Take *e.g.* cyclohexane, which is thermally stable up to several hundreds °C, while cycloazagallane, $Ga_3N_3H_{12}$, decomposes at +150 °C to yield pure GaN and H_2.[4]

This paper presents the results of the DFT/B3LYP theoretical calculations‡ for hypothetical hydrocarbons in which half of the carbon atoms have been substituted by Ti in an ENP.[5,6] This novel family of molecules will be subsequently referred to as "Titanium-Substituted Hydrocarbons" (TSHs).[7] The optimized geometries of TSHs, possible transformations among them, and the calculated enthalpies of clustering and H_2 elimination reactions,[8] are shown in Fig. 1.†

$TiCH_6$, the most H-rich TSH (9.6 wt% H) and an analogue of ethane, can formally be viewed as a donor–acceptor adduct of the CH_3^- to elusive $Ti^{IV}(H^-)_3^+$, or alternatively as a product of the oxidative addition of methane to $Ti^{II}H_2$. As far as we know it has not yet been isolated in bulk, or observed in noble gas matrixes, in contrast to TiH_4, another hydride of tetravalent Ti.[9] The calculated enthalpies of elimination of H_2, CH_4 and ½ C_2H_4 from $TiCH_6$ are +0.77 eV, +0.92 eV and +1.24 eV per molecule, thus suggesting thermodynamic stability of gaseous $TiCH_6$ at ambient temperatures (even if an entropy term is considered[10]).

$Ti_2C_2H_4$ takes a rather non-classical geometry, with all H atoms attached to C and not to Ti (the cyclobutadiene-like isomer lays +0.16 eV above in energy). The ease of H transfer from Ti to C, seen also for $TiCH_4$ and $TiCH_2$, is typical of small TSHs. This feature has been previously observed also for other compounds with poor π overlap, such as $H_2C{=}TiHF$[11a] and unsaturated

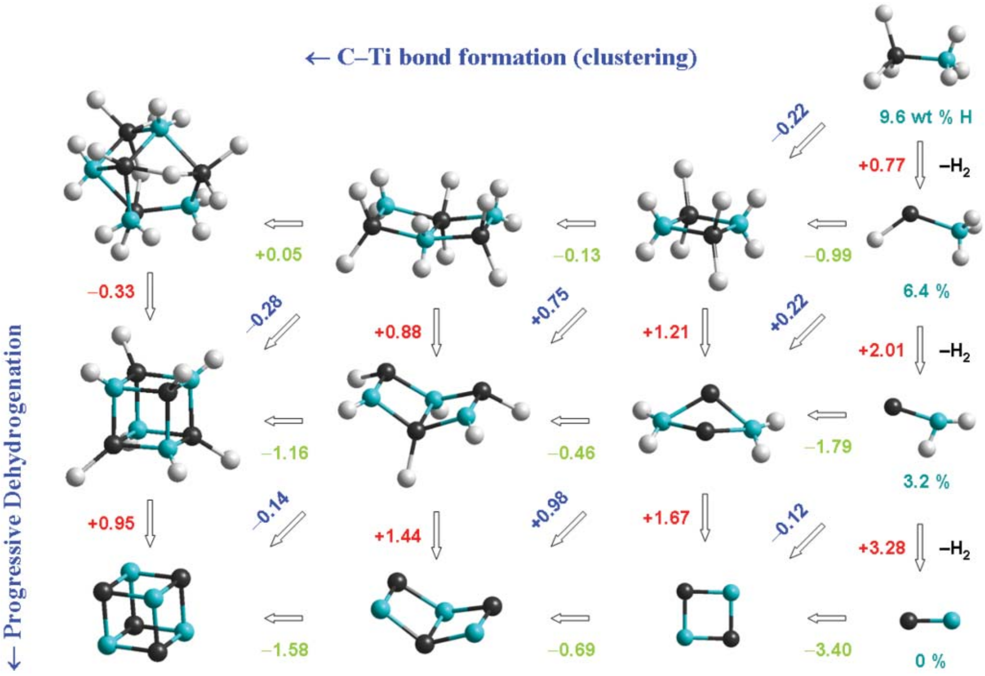

Fig. 1 Selected chemical transformations of TSHs (oligomerization or clustering and H_2 elimination) along with their calculated enthalpy/eV per TiC unit. Ti – black spheres, C – blue spheres, H – white spheres.

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† Electronic supplementary information (ESI) available: optimized geometries and molecular parameters, enthalpies of hydrocarbon elimination reactions and auxiliary numerical data. See http://www.rsc.org/suppdata/cc/b4/b418316a/

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silanes ($H_2Si{=}SiH_2$).[11b] However, it is diminished for larger $TiCH_{2n}$ oligomers, where all H atoms are equally shared between Ti and C.

$Ti_3C_3H_{12}$ and $Ti_3C_3H_6$, respective analogues of cyclohexane (or cycloazagallane, $Ga_3N_3H_{12}$) and benzene (or borazine, $B_3N_3H_6$), also adopt interesting geometries. The Ti_3C_3 core takes the boat conformation, but the Ti stern and the C stem now form a strong bond, thus making the TiC backbone similar to two edge-sharing Ti_2C_2 squares. A similar structural feature is seen for $(TiC)_3$. Great stability of the square TiC framework, confirmed by substantially negative values of enthalpy of oligomerization for odd members $(TiC)_1H_{2n}$ and $(TiC)_3H_{6n}$ (n = 1, 2), is seen also for fully dehydrogenated molecular $(TiC)_n$ species (*viz.* large enthalpy of formation of the $(TiC)_4$ cube). Recollect, solid TiC crystallizes in the NaCl structure; we estimate that its enthalpy of vaporization exceeds the impressive value of +6.45 eV per one TiC molecule.

$Ti_2C_2H_8$ and $Ti_4C_4H_8$ – despite the presence of early transition metal atoms – strongly resemble their hydrocarbon siblings (cyclobutane and cubane). The TiC separation is 2.03–2.04 Å, slightly smaller than the 2.16 Å seen for solid TiC. Both molecules are computed to be stable thermodynamically with respect to H_2 and hydrocarbon elimination even if entropy effects are accounted for.[10]

The HOMO and LUMO of $Ti_4C_4H_8$ are shown in Fig. 2. The HOMO is composed mainly of a σ bonding combination of $d(z^2)$ orbitals of Ti and 1s orbitals of H^- ions bound to Ti. The LUMO is formed from a σ* antibonding combination of $d(z^2)$ orbitals of Ti and 1s orbitals of H^- ions bound to Ti, with little contribution from 1s orbitals of H bound to C. The LUMO is essentially weakly bonding between Ti atoms. Donor function of a molecule is mainly hydride-centered, while acceptor function is based predominantly on Ti. Such a frontier orbital picture is representative of the majority of TSHs studied here. The Ti–H bonds are weak, long and quite ionic[12] (as compared to the Ti–C and C–H ones), and they form the uppermost σ manifold of a molecule.

For $Ti_4C_4H_8$ we predict the relaxed ionization potential, I_P, of 8.47 eV and relaxed electron affinity, E_A, of 2.10 eV. From these values one can calculate Mulliken electronegativity of 5.29 eV, and Pearson hardness of 3.19 eV. These parameters are comparable to those for an 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 eV, 2.27 eV, 5.94 eV, 3.67 eV). Comparison indicates that $(TiHCH)_4$ could form moderately stable anions, by analogy to known Au^- and NO_2^-; these anions could occur *e.g.* for alkali metal salts, such as $Cs_x(TiHCH)_4$. $(TiHCH)_4$ is also expected to undergo nonoxidative addition of Lewis bases at the Ti site, *e.g.* with formation of $(TiHCH)_4(H^-)_n$ or $(TiHCH)_4(CsH)_n$. The quite large electronegativity of TSHs and the interconnected substantial electrophilicity of the Ti site also explain the tendency of TSHs for dimerization through formation of Ti···H···Ti bridges. Interestingly, sharing hydride anions between Ti's stabilizes dimer more than intermolecular $CH^+\cdots{}^-HTi$ interactions. The former process, and progressive oligomerization *via* formation of new TiC bonds, are thought to predominate solidification paths of TSHs.

TSHs are hydrogen-rich molecules. The hydrogen content decreases from 9.6 wt% for $TiCH_6$, *via* 6.4 wt% for $(TiCH_4)_n$, down to 3.2 wt% H for $(TiCH_2)_n$. The overall H content for $(TiCH_4)_n$ homologues is slightly smaller than that for $NaAlH_4$ (7.4%), and is very close to the US DOE target of 6.5 wt%.[2b]

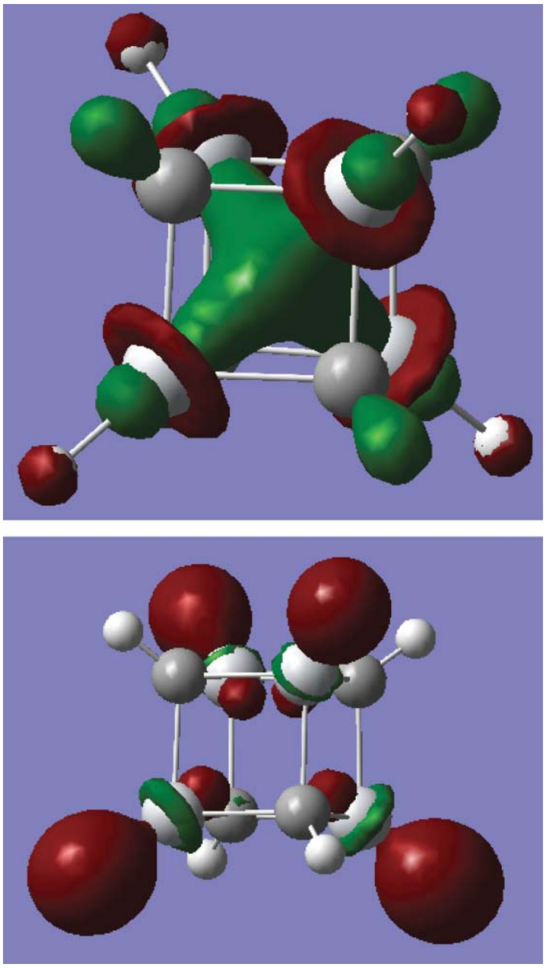

Fig. 2 The DFT HOMO (bottom) and LUMO (top) of $Ti_4C_4H_8$ cubane. Ti – big white spheres, C – big gray spheres, H – small white spheres.

There are two straightforward trends of H_2 evolution from TSHs. (i) At a constant size of the TiC core, H_2 release is least prohibited for the most H-rich TSH (analogue of alkanes), and more difficult for analogues of alkenes and alkynes.[13] (ii) At a constant H content, H_2 desorption is easier from oligomeric TSHs than from the monomers. It can therefore be anticipated that enthalpy of dihydrogen release of +0.40 eV (equal to entropy factor $S(H_2)T$ at 298 K) could be achieved for TiC clusters ('metcars'[14]) of moderate size. Such species are supposed to bind and release H_2 at ambient temperatures.[15] The surface of other prefabricated TiC nanostructures could also be decorated with H atoms *via* heterolytic splitting of H_2, as seen for related collapsed BN nanotubes.[16] This process could be reversible for moderate quantities of H_2 and in a narrow temperature range if polymerization is avoided of $(TiC)_n$ clusters after H_2 gas release.

Prompted by the possibility of feasible hydrogen absorption by TiC nanostructures, we have analyzed the reaction path for absorption of one H_2 molecule by $^1Ti_4C_4H_6$. This species exemplifies the smallest partially hydrogenated nanocluster with the 3D $(TiC)_4$ core. In Fig. 3 we show a diagram of the changes of electronic energy and HH distance along the reaction path.

It turns out that the H_2 molecule reacts exothermally with $^1Ti_4C_4H_6$ to yield the dihydrogen complex (H_2C); the reaction shows no energy barrier at this stage.[17] Remarkably, subsequent

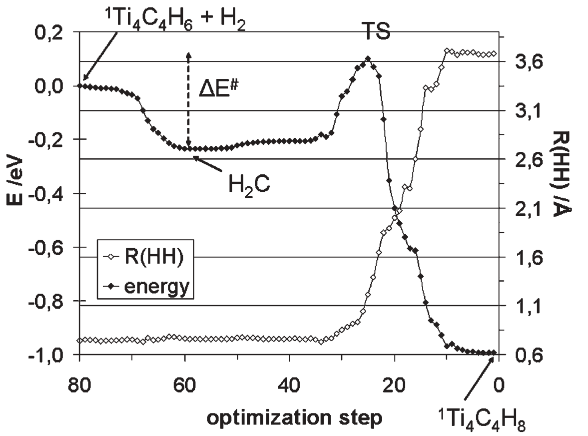

Fig. 3 Reaction path for attachment of H_2 to the non-hydrogenated edge of the $^1Ti_4C_4H_6$ nanocluster. Heterolytic splitting of the H_2 molecule yields a small energy barrier, $\Delta E^\#$, of 0.33 eV. H_2C stands for dihydrogen complex intermediate, TS for transition state.

activation of H_2C requires only 0.33 eV to reach the transition state on the way to product ($^1Ti_4C_4H_8$), despite the necessity of highly endothermic heterolytic splitting of the H_2 molecule. We anticipate that other partially hydrogenated TiC nanostructures are likely to store H_2 on their own and serve as catalysts of H_2 attachment/detachment reactions from other, more stable, hydrogen stores.[18]

Selected TSHs could also be used for chemical vapour deposition of mechanically and thermally resistant TiC coatings (by analogy with their BNH_{2n} and $GaNH_{2n}$ cousins which yield BN[19] and GaN[4], respectively). This process requires full thermal desorption of H_2 from volatile material, and in consequence demands an elevated temperature. At present, mixtures of $TiCl_4$ and CH_4 are used for TiC deposition, typically at 850–1050 °C in a H_2 atmosphere.[2] Such harsh conditions obviously eliminate thermally-sensitive materials from the substrate list. We estimate (see Supplementary Information) that TiC could be deposited under much milder conditions (300–450 °C) if TSHs are used for this purpose.

In conclusion we predict a novel family of potentially useful compounds, the Ti-substituted hydrocarbons. Many of these should be sufficiently stable towards H_2 and CH_4 elimination to survive at ambient temperatures without decomposition.[20] TSHs could possibly be obtained *via* metathetical (halide and cyclopentadienyl for hydride) substitutions for known methyltitanium halides.[5,21]

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Notes and references

‡ We used the 6-311++G** basis set for C and H, and the 6-31G** set for Ti.

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5 Compounds containing only Ti, C and H are scarce. $Ti(CH_3)_4$, which is a tetramethylmethane in which 1/5 of the C atoms have been substituted by Ti, has been obtained only in the form of THF or ether solvates, which decompose above −40 to −30 °C. For the most recent report see: S. Kleinhenz and K. Seppelt, *Chem. Eur. J.*, 1999, **12**, 3573 and references therein.
6 Titanium seems to be an ideal partner for carbon among metallic elements which are typically tetravalent (Groups 4 and 14, Ce, and Th). Ti can form multiple bonding to carbon, as exemplified by $^3Ti{\equiv}C$ or $Cp_2Ti{=}CCH_2$ (Cp = cyclopentadienyl). Tetravalent Ti ($3d^0$) readily adopts tetrahedral coordination, thus resembling the sp^3 C atom. (*a*) C. W. Bauschlicher and P. E. M. Siegbahn, *Chem. Phys. Lett.*, 1984, **104**, 331; (*b*) M. D. Hack, R. G. A. R. Maclagan, G. E. Scuseria and M. S. Gordon, *J. Chem. Phys.*, 1996, **104**, 6628; (*c*) M. Niehues, G. Erker, G. Kehr, P. Schwab, R. Frölich, O. Blacque and H. Berke, *Organometallics*, 2002, **21**, 2905.
7 The ENP is similar for TSHs and for BN compounds. The differences between Pauling and Mulliken electronegativities for Ti and C (1.01 au and 2.82 eV) are very close to respective values for B and N (1.00 au and 3.01 eV). Here au stands for arbitrary units of Pauling electronegativity. These values might suggest that the Ti–C bonds should be moderately ionic, similarly to the BN ones.
8 Some organometallic complexes of Ti are known to activate and/or eliminate methane, acetylene and H_2. See Ref. 6*c*, and (*a*) T. R. Cundari, *J. Am. Chem. Soc.*, 1992, **114**, 10557; (*b*) J. R. Hagadorn and M. J. McNevin, *Organometallics*, 2003, **22**, 609.
9 G. V. Chertihin and L. Andrews, *J. Am. Chem. Soc.*, 1994, **116**, 8322.
10 Entropies of gaseous H_2, CH_4 and ½ C_2H_4 translate to the following contributions to ΔG^0 at T = 298 K: −0.40 eV, −0.58 eV, and −0.34 eV.
11 (*a*) H. G. Cho and L. Andrews, *J. Phys. Chem. A*, 2004, **108**, 6294; (*b*) L. Sari, M. C. McCarthy, H. F. Schaefer and P. Thaddeus, *J. Am. Chem. Soc.*, 2003, **125**, 11409. For such compounds an inherent structural flexibility can influence the potential energy surface of the ground state.
12 Despite similar ENP for BN and TiC, the ionicity of the TiC bonds is much larger than that of the BN bonds in analogous molecules. For example, Mulliken charges are +1.02 e and −1.09 e for Ti and C ($Ti_4C_4H_8$), and +0.32 e and −0.54 e for B and N ($B_4N_4H_8$).
13 Similar behaviour is seen for other hydrides with substantial ENP, for which gradual thermal dehydrogenation occurs; see Ref. 3*b* and compare to G. Wolf, J. Baumann, F. Baitalow and F. P. Hoffmann, *Thermochim. Acta*, 2000, **343**, 19. Also for $^1H_3Ti^{IV}CH_3$, a two-step reaction is anticipated, the first step leading to $^2H_2Ti^{III}CH_3$ (+0.27 eV), and the second one to $^3HTi^{II}CH_3$ (+0.50 eV).
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17 The optimization path, rather than the process taking place along the intrinsic reaction coordinate, is calculated here (note: DFT underestimates energy barriers). The effective barrier is thought to be small due to immense zero-vibrational energy of C–H and Ti–H oscillators (> 0.5 eV per pair of H atoms). See also: I. I. Zakharov, G. M. Zhidomirov and V. A. Zakharov, *J. Mol. Catal.*, 1991, **68**, 149.
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19 See *e.g.*: (*a*) T. Yanagihara, *Diamond Relat. Mater.*, 2004, **13**, 616; (*b*) M. P. Chowdhury and A. K. Pal, *J. Phys. D*, 2004, **37**, 261.
20 This is especially true for gaseous TSHs at low concentrations; under such conditions H_2 detachment interconnected with simultaneous oligomerization could be avoided.
21 (*a*) S. Zhang and W. E. Piers, *Organometallics*, 2001, **20**, 2088; (*b*) J. R. Hagadorn and M. J. McNevin, *Organometallics*, 2003, **22**, 609.