



## Research paper

# Probing the structural evolution and bonding properties of $\text{Pt}_n\text{C}_2^{-/0}$ ( $n = 1-7$ ) clusters by density functional calculations

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## ABSTRACT

We present a theoretical investigation on the structural evolution and bonding properties of  $\text{Pt}_n\text{C}_2^{-/0}$  ( $n = 1-7$ ) clusters using density functional theoretical calculations. The results showed that both anionic and neutral  $\text{Pt}_n\text{C}_2$  ( $n = 1-7$ ) clusters primarily adopt 2D planar chain-shaped or ring-based structures. The two C atoms directly interact with each other to form a C–C bond for  $n = 1-3$ , while the two C atoms are separated by the Pt atoms for  $n = 4-7$ , except for neutral  $\text{Pt}_5\text{C}_2$ .  $\text{Pt}_4\text{C}_2^-$  anion and  $\text{Pt}_4\text{C}_2$  neutral both show  $\sigma$  plus  $\pi$  double delocalized bonding patterns.

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## 1. Introduction

Owing to metal-carbide compounds have important application in catalytic fields [1–3], metal-carbide clusters have received a great deal of attention. Additionally, they are ideal research models for investigating the microscopic catalytic mechanisms in organometallic reactions [4]. Especially,  $\text{M}_n\text{C}_2$  clusters have been extensively investigated by various experimental techniques and theoretical calculations. Anion photoelectron spectroscopy and theoretical calculations on the interactions between the M and  $\text{C}_2$  of  $\text{MC}_2^-$  ( $M = \text{Sc}, \text{V}, \text{Cr}, \text{Mn}, \text{Fe}, \text{and Co}$ ) found that they are similar to those between the M and O [5]. The most stable isomer of  $\text{FeC}_2$  is predicted to a cyclic structure by theoretical calculations [6]. The experimental photoelectron spectrum of  $\text{MnC}_2^-$  was found to contribute by only the cyclic isomer, whereas that of  $\text{CrC}_2^-$  was contributed by both the cyclic and linear isomers [7–9]. Anion photoelectron spectroscopy and theoretical studies of  $\text{Co}_n\text{C}_2^-$  ( $n = 1-5$ ) found that their geometric structures can be considered as adding  $\text{C}_2$  to the top sites, bridge sites, or hollow sites of  $\text{Co}_n$  frameworks [10], while the two C atoms of  $\text{V}_n\text{C}_2^-$  ( $n = 1-6$ ) were separated gradually with increasing number of V atoms [11]. Combined experimental and theoretical investigations of  $\text{Au}_{1-2}\text{C}_2^{-/0}$  clusters revealed that their ground-state structures are linear configurations and the bonding properties of Au atom are similar to those of H atom [12–15]. Numerous experimental and theoretical calculations investigated the encapsulation of  $\text{M}_x\text{C}_2$  ( $x = 2-4$ ,  $M = \text{Sc}, \text{V}, \text{Cr}, \text{Mn}, \text{Fe}, \text{and Co}$ ) clusters into fullerene carbon cages [16–21]. Theoretical investigations on the isolated  $\text{Au}_n\text{C}_2^{-/0}$  ( $n = 1, 3$  and 5)

and  $\text{Au}_n\text{C}_2^{0/+}$  ( $n = 2, 4$  and 6) found that gold atoms serve as terminals and bridges in small dicarbon aurides and the triangle structures can form when the number of gold atoms reaches four [22]. Recently, two-dimensional sheets of  $\text{TiC}_2$  are predicted to be formed when the ratio of carbon increases and  $\text{C}_2$  dimers act as the basic building blocks rather than the individual carbon atoms [23].

Platinum is one of the most important metal catalysts used for mediating C–C bond formation in cross-coupling reactions [24–28]. Investigating the interactions of platinum clusters with  $\text{C}_2$  radical can help understand the microscopic catalyzed mechanisms of C–C bond formation on the platinum surface. In our previous work of  $\text{Pt}_3\text{C}_2^{-/0}$ , we found that both anionic and neutral  $\text{Pt}_3\text{C}_2$  adopt  $\text{PtC}_2$  planar triangular structures with each C atom coordinating with two Pt atoms. Additionally,  $\text{Pt}_3\text{C}_2^-$  anion and  $\text{Pt}_3\text{C}_2$  neutral both show aromaticity [29]. As far as we know, the investigations on the platinum clusters reacted with  $\text{C}_2$  radical are rather rare. In this work, the structural evolution and bonding properties of  $\text{Pt}_n\text{C}_2^{-/0}$  ( $n = 1-7$ ) clusters were investigated by using density functional theoretical calculations.

## 2. Theoretical methods

Full structural optimizations and frequency analyses of  $\text{Pt}_n\text{C}_2^-$  ( $n = 1-7$ ) anions and its neutral counterparts were carried out employing DFT in the context of Beck's three-parameter and Lee–Yang–Parr's gradient-corrected correlation hybrid functional (B3LYP) [30–32], and the augmented correlation-consistent polarized valence triple-zeta (aug-cc-pVTZ) basis set was used for C atoms [33], and the aug-cc-pVTZ-PP basis set was used for Pt

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atoms [34]. No symmetry constraint was imposed during the overall geometry optimizations for both anionic and neutral clusters. The initial structures were obtained by putting these Pt atoms to different adsorption sites of C–C framework and also obtained by adding the C atoms to different sites of the stable structures of  $Pt_n$  clusters reported in the literature [35] at all possible spin states. Also, the crystal structure analysis by particle swarm optimization (CALYPSO) software [36] was used to search the global minima of  $Pt_nC_2^-$  ( $n = 1-7$ ) anions and its neutral counterparts. The theoretical vertical detachment energies (VDEs) were calculated as the energy differences between the neutrals and anions both at the geometries of anionic species, while the theoretical adiabatic detachment energies (ADEs) were calculated as the energy differences between the neutrals and anions with the neutrals relaxed to the nearest local minima using the geometries of the corresponding anions as initial structures (Table S1, supplementary data). Perdew-Wang correlation functional (BPW91) [37] and HSE 06 functional [38] were also tested for comparison, which provide results agreeing well with those of the B3LYP functional. Harmonic vibrational frequency analyses were carried out to confirm that the obtained structures were true local minima on the potential energy surfaces. Zero-point energy (ZPE) corrections obtained from the B3LYP functional were considered in all the calculated energies. Natural population analysis (NPA) was performed to gain insight into the charges distribution of  $Pt_nC_2^{0-}$  ( $n = 1-7$ ) using the Natural Bond Orbital (NBO) version 3.1 programs [39–43]. All the calculations and analyses were accomplished using the Gaussian 09 program package [44].

### 3. Theoretical results

The optimized geometries of low-lying isomers of  $Pt_nC_2^-$  ( $n = 1-7$ ) anions are presented in Fig. 1 and its corresponding neutrals are displayed in Fig. 2. The most stable structures of  $Pt_nC_2^{0-}$  ( $n = 1-7$ ) clusters calculated at different levels of theory are similar and the relative energies of low-lying isomers at different levels of theory are slightly different.

#### 3.1. Anionic $Pt_nC_2^-$ ( $n = 1-7$ )

The lowest-lying isomer of  $Pt_1C_2^-$  (1A) is a  $C_{\infty v}$  symmetric Pt–C–C linear chain-shaped structure with  $^2\Sigma$  electronic state. The C–C and Pt–C bond lengths of isomer 1A are 1.28 and 1.82 Å, respectively. Isomer 1B is a  $C_{2v}$  symmetric isosceles triangular structure with  $^2B_1$  electronic state. It is higher in energy than isomer 1A by 0.78 eV. As for  $Pt_2C_2^-$ , the lowest-lying isomer (2A) is a  $D_{\infty h}$  symmetric Pt–C–C–Pt linear chain-shaped structure with  $^2\Sigma_u$  electronic state. The C–C and Pt–C bond lengths of isomer 2A are 1.26 and 1.81 Å, respectively. Isomer 2B can be viewed as an additional Pt atom attaching to one C atom of  $PtC_2$  isosceles triangular structure and it is higher in energy than isomer 2A by 0.74 eV.

For  $Pt_3C_2^-$ , the lowest-lying isomer (3A) has a  $PtC_2$  planar triangular framework with the remaining two Pt atoms independently interacting with the two C atoms. Isomer 3A has  $C_{2v}$  symmetry with an electronic state of  $^2B_1$ . The second isomer (3B) of  $Pt_3C_2^-$  adopts a  $C_s$  symmetric five-membered ring structure with the two C atoms separated by the three Pt atoms and has a  $^2A'$  electronic state. The third isomer (3C) of  $Pt_3C_2^-$  has a Pt–C–C–Pt chain with the third Pt atom bonding with one of two terminal Pt atoms. Isomers 3B and 3C are higher in energy than isomer 3A by 0.50 and 0.65 eV, respectively.

The global minimum (4A) of  $Pt_4C_2^-$  has a  $D_{2h}$  symmetric planar  $Pt_4C_2$  six-membered ring structure with each C atom interacting with two Pt atoms and has an electronic state of  $^2B_{3g}$ . The second

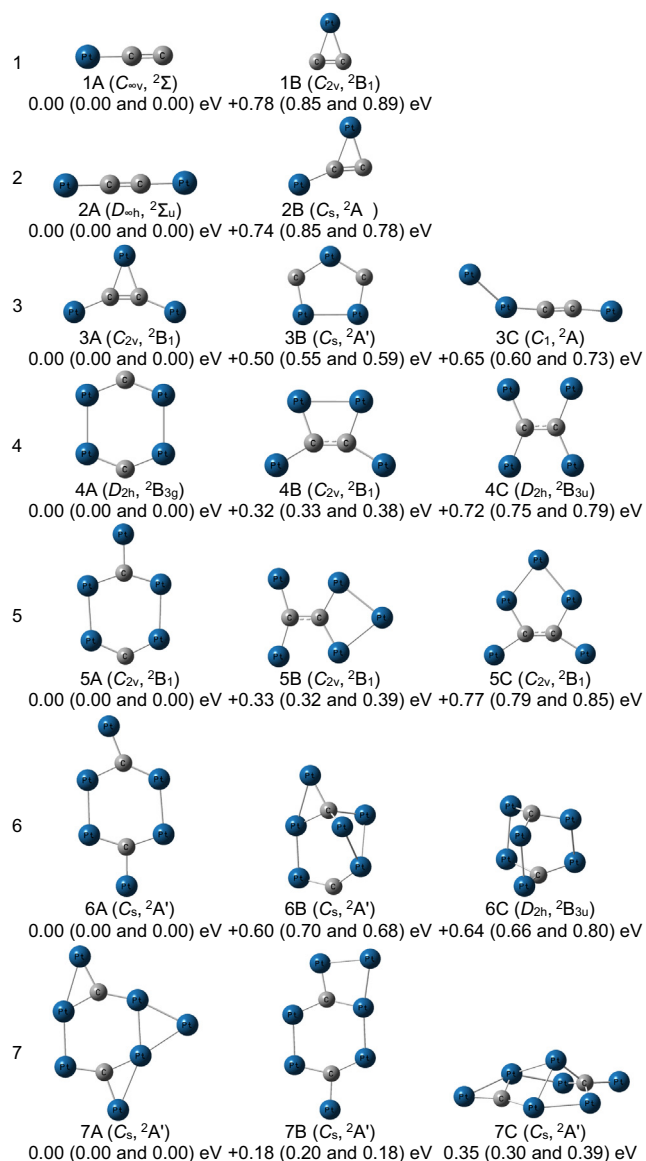


Fig. 1. Typical low-lying isomers of  $Pt_nC_2^-$  ( $n = 1-7$ ) anions obtained at the B3LYP level of theory. The relative energies in parentheses are calculated at BPW91 level of theory and HSE 06 level of theory.

isomer (4B) adopts a  $Pt_2C_2$  four-membered ring structure with the remaining two Pt atoms independently interacting with the two C atoms. Isomer 4B has  $C_{2v}$  symmetry and a  $^2B_1$  electronic state. The third isomer (4C) of  $Pt_4C_2^-$  has a  $D_{2h}$  symmetric ethylene-shaped structure with and has an electronic state of  $^2B_{3u}$ . Isomers 4B and 4C are higher in energy than isomer 4A by 0.32 and 0.72 eV, respectively.

As for  $Pt_5C_2^-$ , the global minimum (5A) is a  $C_{2v}$  symmetric Pt-capped planar  $Pt_4C_2$  six-membered ring structure and has a  $^2B_1$  electronic state. Isomer 5A can be obtained by an additional Pt atom attaching to one C atom of isomer 4A. Isomer 5B is a  $C_{2v}$  symmetric Pt-capped ethylene-shaped structure and has a  $^2B_1$  electronic state. Isomer 5C has a  $Pt_3C_2$  planar five-membered ring structure with the remaining two Pt atoms independently interacting with the two C atoms. It has  $C_{2v}$  symmetry and a  $^2B_1$  electronic state. Isomers 5B and 5C are higher in energy than isomer 5A by 0.33 and 0.77 eV, respectively.

The global minimum (6A) of  $Pt_6C_2^-$  is a bicapped planar  $Pt_4C_2$  six-membered ring structure with the two capped Pt atoms

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