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Research paper

Structures and bonding properties of $Pd_nC_2^{-/0}$ (n = 1–7) clusters

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ABSTRACT

We present a theoretical investigation on the structural evolution and bonding properties of $Pd_nC_2^{-/0}$ (n = 1–7) clusters using density functional theory calculations. The results showed that the two C atoms in $Pd_{1-7}C_2^{-/0}$ directly interact with each other to form a C—C bond, except for neutral Pd_6C_2. The Pd atoms can be viewed as an integral cluster unit interacting with C_2 frameworks and have very weak interactions with each other. Interestingly, Pd_6C_2 neutral has a D_{3d} symmetric bicapped trigonal antiprism structure with the two C atoms located at the apex positions and shows σ plus π double delocalized bonding patterns.

1. Introduction

Metal-carbide clusters have received considerable attention from both experimental and theoretical points of view because metal-carbide compounds have important application in catalytic fields [1,2], and they are ideal research models for giving insights into the microscopic catalytic mechanisms in organometallic reactions [3]. Especially, M_nC_2 clusters have been extensively investigated by various experimental techniques and theoretical methods. The interactions between M and C_2 units in MC_2^- (M = Sc, V, Cr, Mn, Fe, and Co) were found to be similar to those between M and O atoms by anion photoelectron spectroscopy combined with theoretical calculations [4]. Theoretical calculations predicted that FeC_2 is a cyclic structure [5]. Both the cyclic and linear isomers have contribution to the photoelectron spectrum of CrC_2^-, while only the cyclic isomer has contribution to the photoelectron spectrum of MnC_2^- [6–8]. Anion photoelectron spectroscopic and theoretical studies of $Co_nC_2^-$ (n = 1–5) and $V_nC_2^-$ (n = 1–6) revealed that the geometric structures of $Co_nC_2^-$ can be obtained by adding C_2 unit to the top sites, bridge sites, or hollow sites of Co_n frameworks [9], whereas the two C atoms in $V_nC_2^-$ were separated gradually with increasing number of V atoms [10]. Combined experimental and theoretical investigations of $Au_{1-2}C_2^{-/0}$ clusters found that they have linear structures and the bonding properties between Au and H atoms are very similar [11–14]. Theoretical investigations of isolated $Au_nC_2^{-/0}$ (n = 1, 3, and 5) and $Au_nC_2^{0/+}$ (n = 2, 4, and 6) suggested that the Au atoms behave as terminals and bridges in small dicarbon aurides, and the triangle structures can form with the increasing number of Au atoms [15]. Recently, Two-dimensional sheets of TiC_2 were calculated to be formed with C_2 dimer acting as the basic building blocks [16]. Mass-selected photoelectron spectroscopy and density functional theory (DFT) calculations found that the carbon atoms of $Co_nC_3^{-/0}$ and $Co_nC_4^{-/0}$ (n = 1–4) are separated from each other gradually with increasing number of Co atoms, but a C_2 unit still remains at n = 4 [17]. Very recently, DFT calculations found that both anionic and neutral Pt_3C_2 adopt PtC_2 planar triangular structures [7]. The structural evolution and bonding properties of $Pt_nC_2^{-/0}$ (n = 1–7) clusters were probed by DFT calculations [18].

Palladium is one of the most important metal catalysts used for mediating C—C bond formation in cross-coupling reactions [19–22]. Dispersed fluorescence spectroscopy of the diatomic molecule PdC was previously measured [23]. The electrical transport properties and growth conditions of PdC nanostructures on the Si substrate were investigated by using a focused ion beam and scanning electron microscope [24]. Investigating the structures and bonding properties of $Pd_nC_2^{-/0}$ can provide the valuable information for understanding the microscopic mechanisms of C—C bond formation on the palladium surface. However, the regarding investigations are rather rare. In this work, the structural evolution and bonding properties of $Pd_nC_2^{-/0}$ (n = 1–7) clusters were investigated by *ab initio* calculations.

2. Theoretical methods

Full structural optimizations and frequency analyses of $Pd_nC_2^-$ (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) [25–27]. The augmented correlation-consistent polarized

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valence triple-zeta (aug-cc-pVTZ) basis set [28] was used for C atoms and the aug-cc-pVTZ-PP basis set [29] was used for Pd atoms. The B3LYP functional has been widely used for organic transition-metal compounds [1,2,7,18,30–32]. Many density functionals can be employed to study the complexes involving transition metals, which have been discussed in details in a number of references [30,33,34]. No symmetry constraint was imposed during the overall geometry optimizations for both anionic and neutral clusters. The initial structures were obtained by putting these Pd 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 Pd_n and by adding the C atoms to different sites of Au_n clusters replacing by Pd atoms at all possible spin states [8,35]. Also, the crystal structure analysis by particle swarm optimization (CALYPSO) software [36] was used to search the global minima of $Pd_nC_2^-$ (n = 1–7) anions and its neutral counterparts. Harmonic vibrational frequency analyses were carried out to confirm that the obtained structures were true local minima on the potential energy surfaces. 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. To further evaluate the relative energies of the low-lying isomers, the single-point energies of $Pd_{1-7}C_2^{-/0}$ were also calculated by using the more accurate coupled-cluster methods including single, double, and perturbative contributions of connected triple excitations (CCSD(T)) [37,38] based on the optimized B3LYP geometries. 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 charge distributions of $Pd_nC_2^{-/0}$ (n = 1–7) using the Natural Bond Orbital (NBO) version 3.1 programs [39,40]. All the calculations and analyses were accomplished using the Gaussian 09 program package [41].

3. Theoretical results

The optimized geometries of low-lying isomers of $Pd_nC_2^-$ (n = 1–7) anions are presented in Fig. 1 and its corresponding neutrals are displayed in Fig. 2. The relative energies of low-lying isomers calculated at the B3LYP and CCSD(T) levels of theory are slightly different. Theoretical VDEs and ADEs of low-lying isomers at the B3LYP and CCSD(T) levels of theory are summarized in Table 1. As shown in Table 1, the theoretical VDEs and ADEs of low-lying isomers at the B3LYP and CCSD(T) levels of theory are close. The bond lengths of the most stable isomers of $Pd_nC_2^{-/0}$ (n = 1–7) clusters are displayed in Table 2. Furthermore, the photoelectron spectra of the most stable isomers of $Pd_nC_2^-$ are simulated based on the generalized Koopmans' theorem (GKT) [42,43], and are displayed in Fig. 3. In the simulated spectra, the peak of each transition corresponds to the removal of an electron from an individual molecular orbital of $Pd_nC_2^-$ anions. The first peak associated with the HOMO is set to the position of calculated VDE of each isomer, and the other peaks associated with the deeper transitions are shifted toward higher binding energies according to their relative energies compared to the HOMO. Then all the calculated peaks are fitted with unit-area Gaussian functions of 0.20 eV full width at half maximum (FWHM). The peak intensities in simulated spectra are treated equally in the simulations.

Anionic $Pd_nC_2^-$ (n = 1–7). The lowest-lying isomer of $Pd_1C_2^-$ (1A) is a $C_{\infty v}$ symmetric Pd—C—C linear chain-shaped structure with $^2\Sigma$ electronic state. The C—C and Pd—C bond lengths of isomer 1A are 1.31 and 1.86 Å, respectively. Isomer 1B is a C_{2v} symmetric

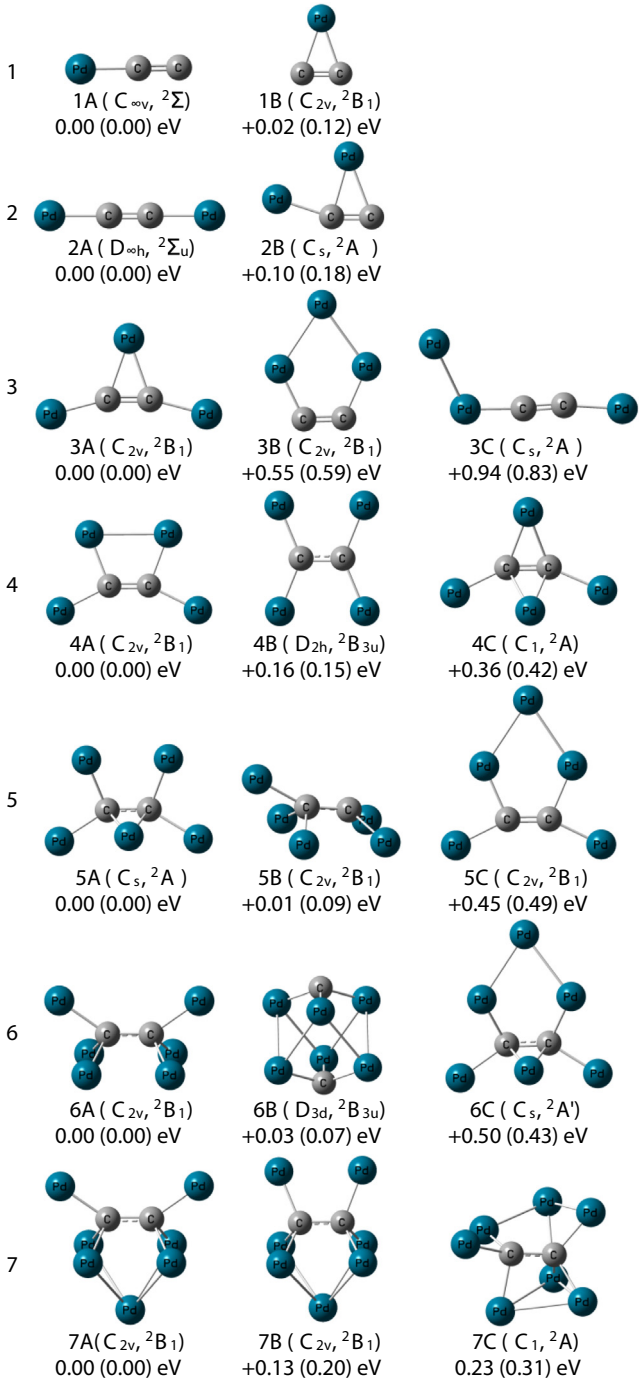

Fig. 1. Typical low-lying isomers of $Pd_nC_2^-$ (n = 1–7) anions obtained at the B3LYP level of theory. The relative energies in parentheses are calculated at the CCSD(T) level of theory.

isosceles triangular structure with $^2B_1$ electronic state and it is higher in energy than isomer 1A by 0.02 and 0.12 eV, calculated at the B3LYP and CCSD(T) levels of theory, respectively.

As for $Pd_2C_2^-$, the lowest-lying isomer (2A) is a $D_{\infty h}$ symmetric Pd—C—C—Pd linear chain-shaped structure with $^2\Sigma_u$ electronic state. The C—C and Pd—C bond lengths of isomer 2A are 1.29 and 1.87 Å, respectively. Isomer 2B can be viewed as an additional Pd atom attaching to one C atom of PdC_2 isosceles triangular structure and it is higher in energy than isomer 2A by 0.10 and 0.18 eV, calculated at the B3LYP and CCSD(T) levels of theory, respectively.

For $Pd_3C_2^-$, the lowest-lying isomer (3A) has a PdC_2 planar triangular framework with the remaining two Pd atoms independently