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The flexibility of the cycloheptatrienyl ring in cycloheptatrienylvanadium carbonyl derivatives

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ABSTRACT

The cycloheptatrienylvanadium carbonyl (η^7-C_7H_7)V(CO)$_3$ is a stable species that can be synthesized by the reaction of V(CO)$_6$ with cycloheptatriene. The related species of the types (C_7H_7)V(CO)$_n$ ($n = 5, 4, 3$) and (C_7H_7)$_2$V$_2$(CO)$_n$ ($n = 5, 4, 3, 2, 1, 0$), which are potentially accessible from (η^7-C_7H_7)V(CO)$_3$, have now been investigated by density functional theory. For the lowest energy singlet mononuclear (C_7H_7)V(CO)$_n$ ($n = 5, 4, 3$) structures, the hapticity of the C_7H_7 ring is adjusted to give the vanadium atom the favored 18-electron configuration. Furthermore, for the lowest energy singlet binuclear (C_7H_7)$_2$V$_2$(CO)$_n$ ($n = 5, 4, 3$) structures the hapticity of the C_7H_7 ring is adjusted to give a V$\equiv$V triple bond of ~2.5 Å length with an 18-electron configuration for each vanadium atom similar to the known binuclear cyclopentadienylvanadium carbonyl (η^5-C_5H_5)$_2$V$_2$(CO)$_5$. Evidence is presented for the presence of higher order multiple V–V bonds in the more highly unsaturated singlet (C_7H_7)$_2$V$_2$(CO)$_n$ ($n = 2, 1, 0$) structures including a formal sextuple bond in the bent singlet (C_7H_7)$_2$V$_2$ structure. A lower energy coaxial triplet (C_7H_7)$_2$V$_2$ structure exhibiting the rare D_{7d} point group symmetry is shown to have a $\sigma + 2\pi$ V$\equiv$V triple bond by analysis of its frontier molecular orbitals. The thermochemistry of the (C_7H_7)$_2$V$_2$(CO)$_n$ system suggests (η^7-C_7H_7)$_2$V$_2$(μ-CO)$_3$ to be a viable synthetic target analogous to the experimentally known and structurally characterized species (η^6-C_6H_6)$_2$Cr$_2$(μ-CO)$_3$ and (η^5-C_5H_5)$_2$Mn$_2$(μ-CO)$_3$.

1. Introduction

Various compounds containing a transition metal bonded to the cycloheptatrienyl ring have been synthesized since the original discovery of the cation [(η^7-C_7H_7)Mo(CO)$_3$]$^+$ by Dauben and Honnen in 1958 [1,2] as the first example of a C_7H_7 metal complex (Fig. 1). Subsequent work led to the discovery of the chromium and tungsten analogues [(η^7-C_7H_7)M(CO)$_3$]$^+$ (M = Cr, W) [3,4]. Furthermore, the other early examples of cycloheptatrienyl metal complexes, such as the vanadium derivatives (η^7-C_7H_7)V(η^5-C_5H_5) [5,6] and (η^7-C_7H_7)V(CO)$_3$ [7], were also heptahapto derivatives, in which all seven carbon atoms of the C_7H_7 ring are within bonding distance of the metal atom.

The subsequent development of cycloheptatrienylmetal chemistry soon led to the discovery of species in which the C_7H_7 ring is only partially bonded to the central metal atom [8–11]. The first such compounds were the trihapto complexes (η^3-C_7H_7)Mo(CO)$_2$(η^5-C_5H_5) [9] and (η^3-C_7H_7)Co(CO)$_3$ [11] (Fig. 2). The pair of cycloheptatrienylmetal tricarbonyls (C_7H_7)M(CO)$_3$ (M = V, Co) is of particular interest since in the vanadium derivative the η^7-C_7H_7 ring is a heptahapto ligand whereas in the cobalt derivative the η^3-C_7H_7 ring is a trihapto ligand with two uncomplexed C=C double bonds. In both cases the central metal atom has the favored 18-electron configuration. This phenomenon indicates considerable flexibility of C_7H_7 rings in bonding to transition metals. This flexibility of the C_7H_7 ring in exhibiting variable hapticity contrasts with the smaller C_6H_6 and C_5H_5 rings, which exhibit hexahapticity and pentahapticity, respectively, in almost all of their transition metal complexes.

The cycloheptatrienylvanadium carbonyl system is of particular interest since (C_7H_7)V(CO)$_3$ has been synthesized as a stable compound [7], which is a potential precursor to a variety of other cycloheptatrienylvanadium carbonyl derivatives. In order to investigate the possible extent of cycloheptatrienylvanadium carbonyl derivatives without other ligands, we have investigated the systems (C_7H_7)V(CO)$_n$ ($n = 5, 4, 3$) and (C_7H_7)$_2$V$_2$(CO)$_n$ ($n = 5, 4, 3, 2, 1, 0$) by density functional theory using methods similar to those

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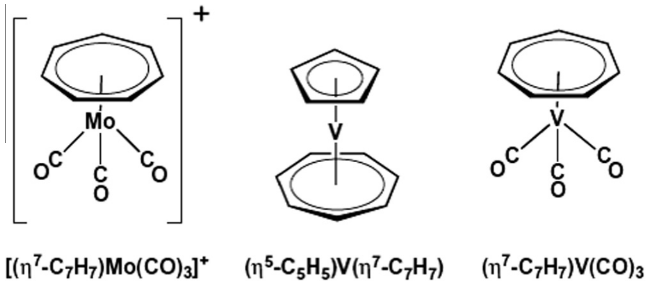

Fig. 1. Early examples of η^7-C_7H_7M derivatives.

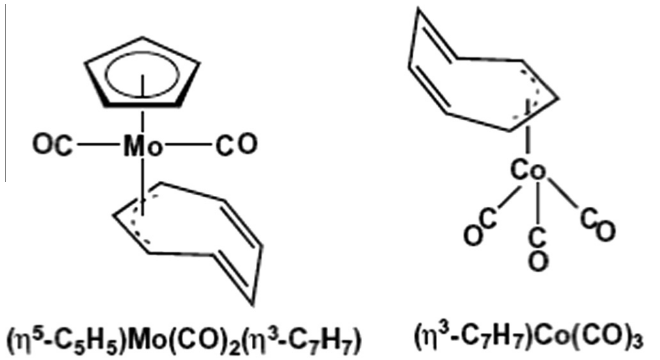

Fig. 2. Early examples of η^3-C_7H_7M derivatives.

used for a previously reported [12] study of the binuclear cycloheptatrienylchromium carbonyls $(C_7H_7)_2Cr_2(CO)_n$ (n = 6, 5, 4, 3, 2, 1, 0).

2. Theoretical methods

The geometry optimizations of the mononuclear and binuclear cycloheptatrienyl vanadium carbonyls were performed using the two density functional theory (DFT) methods B3LYP [13,14] and BP86 [15,16] with double-ζ plus polarization (DZP) basis sets. These two DFT methods have been shown to be effective and practical computational tools for organometallic compounds [17–23]. For carbon and oxygen, the DZP basis set used here (9s5p/4s2p) adds one set of pure spherical harmonic d functions with orbital exponents $\alpha_d(C) = 0.75$ and $\alpha_d(O) = 0.85$. For hydrogen, the DZP basis set (4s1p/2s1p) is used with $\alpha_p(H) = 0.75$ [24,25]. The loosely contracted DZP basis set for vanadium uses the Wachters' primitive sets augmented by two sets of p functions and one set of d functions and contracted following Hood et al. leading to a (14s11p6d/10s8p3d) basis set [26].

The geometries of the mononuclear and binuclear cycloheptatrienyl vanadium carbonyls were optimized for the lowest energy singlet and triplet electronic states using both the DZP B3LYP and BP86 methods. All computations were carried out with the Gaussian 09 program package [27] in which a fine integration grid (75, 302) was used.

The optimized geometries of the energetically low lying $(C_7H_7)V(CO)_n$ and $(C_7H_7)_2V_2(CO)_n$ structures are depicted in Figs. 3–9. The optimized structures are designated as **mV–nX** where **m** represents the number of vanadium atoms, **n** represents the number of carbonyl groups, and **X** represents the spin state as singlet (**S**) or triplet (**T**). The carbonyl-free $(C_7H_7)_2V_2$ structures are analogously designated as **2V-X**.

3. Results

3.1. Molecular structures of the mononuclear derivatives $(C_7H_7)V(CO)_n$ (n = 5, 4, 3)

The mononuclear $(C_7H_7)V(CO)_n$ (n = 5, 4, 3) structures have been optimized in the singlet and triplet spin states. However, since each of the singlet $(C_7H_7)V(CO)_n$ (n = 5, 4, 3) structures has a lower energy than the corresponding triplet structure, only the singlet structures are presented here (Fig. 3). In these three singlet $(C_7H_7)V(CO)_n$ (n = 5, 4, 3) structures the hapticity of the C_7H_7 ring is adjusted to give the central vanadium atom the favored 18-electron configuration leading to $(\eta^3\text{-}C_7H_7)V(CO)_5$, $(\eta^5\text{-}C_7H_7)V(CO)_4$, and $(\eta^7\text{-}C_7H_7)V(CO)_3$ with trihapto, pentahapto, and heptahapto C_7H_7 rings, respectively, as the low energy structures. The optimized $(\eta^7\text{-}C_7H_7)V(CO)_3$ structure is in agreement with the experimental structure, determined by X-ray crystallography [28]. Structure **V-4S** for the tetracarbonyl $(\eta^5\text{-}C_7H_7)V(CO)_4$ is closely related to the well-known [29] cyclopentadienylvanadium tetracarbonyl, $(\eta^5\text{-}C_5H_5)V(CO)_4$, which likewise has a pentahapto ring bonded to the vanadium atom.

3.2. Molecular structures of binuclear derivatives $(C_7H_7)_2V_2(CO)_n$ (n = 5, 4, 3, 2, 1, 0)

3.2.1. $(C_7H_7)_2V_2(CO)_5$

The singlet and triplet structures **2V-5S** and **2V-5T** (Fig. 4 and Table 1) were optimized for $(C_7H_7)_2V_2(CO)_5$. The triplet structure $(\eta^7\text{-}C_7H_7)(OC)_2V{-}V(CO)_3(\eta^5\text{-}C_7H_7)$ **2V-5T** with one heptahapto η^7-C_7H_7 ring and one pentahapto η^5-C_7H_7 ring is the global minimum with all real vibrational frequencies. Two of the CO groups in **2V-5T** are semibridging CO groups whereas the remaining three CO groups are terminal CO groups. The V–V distance of 3.305 Å (B3LYP) or 3.048 Å (BP86) suggests a formal single bond giving each vanadium atom a 17-electron configuration for a binuclear triplet. The singlet $(C_7H_7)_2V_2(CO)_5$ structure **2V-5S** lies 14.4 kcal/mol (B3LYP) or 6.4 kcal/mol (BP86) above **2V-5T**. Structure **2V-5S** has two pentahapto η^5-C_7H_7 rings and is closely related to the known $(\eta^5\text{-}C_5H_5)_2V_2(CO)_5$ [30,31]. The V$\equiv$V distance of ~2.55 Å in **2V-5S** is close to the experimental V$\equiv$V formal triple bond distance of

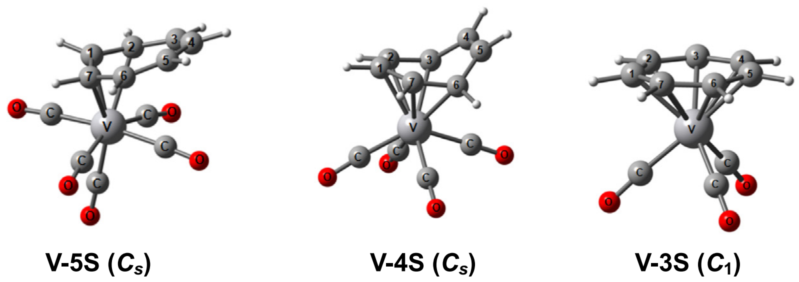

Fig. 3. Optimized singlet $(C_7H_7)V(CO)_n$ (n = 5, 4, 3) structures.