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Oligomerization of Early Transition Metal $\{M(OH)_3\}_2(\mu\text{-}C_2)$ Acetylides toward the Formation of $[(OH)_3MC]_n$ ($n = 4, 6$) Metalla Carbides: A Theoretical Study by Density Functional Theory

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Density functional calculations were performed on a series of $M(OH_3)$-substituted ($M = Ti,V$) cyclopolyenes as simple models of metal carbides. We studied the oligomerization of the metal acetylide complexes $\{ML_n\}_2$ (μ-C_2) as a possible precursor of these $[(OH)_3MC]_n$ ($n = 4,6$) hypothetical species. Special emphasis was placed on the comparison of the main properties of these metal substituted cyclopolyenes with those of the corresponding cyclopolyenes in an attempt to study the effects of the metal substituents on the organic C_4 and C_6 cyclic moieties. Whereas for the titanium species, the π system of the polyene moiety is slightly perturbed, the electronic structures and molecular geometries found for the vanadium species suggest a metalla radialene nature for these compounds, with the endocyclic conjugation of carbon−carbon double bonds replaced by an exocyclic arrangement of carbon−metal double bonds.

1. Introduction

Extended metal-carbides are materials of remarkable practical interest, whereas very rare examples of molecular carbides have also been reported.[1−9] In this context, it is very interesting to investigate the generation of metal carbides in order to discover low mass weight $(MC)_n$ fragments as plausible precursors of carbides of higher molecular complexity. A possible approach that can be undertaken is the oligomerization of metal-acetylides or metal-vinylidenes. This approach consists of considering metal acetylides, $\{L_nM\}_2(\mu\text{-}C_2)$, as compounds which should undergo oligomerization to different forms of molecular metal carbides.

In a previous paper, we investigated the oligomerization of the copper acetylide $PH_3Cu{-}C{\equiv}C{-}CuPH_3$ as a possible precursor of hypothetical $Cu(PH_3)$ substituted cyclobutadiene, benzene, and cyclooctatetraene species.[10] Our calculations showed that metal substitution affects essentially the σ skeleton of the polyene units, whereas negligible π interactions between the metal d orbitals and the π system of the polyene moieties were observed. This could be easily rationalized on the basis of the low energies of the d_π orbitals of this $(PH_3)Cu$, d^{10} fragment.

A significant π interaction between the metal d orbitals and the π system of the polyene moiety is expected only for early transition metal fragments, which may show high-lying empty d orbitals. Such an approach has been suggested by the analogy with the recently developed class of dinuclear transition metal complexes containing an acetylide bridge. Several μ-C_2 bridged dinuclear complexes have been synthesized, with structures consistent with all the three possible valence bond descriptions:[11]

$$LnM{-}C{\equiv}C{-}MLn \quad LnM{=}C{=}C{=}MLn \quad LnM{\equiv}C{-}C{\equiv}MLn$$

Whereas for late transition metals (from the manganese triad to the right) in low oxidation states with mainly π-acceptor ligands (like carbonyls or phosphines) only the acetylenic μ-$C{\equiv}C$ structure has been found, irrespective of the metal d configuration, a different situation is observed for early transition

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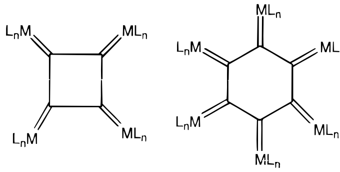
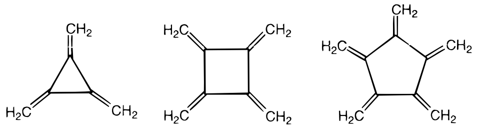


1 **2**

Figure 1. Geometrical structures of the considered metal substituted radialenes with four **1** and six **2** members in the ring.



3 **4** **5**

Figure 2. Geometrical structures of the all-*exo*-alkylidene-cycloalkanes. The lower members of this series **3**−**5** are shown.

metals. Indeed, for early transition metals (those of the titanium, vanadium, and chromium triads) in high oxidation states with mainly donor ligands such as RO^-, all three possible valence bond structures have been found, depending on the metal d^n configuration. Referring to the isolated ML_n fragment, an acetylenic $M-C\equiv C-M$ structure is found for a d^1 configuration, a cumulenic $M=C=C=M$ structure for a d^2 configuration, and a dimetallabutadyyne $M\equiv C-C\equiv M$ structure for a d^3 configuration. Therefore, a $\{L_nM\}_2(\mu\text{-}C_2)$ acetylide complex based on a d^2 metal fragment will show a cumulenic structure, and its oligomerization is expected to form an exocyclic arrangement of metal−carbon double bonds rather than the usual endocyclic conjugation of carbon−carbon double bonds. In other words, the d^2 metal fragment could form π bonds with the polyene carbon atoms leading to all- *exo*-alkylidene-cycloalkanes such as **1** and **2** in Figure 1. These compounds are strictly related to the class of all- *exo*-methylene-cycloalkanes, a homologue series of organic compounds with the general formula C_nH_n, also known as radialenes.[12] The lower members of this series, **3**−**5** are shown in Figure 2. The analogy between the two classes of compounds is intuitively evident and is related to the quasi isolobal analogy between methylene and the d^2 ML_n fragments.[13] Moreover, there is also a synthetic analogy, since it is known that the dimerization of 1,2,3-trienes leads to [4]radialenes.[12]

In the present paper, we explored the oligomerization of the titanium and vanadium complexes, $(OH)_3Ti-C\equiv C-Ti(OH)_3$, **6**, and $(OH)_3V=C=C=V(OH)_3$, **7**, to the corresponding tetrametallacyclobutadiene and hexametallabenzene model species, that is, $[(OH)_3TiC]_4$, **8**, $[(OH)_3TiC]_6$, **9** and $[(OH)_3VC]_4$, **10**, $[(OH)_3VC]_6$, **11**. Our attention will be focused on the geometric structures of the monomeric and oligomeric compounds and on their relative, thermodynamical stabilities on the basis of detailed density functional calculations. Special emphasis will be placed on the comparison of the main properties of these metal substituted cyclopolyenes with those of the corresponding cyclopolyenes in an attempt to study the effects of the metal substituents on the organic C_4 and C_6 cyclic moieties and the possible formation of all-*exo*-alkylidene-butane and -hexane.

2. Computational Details

All calculations reported in this work were carried out using the ADF program package described elsewhere.[14−16] Molecular structures were optimized at the NLDA level of theory, in which the nonlocal exchange (Becke[17]) and correlation (Perdew[18]) corrections are included. It has been already demonstrated how the nonlocal corrections lead to optimized geometries of transition metal complexes, in good agreement with experimental data.[19]

The basis set employed for both titanium and vanadium was of uncontracted double-ζ quality for 3s and 3p and of triple-ζ quality for 3d and 4s, which was augmented by one 4p STO. The main group elements were described by a double-ζ basis augmented by one 2p function for hydrogen and one 3d polarization function for the other elements. The cores (Ti,V: 1s-2p; C,O: 1s) were kept frozen, according to the method by Baerends et al.[14] Better quality basis sets, including more diffuse functions on the carbon, oxygen, and hydrogen atoms (triple-ζ plus polarization), in test calculations on dinuclear complexes did not give significantly different results.

A density fitting procedure was used to obtain accurate Coulomb and exchange potentials in each SCF cycle, and the effective one-electron Hamiltonian matrix elements were calculated by an accurate and efficient numerical integration scheme.

The structures of $(OH)_3MCCM(OH)_3$, M = Ti,V model systems **6**−**7** considered in the calculations were fully optimized within the D_{3d} symmetry constraint at the NLDA level. A removal of the symmetry constraint did not change significantly either the geometry or the ground state. The geometries of the model systems $[(OH)_3MC]_4$, **8** and **10**, and $[(OH)_3MC]_6$, **9** and **11**, have been fully optimized at the NLDA level, according to the D_{2d} (D_2 for the rectangular and C_{2v} for the rhombic distortion) and D_{3d} symmetry constraints, respectively.

3. Results and Discussion

The optimized geometries of the monomeric $[(OH)_3MC]_2$, M = Ti, V, species **6**−**7** are shown in Table 1. Note that whereas for the titanium complex, the geometrical parameters refer to a singlet ground state, $^1A_{1g}$, for the vanadium complex they refer to a triplet ground state $^3A_{2g}$.

We have fully optimized the structures of the corresponding dimeric and trimeric species **8**−**11**, and the calculated geometrical parameters and bonding energies are also reported in Table 1. In Table 2, the geometrical parameters of these oligomeric systems are compared with those of the corresponding polyenes and radialenes.

Table 1 shows that the monomeric titanium acetylide species **6** has a CC bond distance of 1.241 Å, which is only 0.029 Å longer than in ethyne (1.212 Å), and a Ti−C bond distance of 2.047 Å, which is characteristic of a titanium−carbon single bond. On the other hand, the monomeric vanadium acetylide species **7** has a CC bond distance of 1.268 Å, 0.016 Å shorter than the central CC distance in cumulene (1.284 Å), and a V−C bond distance of 1.882 Å, typical of a vanadium−carbon double bond, which clearly indicate a cumulenic structure.

When we consider the oligomeric species, Table 2 shows that in the titanium complexes **8**−**9**, the CC bond distances are quite close to the values characteristic of the corresponding cyclopolyenes, that is, cyclobutadiene and benzene. The TiC bond length also shows a slight increase on passing from the

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Table 1. Main Geometrical Parameters and Bonding Energies (Ground States) from Atoms as Fragments of Titanium and Vanadium Oligomers

molecule	symmetry	state	param	NLDA[a]	energy (eV)
$\{CTi(OH)_3\}_2$ **6**	D_{3d}	$^1A_{1g}$	C−C	1.241	−97.253
			Ti−C	2.047	
			Ti−O	1.817	
$\{CTi(OH)_3\}_4$ **8**	D_{2d}	$^3A_2$	C−C	1.459	−193.930
			Ti−C	2.081	
			Ti−O	1.844	
$\{CTi(OH)_3\}_4$ **8**	D_2	^1A	C1−C2	1.365	−195.245
			C1−C3	1.602	
			Ti−C	2.071	
			Ti−O	1.842	
$\{CTi(OH)_3\}_4$ **8**	C_{2v}	$^1A_1$	C−C	1.445	−195.489
			Ti−C1	2.142	
			Ti−C2	2.008	
			Ti−O	1.837	
$\{CTi(OH)_3\}_6$ **9**	D_{3d}	$^1A_{1g}$	C−C	1.406	−295.948
			Ti−C	2.098	
			Ti−O	1.853	
$\{CV(OH)_3\}_2$ **7**	D_{3d}	$^3A_{2g}$	C−C	1.268	−96.791
			V−C	1.882	
			V−O	1.806	
$\{CV(OH)_3\}_4$ **10**	D_{2d}	$^1A_1$	C−C	1.474	−194.744
			V−C	1.861	
			V−O	1.823	
$\{CV(OH)_3\}_4$ **10**	D_2	^1A	C1−C2	1.454	−195.742
			C1−C3	1.519	
			V−C	1.870	
			V−O	1.813	
$\{CV(OH)_3\}_4$ **10**	C_{2v}	$^3B_1$	C−C	1.480	−196.045
			V1−C	1.856	
			V2−C	1.876	
			V−O	1.812	
$\{CV(OH)_3\}_6$ **11**	D_{3d}	$^1A_{1g}$	C−C	1.453	−295.435
			V−C	1.926	
			V−O	1.826	

[a] Bond lengths in Å.

monomeric unit (2.047 Å) to the trimeric species (2.098 Å), probably because of the change in the carbon hybridization.

A different situation is observed for vanadium complexes **10**−**11**, for which the calculated CC bond distances are much longer than in the corresponding organic cyclopolyenes and show values close to those of single bonds. Simultaneously, the VC bond lengths mantain their short values that are typical of vanadium−carbon double bonds, showing only a small decrease in the dimeric species and a slight increase in the trimeric species. These results suggest, for the vanadium complexes **10**−**11**, a metalla radialene structure with an exocyclic arrangement of metal−carbon double bonds rather than the endocyclic conjugation of carbon−carbon double bonds characteristic of substituted cyclopolyenes. The X-ray data for some substituted [4]radialenes are known; the experimental values for the C−C bonds of the cyclobutane ring vary from 1.466 to 1.508 Å, and those for the exocyclic C═C bonds vary from 1.292 to 1.347 Å.[12] These values are in good agreement with those calculated for **4**, that is, 1.490 and 1.337 Å (Table 2). Table 2 shows that the CC bond distances calculated for vanadium complexes **10** and **11** compare very well with those calculated for the corresponding [4] and [6]radialenes.

The different behavior of the titanium and vanadium monomeric species in oligomerization can be understood on the basis of the isolobal analogy between the $\cdot CH_3$ radical and the d^1 $Ti(OH)_3$ fragment and between the $:CH_2$ biradical and the d^2 $V(OH)_3$ fragment. The metal orbitals of the two $M(OH)_3$ fragments are made up of a $6a_1$, which is an s-d_{z^2} hybrid, a slightly higher doubly degenerate 6e, whose components are mainly d_{xz} and d_{yz} orbitals of d_π character, and a much higher doubly degenerate 7e, whose components are mainly d_{xy} and $d_{x^2-y^2}$ orbitals of d_δ character.

For both d^1 $Ti(OH)_3$ and CH_3, the singly occupied orbital is of a_1 symmetry and is directed out away from the ligands, thus indicating their isolobal relationship. In the d^2 $V(OH)_3$ fragment, the two electrons occupy the $6a_1$ (σ) and one of the doubly degenerate 6e (d_π) orbitals. This situation differs from that of the CH_2 triplet fragment, where the two electrons occupy an a_1 (σ) and a b_1 (p_π) orbital, essentially for the presence of a further d_π empty orbital. However, in the interaction with a carbon of the polyene cycle, the latter orbital may only give a minor in-plane interaction with the low-lying orbitals describing the σ skeleton, so that the two fragments can be regarded as quasi isolobal.

One of the aims of this work is to determine if any of the hypothetical oligomers **8**−**11** are sufficiently stable to be feasible synthetic targets. To give a quantitative measure of the stability of these molecules, we considered the inverse of the oligomerization reaction from a suitable number of metal acetylide molecules,

$$[CM(OH)_3]_n \rightarrow n/2[CM(OH)_3]_2 \qquad (1)$$

Although a complete characterization of the stability of these species would require the evaluation of the activation energy of the corresponding oligomerization reactions, we will calculate only the energetics of these reactions because of the dimensions of the considered systems. Moreover, as these ring systems may exhibit aromatic stabilization or destabilization, we have also evaluated their delocalization stabilization. As a quantitative measure of the delocalization stabilization of these potentially aromatic compounds, we calculated the energy difference ΔE for the appropriate bond separation reaction. This reaction gives the stability of the considered molecule relative to the smallest possible molecules having the same types of isolated bonds and has been extensively applied to study the aromatic character of several compounds.[20] Thus, for instance, the aromatic or conjugation stabilization associated with **9** is obtained by

Table 2. Geometrical Parameters of Cyclopolyenes, Radialenes and Their Metal Derivatives[a]

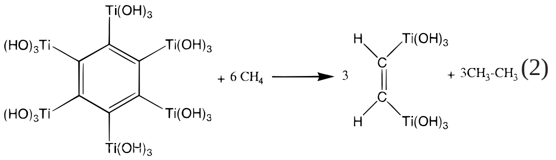
molecules	symmetry	param	X = $Ti(OH)_3$	X = $V(OH)_3$	X = CH_2	X = H
$(X_2C_2)_2$	$D_{2d}/D_{4h}/C_{4v}$	C−C	1.459	1.474	1.490	1.430
		X−C	2.081	1.861	1.338	1.090
$(X_2C_2)_2$	$D_2/D_{2h}/C_{2v}$	C−C	1.365, 1.602	1.454, 1.519	1.487, 1.497	1.330, 1.570
		X−C	2.071	1.870	1.337	1.096
$(X_2C_2)_2$	$C_{2v}/C_{2h}/C_{2v}$	C−C	1.445	1.480	1.490	1.430
		X−C1	2.142	1.876	1.337	1.090
		X−C2	2.008	1.856	1.337	1.090
$(X_2C_2)_3$	$D_{3d}/D_{6h}/C_{6v}$	C−C	1.406	1.453	1.498	1.384
		X−C	2.098	1.926	1.349	1.095

[a] Bond lengths (NLDA) in Å.

Table 3. Dissociation Energies (ΔE_{olig}) (kcal mol^{-1}) of the Oligomers with Respect to the Relative Monomer Units and Conjugation Stabilization Energies (ΔE_{conj}) (kcal mol^{-1}) of the Oligomers Calculated According to Equations in the Text

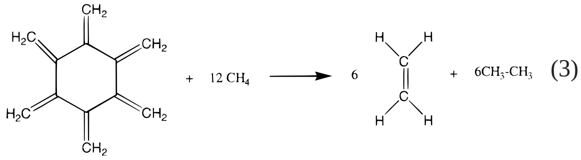
molecules	symmetry	X = Ti(OH)$_3$	X = V(OH)$_3$	X = H	X = CH$_2$
		ΔE_{olig}			
(X$_2$C$_2$)$_2$	$D_{2d}/D_{4h}/C_{4v}$	−13.3	+26.8	+2.5	+53.5
(X$_2$C$_2$)$_2$	$D_2/D_{2h}/C_{2v}$	+17.0	+49.8	+8.0	+53.5
(X$_2$C$_2$)$_2$	$C_{2v}/D_{2h}/C_{2v}$	+22.7	+56.8	+8.0	+53.5
(X$_2$C$_2$)$_3$	$D_{3d}/D_{6h}/C_{6v}$	+96.6	+116.7	+154.6	+94.2
		ΔE_{conj}			
(X$_2$C$_2$)$_2$	$D_{2d}/D_{4h}/C_{4v}$	−56.7	−25.0	−58.8	+17.5
(X$_2$C$_2$)$_2$	$D_2/D_{2h}/C_{2v}$	−26.4	−2.0	−53.3	+17.5
(X$_2$C$_2$)$_2$	$C_{2v}/D_{2h}/C_{2v}$	−20.8	+5.0	−53.3	+17.5
(X$_2$C$_2$)$_3$	$D_{3d}/D_{6h}/C_{6v}$	+31.4	+39.0	+62.6	+40.1

computing ΔE for the following reaction:



(2)

whereas the conjugation stabilization associated with the [6]-radialene is obtained by computing ΔE for the following reaction:



(3)

Although the above definition of aromatic stabilization is not fully appropriate for the description of the aromatic properties of nonbenzenoid systems such as radialenes,[21] it is useful to compare the stabilization properties of organic and metalla radialenes.

In Table 3, we compare the oligomerization energies, ΔE_{olig}, and the delocalization stabilizations, ΔE_{conj}, of the metal substituted cyclopolyenes **8**−**11** with those for the corresponding organic radialenes and cyclopolyenes. First of all, we note that the results obtained for the organic cyclopolyenes at this level of theory are in agreement with the available experimental data. For instance, the experimental oligomerization and aromatization energies for benzene are −142.8 and −64.2 kcal mol^{-1}, in reasonable agreement with the calculated values reported in Table 3.

The titanium dimer species **8** with a square geometry (D_{2d}) is 13.3 kcal mol^{-1} more unstable with respect to two monomer species **6**. Actually, the triplet ground state of this dimer could be subjected to a second-order Jahn−Teller distortion from the square geometry to a rectangle or rhombus structure.[22,23] This is essentially due to the intrinsic instability of this cyclobutadiene-like system. Indeed, cyclobutadiene is considered to be antiaromatic according to the Hückel 4n+2 rule, as it has four π electrons. On the basis of the long history of the cyclobutadiene molecules for which a rectangular singlet ground state has been found,[24−27] we investigated the deformation of **8** to a rectangle of D_2 symmetry. We found a rectangular singlet ground state with an optimized geometry strongly deformed from a square (R_{CC} = 1.602, 1.365 Å) and similar to that calculated for cyclobutadiene. Such a deformation leads to a stabilization of 30.3 kcal mol^{-1}, and **8** becomes 17.0 kcal mol^{-1} more stable with respect to two monomers. The deformation of **8** to a rhombus of C_{2v} symmetry gives a rhombic singlet ground state with an optimized geometry not far from that of the square structure. Such a deformation leads to an additional stabilization of 5.7 kcal mol^{-1}, so that **8** is 22.7 kcal mol^{-1} more stable with respect to two monomers. On the other hand, the titanium trimeric species **9** has a sizeable oligomerization energy of 96.6 kcal mol^{-1}, although it is quite smaller than that of benzene (154.6 kcal mol^{-1}). The aromatic stabilization energy for **9** is ca. 31 kcal mol^{-1} smaller than that for benzene, thus implying that about half of the observed destabilization of the metal substituted species (58 kcal mol^{-1}) is due to the diminished ring conjugation.

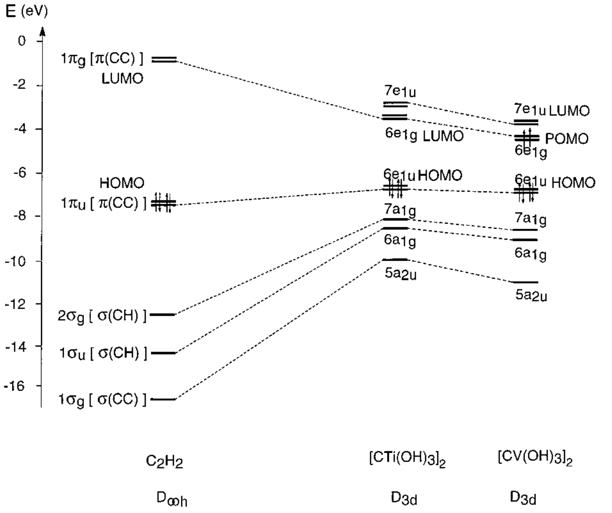


Figure 3. Molecular orbital diagram showing the effect of metal substitution on the frontier energy levels of acetylene.

When the vanadium dimer species **10** with a square geometry (D$_{2d}$) is considered, a singlet ground state is observed with the triplet state only 2.4 kcal mol^{-1} higher in energy. Note that this dimer is 26.8 kcal mol^{-1} more stable than two monomer species **7**. This reflects the radialene nature of **10**, which removes the orbital degeneracy (and the connected antiaromatic nature) of cyclobutadiene and its σ-substituted derivative. Therefore, no significant stabilization is expected by its deformation to a rectangular or rhombic geometry. However, two independent optimizations in D_2 and C_{2v} symmetry for the singlet state led to a significant stabilization of 23.0 and 29.0 kcal mol^{-1}, respectively, although the geometries are only slightly deformed from a square shape. However, it is experimentally known that, due to steric repulsion, [4]radialenes with large substituents adopt lower than D_{4h} symmetries with either planar or puckered cyclobutane rings.[12] Therefore, the energy lowering caused by deformation can be explained in terms of steric hindrance. Note that the rhombic structure shows a dissociation energy (ΔE_{olig}) which is very close to that of the corresponding radialene system (56.8 vs 53.5 kcal mol^{-1}). The vanadium trimeric species **11** has an even larger oligomerization energy of 116.7 kcal mol^{-1} than that of the organic analogue (94.2 kcal mol^{-1}). The

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Table 4. Mulliken Atomic Charges of Cyclopolyenes, Radialenes, and Metal Derivatives

			charge			
molecules	symmetries	atom	X = Ti	X = V	X = H	X = CH_2
$(X_2C_2)_2$	$D_{2d}/D_{4h}/C_{4v}$	C	−0.43	−0.50	+0.004	−0.001
		X	+1.87	+1.84	−0.004	+0.001
$(X_2C_2)_2$	$D_2/D_{2h}/C_{2v}$	C	−0.43	−0.49	−0.004	−0.003
		X	+1.85	+1.80	+0.004	+0.003
$(X_2C_2)_2$	$C_{2v}/D_{2h}/C_{2v}$	C	−0.47/−0.38	−0.52/−0.51	−0.004	−0.001
		X	+1.86/+1.85	+1.83/+1.89	+0.004	+0.001
$(X_2C_2)_3$	$D_{3d}/D_{6h}/C_{6v}$	C	−0.41	−0.49	−0.060	−0.134
		X	+1.86	+1.75	+0.060	+0.134

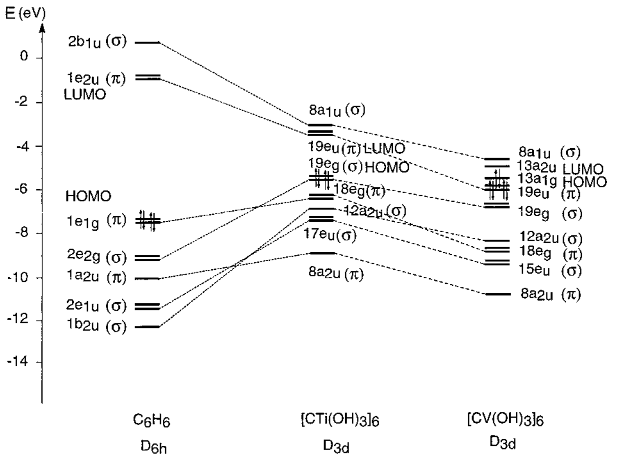

Figure 4. Molecular orbital diagram showing the effect of metal substitution on the frontier energy levels of benzene.

conjugation stabilization energy for **11** is very close to that of the corresponding radialene (39.0 vs. 40.1 kcal mol^{-1}). Together with the results of the geometrical optimization, these results state that **10** and **11** have a metalla radialene structure.

Table 4 reports the Mulliken charges on the carbon atoms and the hydrogen or metal substituents of the cyclopolyenes, radialenes, and their metal derivatives. We see that the charges on the carbon atoms are around −0.40 e for the titanium systems and −0.50 e for the vanadium species, showing more negative values than those observed for the corresponding cyclopolyenes (0.00/−0.06 e) and radialenes (0.00/−0.13 e). This is probably due to the higher polarization of the C−M σ bonds toward the carbon atoms and would suggest a higher reactivity toward electrophilic attack for these metal substituted cyclopolyenes and radialenes.

Figures 3 and 4 show the effect of metal substitution on the frontier energy levels of acetylene and benzene, respectively. We see that metal substitution affects both σ and π orbital energies. In particular, a partial occupation of the antibonding π (CC) orbital is observed for the vanadium substituted acetylene, as expected on the basis of its cumulenic structure (see Figure 3). For benzene, a σ-π crossing among the occupied orbitals is observed upon titanium substitution, whereas upon vanadium substitution, the antibonding π(CC) orbitals are occupied, thus leading to endocyclic single C−C bonds. The HOMO−LUMO gaps are reduced by metal substitution, so that the substituted species are expected to be less stable than the corresponding cyclopolyenes. In particular, the smallest gap is calculated for the vanadium system (0.718 eV). The higher energies of the HOMOs and the lower energies of the LUMOs make these species more reactive toward both electrophilic and nucleophilic attack.

4. Conclusions

This theoretical study has presented a characterization of a series of $M(OH)_3$-substituted cyclopolyenes as simple models of hypothetical molecular metal carbides. Whereas the predicted structures of the titanium species are quite similar to those of the corresponding organic cyclopolyenes, the electronic structures and molecular geometries found for the vanadium species suggest a metalla radialene nature for these compounds, with the endocyclic conjugation of carbon−carbon double bonds replaced by an exocyclic arrangement of carbon−metal double bonds.

Although there is a decrease of the thermodynamical stability upon metal substitution of the organic moieties, the benzene analogues are still quite stable with respect to dissociation into acetylene-like units and are therefore expected to be feasible synthetic targets. However, the comparison of the electronic structure of these metal substituted cyclopolyenes with those of the corresponding cyclopolyenes has shown that these species should be more reactive toward both electrophilic and nucleophilic attacks.

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