Oligomerization of the PH$_3$CuC≡CCuPH$_3$ Acetylide toward the Formation of (PH$_3$CuC)$_n$ (n = 4, 6, 8) Metal Carbides: A Theoretical Study Based on Density Functional Theory

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Density functional calculations were performed on a series of Cu(PH$_3$)-substituted cyclopolyenes as simple models of molecular metal carbides. We studied the oligomerization of the copper acetylide PH$_3$CuC≡CCuPH$_3$ as a possible precursor of these (PH$_3$CuC)$_n$ (n = 4, 6, 8) 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 metal substituents on the organic C$_4$, C$_6$, and C$_8$ cyclic moieties. We found comparable geometries of the C$_n$ units and, for n = 3, a thermodynamically stable species with respect to dissociation toward dinuclear copper acetylides.

Introduction

The field of molecular metal carbides has attracted considerable attention. Extended metal carbides are materials of remarkable practical interest and have been known for long time,[1] while examples of molecular carbides were reported only recently.[2−19] Among them, we can distinguish (i) systems that can be considered as fullerene-like cages or extended carbide fragments where carbons have been replaced by metal atoms as in, for example, M$_8$C$_{12}$ (M = Ti, V, Zr),[5−7] M$_{14}$C$_{13}$ (M = Ti, V),[8−9] and Cu$_{15}$C$_{14}$,[10] and (ii) organometallic polynuclear compounds in which small carbon moieties are bracketed by ML$_n$ metal fragments.[11−19] 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 carbide precursors of higher molecular complexity. A viable approach that can be undertaken is the oligomerization of dinuclear metal acetylides. This approach considers metal acetylides, *i.e.* L$_n$-MC≡CML$_n$, as compounds which should undergo oligomerization to different forms of molecular metal carbides.

In this paper, we explore the oligomerization of the copper acetylide PH$_3$CuC≡CCuPH$_3$, **1**, as a possible precursor of hypothetical Cu(PH$_3$)-substituted species cyclobutadiene, **2**, benzene, **3**, and cyclooctatetraene, **4**; see Figure 1. The choice of copper allows us to work with a "simple" d^{10} metal without including relativistic effects. Moreover, with this choice, we can consider more closely the new class of copper metallocarbohedrenes [Cu$_x$C$_y$]$^+$ [10] in which C$_2$ units are bound by copper atoms. Several species have been detected in the gas phase reaction of copper clusters and acetylene, including a [Cu$_{12}$C$_{12}$]$^+$ ion with a 1:1 copper:carbon ratio.[10] Although essentially all structurally characterized polynuclear aryl-bridged copper(I) complexes have an η^1 geometry,[20] this class of organocopper complexes tends to form aggregate structures which often rearrange in solution so that less stable species are difficult to crystallize. Moreover, a few metal-substituted cyclopolyenes with mainly σ-bonded metal fragments have been characterized[3,19] and theoretically investigated.[21,22] Our attention will focus on the geometric structures of the monomeric and oligomeric compounds, on their thermodynamic stabilities, on their aromatic stabilization, and on their electronic structures. Special emphasis will be placed on the comparison of the above properties of these metal-substituted cyclopolyenes with those of the corresponding cyclopolyenes to study the effects of metal

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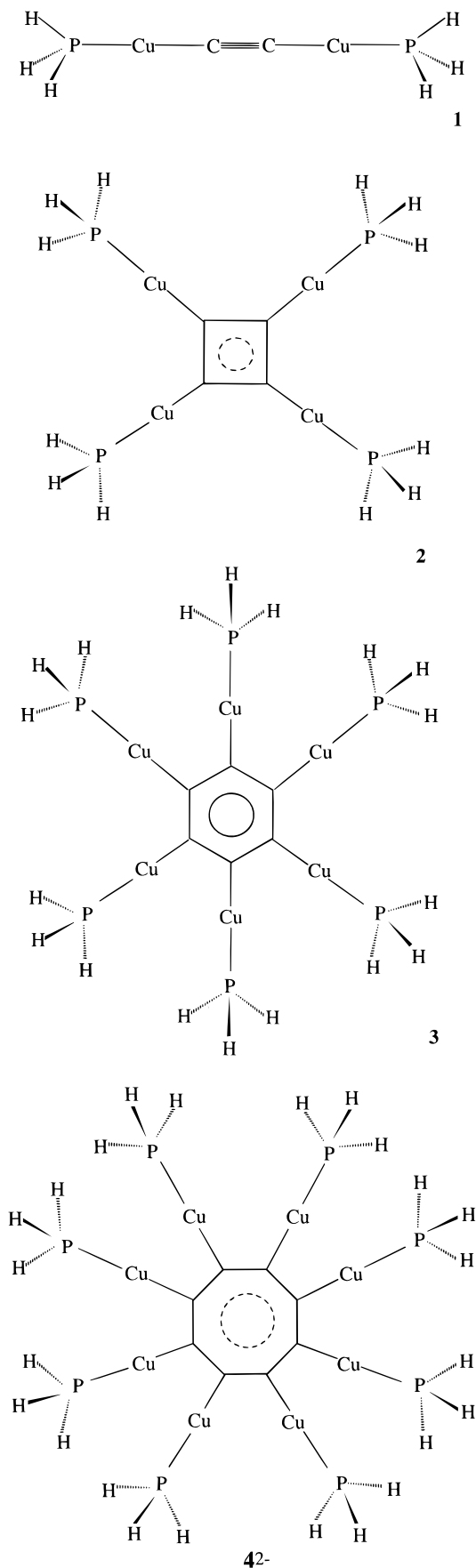
Figure 1. Geometrical structures of the considered metal-substituted cyclopolyenes.

substituents on the organic C_4, C_6, and C_8 cyclic moieties. In particular, we will consider the effect of metal substitution on the energies and the nature of the frontier orbitals of the cyclobutadiene, **5**, benzene, **6**, and cyclooctatetraene, **7**, systems.

Computational Details

All calculations reported in this work were carried out by using the ADF program package described elsewhere.[23−25] Molecular structures were optimized by the LDA method, while its nonlocal extension was applied only to the monomeric, neutral unit (PH₃CuC)₂ **1**. In the latter method, the nonlocal exchange (Becke[26]) and correlation (Perdew[27]) corrections are included. It has already been demonstrated how the nonlocal corrections improve optimized geometries of transition metal complexes, especially metal−ligand bond lengths, otherwise almost uniformly too short (by about 0.05 Å) if calculated by local methods.[28] We chose to perform partial LDA geometry optimizations of the polymeric systems for computational reasons and because of the fact that we are mainly interested in comparative rather than absolute considerations of the various molecules. Although the LDA can overestimate metal−ligand bond energies,[29] we will consider only energy differences of reactions involving no metal−carbon bond dissociation and only carbon−carbon bond dissociation and formation which are known to be reasonably well described at this level of theory.[29]

The basis set employed for copper was of uncontracted double-ζ quality for 3s and 3p and triple-ζ quality for 3d and 4s and 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 (Cu 1s, 2p; C, P 1s) were kept frozen according to the method of Baerends et al.[23] A recent paper reported that sets of this level give a good description of metal−ligand bonds, the basis set incompleteness error being compensated by a BSSE error of opposite sign.[30]

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 general geometry optimization procedure was based on the algorithm developed by Versluis and Ziegler.[28]

The PH₃CuC≡CCuPH₃ model system, **1**, considered in the calculations was constructed by assuming reasonable bond lengths and angles for the starting geometry. This structure was fully optimized within the D_{3h} symmetry constraint, at both LDA and NLDA levels.

The geometries of the model systems (PH₃CuC)₄ (neutral, **2**, with both C_{4v} and C_{2v} symmetries, and dianionic, **2²⁻**), (PH₃CuC)₆, **3**, and (PH₃CuC)₈²⁻, **4²⁻**, were optimized at the LDA level, with only the following bond lengths variable: C−C, Cu−C, and Cu−P. The remaining geometrical parameters were held fixed at the values obtained for the monomeric unit **1**, and C_{4v}, C_{6v}, and C_{8v} symmetry constraints were applied to the respective systems.

A dianionic rather than a neutral (PH₃CuC)₈ allows us to consider a planar rather than a tub-shaped molecule.

Results and Discussion

Table 1 shows the optimized geometry and the bonding energies with respect to atoms of the monomeric (PH₃CuC)₂ species, **1**. We note that the bond distances involving metals

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Table 1. Geometrical Parameters and Bonding Energies for Copper Oligomers[a]

species	symm	param	LDA[b]	energy (eV)
$Cu_2C_2(PH_3)_2$	D_{3h}	C–C	1.238 (1.244)	−50.384
		Cu–C	1.811 (1.857)	
		Cu–P	2.149 (2.217)	
		P–H	1.420 (1.419)	
		∠HPH	119.8 (119.8)	
$[Cu_2C_2(PH_3)_2]^-$	D_{3h}	C–C	1.248	−50.255
		Cu–C	1.807	
		Cu–P	2.128	
		P–H	1.452	
		∠HPH	120.0	
$[Cu_2C_2(PH_3)_2]_2$	C_{4v}	C–C	1.455	−98.790
		Cu–C	1.838	
		Cu–P	2.168	
$[Cu_2C_2(PH_3)_2]_2$	C_{2v}	C_1–C_2	1.556	−98.907
		C_1–C_3	1.332	
		Cu–C	1.838	
		Cu–P	2.168	
$[Cu_2C_2(PH_3)_2]_2^{2-}$	C_{4v}	C–C	1.462	−96.281
		Cu–C	1.824	
		Cu–P	2.151	
$[Cu_2C_2(PH_3)_2]_3$	C_{6v}	C–C	1.400	−152.619
		Cu–C	1.867	
		Cu–P	2.178	
$[Cu_2C_2(PH_3)_2]_4^{2-}$	C_{8v}	C–C	1.407	−200.675
		Cu–C	1.871	
		Cu–P	2.162	

[a] The geometrical values in parentheses and the bonding energies were calculated by including the nonlocal Becke and Perdew corrections. [b] Bond lengths in angstroms; bond angles in degrees.

are underestimated at the LDA level, as is usually observed,[28] and that the nonlocal correction stretches the bonds (generally to distances near the experimental equilibrium lengths, but experimental data are not available in this case for comparison).

The species **2**, **2^{2-}**, **3**, and **4^{2-}** were only partially optimized at the LDA level. The optimized geometrical parameters and the bonding energies of these oligomeric species are also reported in Table 1. A direct comparison of the calculated geometries with experimental data is difficult because few X-ray geometries are available for aryl- and alkynylcopper phosphine complexes and most of them are polynuclear aggregated species.[20] Cu–C distances of ca. 1.95−2.00 Å are observed for the $[Cu(C\equiv CPh)(PMe_3)]_4$[31] and $[Cu_2(C\equiv CBu^t)_2(PCy_3)(PPh_3)_2]$[32] compounds and are therefore 0.10−0.15 Å longer than the values calculated for **2** at the NLDA level. However, in these two complexes, the Cu–C bonds involve two copper−phosphine units combined via a μ_2-η^1-bridging C≡CR alkynyl moiety and are expected to be longer than a corresponding η^1 terminal Cu–C bond. On the other hand, the Cu–P distances are in the range 2.20−2.25 Å, in good agreement with the value calculated for **2** (2.217 Å at the NLDA level). The C–C bond lengths observed for these and other alkynylcopper complexes are close to the value for acetylene (1.21 Å), as is the value calculated for **2** (1.244 Å at the NLDA level), and this has been considered as indicative of negligible π interactions. Cu–C distances for $[Cu(C_6H_2Bu^t_3-2,4,6)(DMS)]$[33] and other mononuclear arylcopper complexes with one neutral two-electron-donor ligand on copper[20] fall in the range 1.90−1.95 Å and are only ca. 0.05 Å longer than that calculated for **3** at the LDA level, but we must bear in mind the usual understimation due to the LDA method.

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Table 2. Dissociation Energies (ΔE_{olig}) (kcal mol^{-1}) of the Oligomers with Respect to the Relative Monomer Units and Aromatic Stabilization Energies (ΔE_{arom}) (kcal mol^{-1}) of the Oligomers Calculated According to Equations in the Text

species	symm	ΔE_{olig}		ΔE_{arom}	
		X = Cu(PH$_3$)	X = H	X = Cu(PH$_3$)	X = H
$(X_2C_2)_2$	C_{4v}/D_{4h}	+45.6	−2.5	+30.8	+58.8
$(X_2C_2)_2$	C_{2v}/D_{2h}	+42.9	−8.0	+28.1	+53.3
$(X_2C_2)_2^{2-}$	C_{4v}/D_{4h}	+97.5	+54.4	+61.7	+89.4
$(X_2C_2)_3$	C_{6v}/D_{6h}	−33.8	−154.6	−56.1	−62.6
$(X_2C_2)_4^{2-}$	C_{8v}/D_{8h}	+13.9	−185.0	−36.8	−88.7

Table 3. Geometrical Parameters of Cyclopolyenes and Their Metal Derivatives

species	symm	param	LDA bond lengths (Å)	
			X = Cu(PH$_3$)	X = H
$(X_2C_2)_2$	C_{4v}/D_{4h}	C–C	1.455	1.430
		X–C	1.838	1.090
$(X_2C_2)_2$	C_{2v}/D_{2h}	C_1–C_2	1.556	1.570
		C_1–C_3	1.332	1.330
		X–C	1.838	1.096
$(X_2C_2)_2^{2-}$	C_{4v}/D_{4h}	C–C	1.462	1.463
		X–C	1.824	1.107
$(X_2C_2)_3$	C_{6v}/D_{6h}	C–C	1.400	1.384
		X–C	1.867	1.095
$(X_2C_2)_4^{2-}$	C_{8v}/D_{8h}	C–C	1.407	1.396
		X–C	1.871	1.099

When we consider the monomeric copper acetylide species **2**, we see that the calculated C–C bond distance (1.244 Å) is ca. 0.03 Å longer than that in acetylene (1.208 Å at the same level of theory) and approaches the C–C bond distance in the acetylide dianion C_2^{2-} (1.287 Å at the NLDA level), reflecting the partial ionic character of this metalated species (see the discussion on Mulliken charges below). The C–C bond distance lengthens in the oligomers to a value intermediate between those of a single and a double bond, as expected from the analogy with cyclopolyenes. The Cu–C bond length increases on passing from the monomeric unit (1.811 Å) to the tetrameric species (1.871 Å). The Cu–P bond distance seems to stretch from monomer to trimer, but in the tetrameric system it decreases. This decrease could be ascribed to the double negative charge because the same trend is found for the neutral and dianionic dimers.

The main purpose of this study is to determine if any of the hypothetical species **2**, **2^{2-}**, **3**, and **4^{2-}** are sufficiently stable to be isolated. To give a quantitative measure of the stability of these molecules, we considered the reaction leading to the most plausible fragments. The most obvious choice is the inverse of the oligomerization reaction involving a suitable number of copper acetylide molecules (which are known to be stable species[34]) and anions for **2^{2-}** and **4^{2-}**:

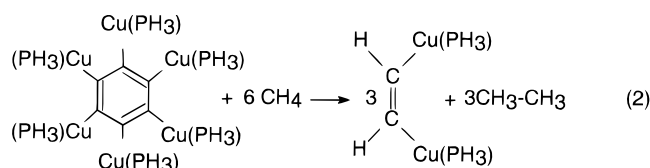$$[CCu(PH_3)]_n^{m-} \rightarrow (n-m)[CCu(PH_3)]_2 + m[CCu(PH_3)]_2^- \quad (1)$$

Although a complete characterization of the stability of these species would require the evaluation of the activation energy of the corresponding oligomerization reactions, we calculated only the energetics of these reactions because of the dimensions of the considered systems. Moreover, because these ring systems may exhibit aromatic stabilization or destabilization, we 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

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**Table 4.** Mulliken Atomic Charges of Cyclopolyenes and Their Metal Derivatives

species	symm	atom	charge X=Cu	charge X=H
$(X_2C_2)_2$	C_{4v}/D_{4h}	C	−0.24	+0.004
		X	+0.03	−0.004
$(X_2C_2)_2$	C_{2v}/D_{2h}	C	−0.35	−0.004
		X	+0.10	+0.004
$(X_2C_2)_2^{2-}$	C_{4v}/D_{4h}	C	−0.39	−0.18
		X	−0.004	−0.32
$(X_2C_2)_3$	C_{6v}/D_{6h}	C	−0.33	−0.06
		X	+0.09	+0.06
$(X_2C_2)_4^{2-}$	C_{8v}/D_{8h}	C	−0.32	−0.15
		X	+0.12	−0.10

calculation 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 the study of the aromatic character of several compounds.[35] Thus the aromatic stabilization associated with **3** was obtained by computing ΔE for the following reaction

$$\text{(benzene-Cu(PH}_3\text{)}_6\text{)} + 6\,CH_4 \longrightarrow 3\,\text{(CCu(PH}_3\text{)}_2\text{=CH}_2\text{)} + 3\,CH_3\text{-}CH_3 \qquad (2)$$

In Table 2 we report the oligomerization energies, ΔE_{olig} for reaction 1, and the aromatic stabilizations, ΔE_{arom} for reaction 2, for the species **2**, **2**$^{2-}$, **3**, and **4**$^{2-}$.

The dimer species **2** with a square geometry (C_{4v}) is 45.6 kcal mol^{-1} higher in energy than two monomer species **1**. Actually, the ground state of the dimer is subjected to a second-order Jahn−Teller distortion from the square geometry to a rectangle or rhombus structure.[36,37] On the basis of the long history of the cyclobutadiene molecules, for which a rectangular singlet ground state has been found,[38−41] we investigated the deformation of **2** to a rectangle of C_{2v} symmetry. We found a rectangular singlet ground state with an optimized geometry strongly deformed from a square (R_{CC} =1.559, 1.365 Å) and similar to that calculated for cyclobutadiene.[39] However, such a deformation leads to a stabilization of only 2.7 kcal mol^{-1}, and **2** remains 42.9 kcal mol^{-1} unstable with respect to two monomers. 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 because it has four π electrons. In order to better investigate this point, we considered also the dianionic dimeric species **2**$^{2-}$, formally aromatic. However, this charged system was even more destabilized with respect to the forming fragments: it is 97.5 kcal mol^{-1} more unstable than two monomeric species $(PH_3CuC)_2^-$. The same effect has been observed in small cyclic dianions and has been attributed to the Coulombic repulsion between nonbonded carbon atoms.[42] A completely different situation is present in the trimeric and tetrameric systems. Species **3** is 33.8 kcal mol^{-1} lower in energy than three monomer species **1**, and the tetramer species **4**$^{2-}$ is only 13.9
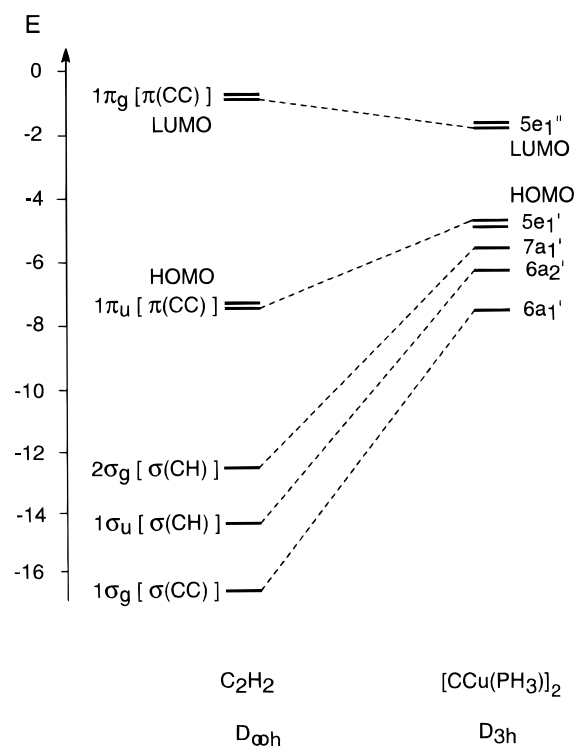
Figure 2. Molecular orbital diagram showing the effect of metal substitution on the frontier energy levels of acetylene (E in eV).

kcal mol^{-1} higher in energy than two species **1** and two anionic species **1**$^-$. The tetrameric species shows a small destabilization due to the destabilizing effect of the double negative charge and to the lower aromatic stabilization expected for a ring having more than six members.[43,44]

In Tables 2 and 3, we compare respectively the oligomerization and aromatic stabilization energies and the main geometrical parameters of the metal-substituted cyclopolyenes **2**, **2**$^{2-}$, **3**, and **4**$^{2-}$ with those for the corresponding organic cyclopolyenes **5**, **5**$^{2-}$, **6**, and **7**$^{2-}$. First, we note that the results obtained for the cyclopolyenes at this level of theory are in good agreement with the available experimental data. For instance, the experimental C−C and C−H bond distances for benzene are 1.39 and 1.10 Å, while the oligomerization and aromatization energies are −142.8 and −64.2 kcal mol^{-1}, in remarkable agreement with the calculated values reported in Tables 2 and 3. Then, from Table 3 we see that the geometrical parameters of the considered cyclopolyenes are slightly affected by the metal substituents: the C−C bond distances are only 0.02−0.03 Å longer in the dimeric species and the difference decreases on increasing the size of the cycle. Table 2 shows that the oligomerization energies of the metal-substituted cyclopolyenes are substantially lower than those for the corresponding cyclopolyenes and only the trimeric species **3** is stable with respect to fragmentation. On the other hand, the aromatic stabilization energies for these metal-substituted cyclopolyenes are only slightly smaller than those for the corresponding cyclopolyenes. This implies that the observed destabilization of the metal-substituted species with respect to cyclopolyenes is due mainly to a destabilization of the C−C and M−C σ skeleton.

Table 4 reports the Mulliken charges on the carbon atoms and the hydrogen or metal substituents of the cyclopolyenes and their metal derivatives. We see that the charges on the carbon atoms all fall in the range −0.20 to −0.40 e for **2**, **2**$^{2-}$,

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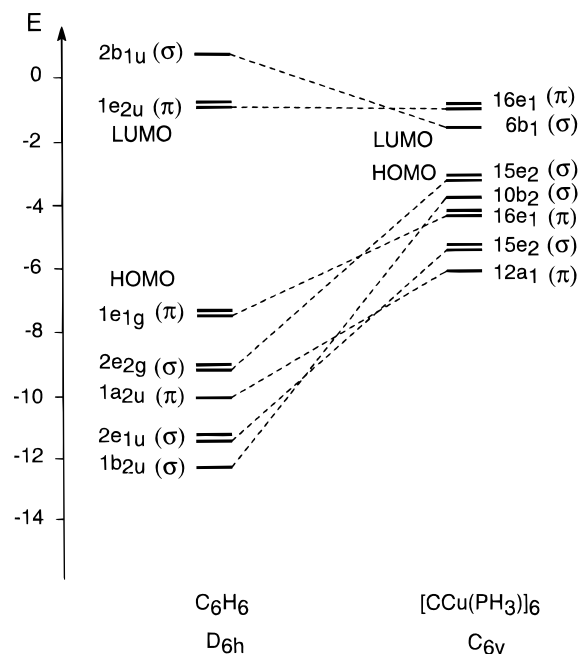
Figure 3. Molecular orbital diagram showing the effect of metal substitution on the frontier energy levels of benzene (E in eV).

3, and **4^{2-}**, showing more negative values than those observed for the corresponding cyclopolyenes (0.00 to -0.20 e). This is probably due to the higher polarization of the C−Cu σ bonds toward the carbon atoms and would suggest a higher reactivity toward electrophilic attack for these metal-substituted cyclopolyenes.

Figures 2 and 3 show the effect of metal substitution on the frontier energy levels of acetylene and benzene, respectively, the latter taken as representative of the behavior for the three cyclopolyenes. As expected, because of the low energies of the Cu d_{π} orbitals, metal substitution affects the σ orbital energies more strongly than the π ones. No $\sigma-\pi$ crossing is observed for acetylene, and both HOMO and LUMO maintain their π character, although the σ orbitals are strongly raised in energy (see Figure 2). A different situation is observed for benzene (see Figure 3), for which a $\sigma-\pi$ crossing is observed for both HOMO and LUMO. Moreover, while the π molecular orbitals are essentially localized on the polyene ring, the σ orbitals are strongly delocalized on the metal and ligand atoms. An analogous $\sigma-\pi$ crossing is observed also for all the other metal-substituted polyenes. Due to this crossing, the HOMO− LUMO gaps are reduced by metal substitution, so that the substituted species **2**, **2^{2-}**, **3**, and **4^{2-}** are expected to be less stable than the corresponding cyclopolyenes. Note that the much stronger destabilization of the σ orbitals with respect to the π orbitals observed for these metal-substituted cyclopolyenes is consistent with the hypothesis above that the reduction of the oligomerization energy is mainly due to a destabilization of the σ skeleton and not of the π system. Finally, it is worth noting that the higher energies of the HOMOs and the lower energies of the LUMOs make these species more reactive toward both electrophilic and nucleophilic attack.

Conclusions

This theoretical study has presented a characterization of a series of Cu(PH$_3$)-substituted cyclopolyenes as simple models of hypothetical molecular metal carbides. The predicted structures of these molecules are quite similar to those of the corresponding organic cyclopolyenes. Although there is a sharp decrease in the thermodynamic stability upon metal substitution of the organic moieties, the benzene analogue is still quite stable with respect to dissociation into acetylene-like units, while the cyclooctatetraene analogue is almost thermoneutral. This suggests that the oligomerization of the copper acetylide PH$_3$-CuC≡CCuPH$_3$, **1**, to the (PH$_3$CuC)$_n$ (n = 6, 8) hypothetical species is a thermodynamically plausible process. However, comparison of the electronic structures 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 attack.