Organometallic Analogs of the Cyclobutadiene Dication: An Ab Initio MO and Density Functional Study of the Symmetrical Planar and Puckered $[WL_2(\mu\text{-}CR)]_2$ Complexes ($L = H, Me, F, OH; R = H, F, Me$)

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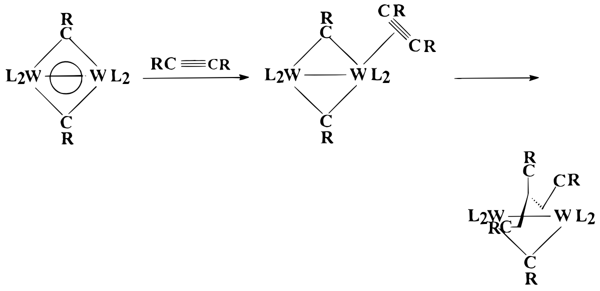
Ab initio MO and density functional theory calculations are reported for tungsten complexes $[WL_2(\mu\text{-}CR)]_2$ ($L = H$, Me, F, OH; $R = H$, F, Me). The general perception that these complexes are always planar is contradicted. The effect of ligand L and substituent R on the puckering of four-membered W_2C_2 ring are studied. With $L = H$, the ring puckering is in the order of $R = F < H < Me$. With $R = H$, the ring puckering is in the order of $L = OH \approx F < Me < H$. The puckering of W_2C_2 ring depends more on the ligand L than on the substituent R. The analogous nature of these complexes to cyclobutadiene dications is also discussed.

Introduction

The chemistry of binuclear complexes continue to fascinate chemists for many reasons.[1] Prime among them are the C−C bond-forming reactions mediated by a variety of binuclear complexes bridged by carbyne ligands.[2,3] Even though the detailed mechanistic pathways are often not known, several of these have found synthetic utility. The chemistry of the binuclear tungsten complexes $[WL_2(\mu\text{-}CR)]_2$ developed by Chisholm and co-workers[3] demonstrates the variety possible. These bridged carbyne complexes form adducts with alkynes,[4,5] allenes,[6] and diazoalkanes.[7] A reactivity order of $[(Me_3SiCH_2)_2W(\mu\text{-}CSiMe_3)]_2 > [(Pr^iO)_2W(\mu\text{-}CSiMe_3)]_2$ was observed in these reactions.[6−8] For example, the former complex reacts rapidly with allenes even at lower temperatures while the latter reacts very slowly over days at room temperature.[6] This reactivity difference was postulated to be an effect of electron donation from the p_π orbital of alkoxy oxygen to the d_π orbital of tungsten.[7] On reaction with acetylenes they form an acetylene adduct and then the didehydroallyl complexes[4,9] as shown in reaction 1. Though many experimental and theoretical studies had been conducted, the details of the mechanism by which this reaction proceeds is not clear. As a first step in this direction, we study the structural aspects of the reactant complexes $[WL_2(\mu\text{-}CR)]_2$. The X-ray structures available so far indicate that $[WL_2(\mu\text{-}CR)]_2$ complexes[5,10−12] have planar four-membered rings with a diagonal metal−metal single bond. These studies were made difficult by the peculiarities of the sample crystals which tended to fracture at low temperatures and caused excessive vibration as the temperature increased. Thus the geometrical parameters obtained from X-ray studies could only be used as a starting point in further structural analysis. Earlier electronic structural studies on these complexes with extended Hückel and Fenske−Hall MO methods considered only planar geometries for W_2C_2 ring.[13,14] These calculations provided a basic understanding of the electronic structure with a metal−metal bonding MO (Figure 1a) and two stabilized π-type MOs (Figure 1b,c). The latter set of orbitals support the circle drawn inside the ring in these systems indicating stabilizing π-delocalization.



(1)

L = CH_2SiMe_3; $-O^tBu$; $-O^iPr$

R = $SiMe_3$; Ph

Though the number of electrons is less by two, the electronic structures of the symmetrical diamagnetic

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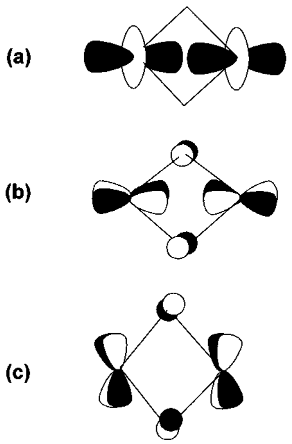
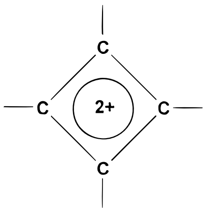
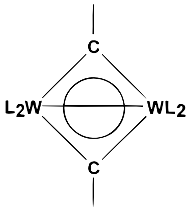


Figure 1. Schematic MOs corresponding to (a) the metal—metal bond and (b,c) delocalized π-bonds.

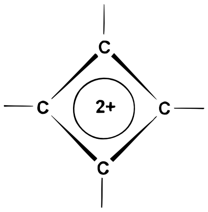
$[WL_2(\mu\text{-}CR)]_2$ complexes with a metal—metal σ-bond and a delocalized π electron system seem to resemble that of the cyclobutadiene dication. It was thought that the dication is planar (**a**) and aromatic. However, detailed theoretical and experimental studies have shown that the parent cyclobutadiene dication[15] and several isoelectronic neutral analogs[16] prefer puckered structures (**c**) and still retain aromaticity. The interactions in the σ-plane in **a** that forces the structure to be puckered has been documented.[15] Substituents such as fluorine reverses this trend; the perfluorocyclobutadiene dication prefers planar structure **a**.[15]



a



b



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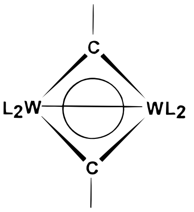

d

Can we expect a puckering similar to that of cyclobutadiene dication (**a** → **c**) among the $[WL_2(\mu\text{-}CR)]_2$ complexes (**b** → **d**)? What is the extend to which the puckering depend on ligand L and substituent R? The puckered geometry was expected only for an unsymmetrical complex when two different ligands are connected to the metal centers. The X-ray structures have shown this puckering very clearly in many cases. For example, the *cis*-$[(WCp^*Me)_2(\mu\text{-}CMe)_2]$ complex[17] has a four-membered ring with puckering angle of 25.1°. A comparison of this unsymmetrical puckered complex with symmetrical complex[13a] using the EHMO method had shown that both have similar orbital patterns; neither a change of ligands nor out-of-plane bending affected the electronic structure. No quantitative study of this system is available in the literature. In order to get quantitative information about the structural variations we have calculated several $[WL_2(\mu\text{-}CR)]_2$ systems using Hartree—Fock (HF) and density functional methods. The results, which show a range of W_2C_2 ring puckering not dictated by symmetry, will be discussed in this paper.

Theoretical Methods

Model complexes for the study were chosen by substituting Me, OH, F, and H for L and Me, F, and H for R. The F and OH ligands with their π-donor character are expected to form a metal—ligand π-bond, in addition to forming σ-bonds. The OH ligand has more π-donor character than the F ligand. The H and Me ligands are predominant σ-donors. Thus the selected models span a range of electronic requirements on the W_2C_2 skeleton, so that any tendency for puckering behavior can be understood.

The geometries of **1**—12 (Chart 1) were fully optimized under the symmetry constraints using the ab initio HF and the hybrid density functional theory (B3LYP) methods.[18] The B3LYP calculations, known for giving results comparable to those at the MP2 level, uses Becke's three-parameter nonlocal exchange functional[18b,c] with the nonlocal correlation functional of Lee, Yang, and Parr.[18d] The relativistic effective core potential of Stevens et al.[19] were used for all atoms along with the split-valence basis sets (4111,411,311) for W, (121,121) for C and F, and (311) for H.

The vibrational frequency calculations have been done at the B3LYP level to characterize the nature of the stationary points using the optimized geometries at the same level. A minimum on the potential energy surface was ascertained by having all positive vibrational frequencies. All the calculations have been performed using the Gaussian 92[20] and Gaussian 94[21] packages.

Results and Discussion

The results at both the Hartree—Fock and B3LYP levels of theory are similar. The nonplanar puckered geometries are preferred among structures **1**—**8**. For structures **9**—**12** the nonplanar geometries were converged to planar geometry except at HF level for **10**.

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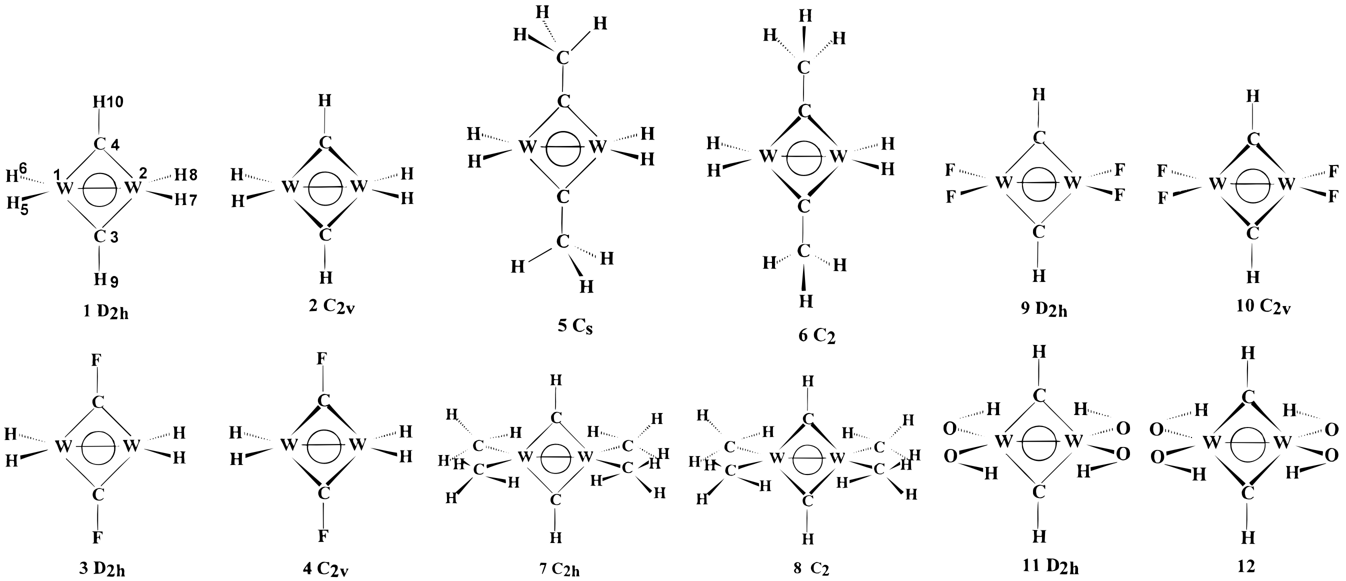
Chart 1



1 D_{2h}
2 C_{2v}
5 C_s
6 C_2
9 D_{2h}
10 C_{2v}
3 D_{2h}
4 C_{2v}
7 C_{2h}
8 C_2
11 D_{2h}
12

Table 1. Total Energies (TE) in au, Relative Energies (RE) in kcal/mol, Dihedral Angles (Dh), Number of Imaginary Frequencies (NIF), Zero Point Vibrational Energies (ZPVE) in kcal/mol, and Lowest Frequency Value (LF) in cm^{-1} at the Hartree–Fock and B3LYP Levels

	HF results				B3LYP results					
molecule	no., sym	TE	RE	Dh	TE	NIF	ZPVE^a	RE^b	Dh	LF
L, R = H	**1**, D_{2h}	−148.386 89	7.8	0.0	−150.318 90	1	34.6	6.0	0.0	−215.3
	2, C_{2v}	−148.399 31	0.0	25.6	−150.329 73	0	35.4	0.0	27.2	217.7
L = H, R = F	**3**, $D_{2h}{}^c$	−194.881 64	3.8	0.0	−197.456 91	0	25.6	0.9	0.0	14.6
	4, C_{2v}	−194.887 75	0.0	24.4	−197.458 92	0	26.0	0.0	24.3	86.9
L = H, R = Me	**5**, C_s	−161.673 69	9.7	0.0	−164.028 99	1	69.1	6.6	0.0	−134.9
	6, C_2	−161.689 22	0.0	27.5	−164.041 42	0	70.3	0.0	28.5	92.8
L = Me, R = H	**7**, C_{2h}	−175.025 39	1.4	0.0	−177.804 10	1	105.3	0.6	0.0	−112.9
	8, C_2	−175.027 79	0.0	18.4	−177.805 58	0	105.6	0.0	18.5	79.4
L = F, R = H	**9**, D_{2h}	−241.779 37	0.1	0.0	−244.964 75	0	24.3		0.0	67.8
	10, C_{2v}	−241.779 58	0.0	10.4						
L = OH, R = H	**11**, D_{2h}	−211.409 08		0.0	−214.480 97	0	50.6		0.0	29.2

[a] Unscaled ZPVE. [b] B3LYP+ZPVE. [c] C_{2h} at B3LYP 14° bending of L = H from the plane of D_{2h}.

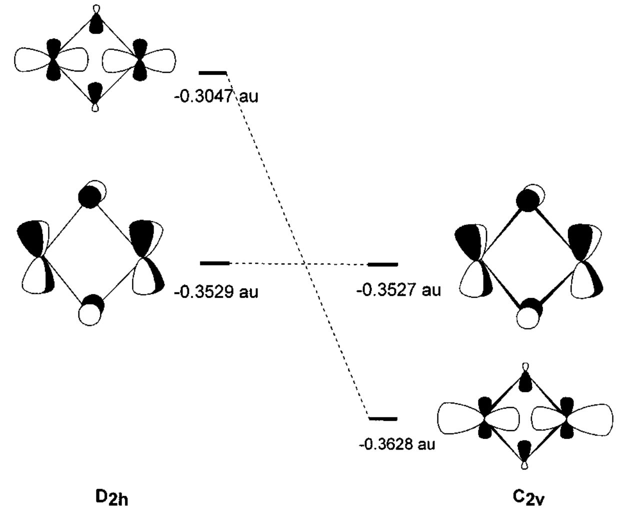


Figure 2. MO correlation diagram of [$WH_2(\mu$-$CH)]_2$ for the HOMO and HOMO-1. Note that the HOMO-1 (C_{2v}) has a decreased antibonding interaction between orbitals on adjacent atoms. On the other hand the bonding interactions between 1,3-atoms are enhanced because these are brought closer on puckering.

The puckering (Table 1) is measured as the dihedral angle of W–C–W–C of the ring as shown in the Chart 1. It varies for R in the order F < H < Me when L = H at the SCF and B3LYP levels. While the W_2C_2 ring is puckered when L = Me and R = H, the ring tends to be planar for L = F or OH. The relative energies reflect variations in the puckering angle.

The relatively smaller values of puckering angles for various R show that there is relatively minor influence exhibited by electronic changes of substituents on carbon. But the ligands L predominantly control the puckering angle. This can be due to the electronic effects of the ligands on the metal.

The calculations done for the parent systems **1** and **2** (Chart 1) showed that the latter is more stable than the former by over 6 kcal/mol. In contrast, the known X-ray geometries of the related derivatives show that the W_2C_2 units are planar. This may result from several factors including the packing of the molecules in the crystal. The temperature of measurement would also mask the puckering, especially if the potential energy surface is flat. The calculations reported here are for the gaseous state species at 0 K. A molecular orbital (MO) correlation analysis (Figure 2) of these two structures illustrates that the HOMO which corresponds to the metal–metal σ-bond in **1** is effected maximum in puckering; this becomes a lower energy MO in **2**. The interaction between adjacent atoms in the HOMO is antibonding. This is decreased by puckering and brings the metal atoms, which are bonding, closer. Thus the

Table 2. Geometrical Parameters of Structures 1−9 and 11 at the B3LYP Level[a]

molecule: no., sym	W(1)−W(2)	W(1)−C(3)	W(1)−C(4)	W(1)W(2)C(3)	W(1)C(3)W(2)	C(3)W(2)C(4)	W(1)C(3)W(2)C(4)	W(1)−L(5)	W(1)−L(6)
1, D_{2h}	2.593	1.966	1.966	48.8	82.5	97.5	0.0	1.751	1.751
2, C_{2v}	2.479	1.977	1.977	51.2	77.7	95.7	27.2	1.730	1.769
3, C_{2h}	2.679	1.976	1.926	47.4	86.7	93.3	0.0	1.744	1.744
4, C_{2v}	2.571	1.964	1.964	49.1	81.8	92.8	24.6	1.728	1.760
5, C_s	2.590	1.979	1.964	49.2	82.1	97.9	0.0	1.757	1.757
6, C_2	2.466	1.986	1.986	51.6	76.8	96.0	28.5	1.736	1.774
7, C_{2h}	2.636	1.975	1.975	48.1	83.7	96.3	0.0	2.128	2.128
8, C_2	2.575	1.978	1.978	49.4	81.2	95.8	18.5	2.124	2.142
9, D_{2h}	2.643	1.960	1.960	47.6	84.8	95.2	0.0	1.896	1.896
11, D_{2h}	2.664	1.972	1.972	47.5	85.0	95.0	0.0	1.891	1.891

[a] Bond lengths are in Å, and bond angles are in deg.

Table 3. Natural Charges on Various Atoms in Structures 1−11 at the HF Level

molecule: no., sym	W(1)	C(3)	L(5)	L(6)	R(9)
1, D_{2h}	1.227	−0.771	−0.304	−0.304	0.153
2, C_{2v}	1.095	−0.673	−0.234	−0.346	0.158
3, D_{2h}	1.135	−0.129	−0.292	−0.292	−0.423
4, C_{2v}	1.022	−0.055	−0.222	−0.334	−0.410
5, C_s	1.200	−0.543	−0.317	−0.317	−0.512
6, C_2	1.060	−0.445	−0.246	−0.358	−0.514
7, C_{2h}	1.361	−0.759	−0.935	−0.935	0.149
8, C_2	1.310	−0.707	−0.903	−0.959	0.152
9, D_{2h}	1.746	−0.705	−0.605	−0.605	0.168
10, C_{2v}	1.737	−0.692	−0.608	−0.606	0.169
11, D_{2h}	1.643	−0.773	−1.019	−1.019	0.147

HOMO is stabilized on puckering. Therefore it is the HOMO of **1**, which controls the puckering of the geometry. For L = H, the relative energy (RE) changes in the order of R = Me > H > F. If the lower energy metal−metal σ-bonding MO in **2** can be tuned to retain its stability, then the planar nature of W_2C_2 ring could be achieved. This can be done only by substituting the ligands L connected to the metal atoms. Thus we have calculated the systems with L = F and OH. The planar arrangement favors the additional π-bonding between the ligand lone pair orbitals and the π-type d-orbitals of the metal. Therefore with π donor ligands the complex prefers to be planar rather than puckered. The results are in agreement with the expectation. The F and OH ligands favor only the planar structure at B3LYP level. The natural charge analysis (Table 3) show less positive charge on W in **11** than in **9** indicating the π-donor characteristic of ligands as F < OH. This is also reflected in thte W−L distance in **9** and **11.** According to the electronegativities of carbon, oxygen, and fluorine, we expect the bond distances in the order W−C > W−O > W−F. On the contrary the W−F and W−OH distances are 1.896 and 1.891 Å, respectively, while W−CH_3 bond distance is 2.124 Å. This change in the order of W−F and W−O bond distances is significant. The Wiberg bond indices of (Table 4) 0.589 and 0.720, respectively, for W−F (**9**) and W−O (**11**) bonds indicate a stronger bonding in the latter than in the former. This demonstrates the pronounced ability of the OH ligand over F for π-donation. Additionally, the MO energy diagram of **11** (Figure 3) shows that, though the HOMO and HOMO-1 are close in energy, the MO corresponding to the metal−metal bond is HOMO-1 as in the case of **2** even though **11** is planar. If the stabilization of the metal−metal bond is indeed the major factor for puckering, systems with a d^0−d^0 configuration such as the $[(Me_3SiCH_2)_2Ta(\mu\text{-}CSiMe_3)]_2$ complex,[22] without the metal−metal bond, should be planar. This complex has also been found to be planar from X-ray diffraction studies. The calculations on the model $[TaH_2(\mu\text{-}CH)]_2$ complex show that the planar structure is a minimum.[23] Thus the effects on the metal−metal bond play a major role in puckering.

The calculated geometries show that W−W bond distance is in agreement with experimental values though these are not directly comparable. As expected, the W−W bond distance is shorter in the nonplanar structures than in the planar structures. The increase in the W−W distance on going from L = Me, **8** (2.575 Å). to L = OH, **11** (2.664 Å), is also reflected in the W−W distances found in the X-ray structures with 2.535 Å for $[(Me_3SiCH_2)_2W(\mu\text{-}CSiMe_3)]_2$ and 2.618/2.622 Å for $[({}^tBuO)_2W(\mu\text{-}CSiMe_3)]_2$. Molecular orbital analysis showed that the pyramidalization at the metal center caused the rehybridization of W orbitals leading to enhanced metal−metal bonding, and the MO corresponding to the W−W bond lowered its energy while puckering. This in turn resulted in the shorter W−W bond distance. The Wiberg bond indices between atoms have also indicated the effective W−W bonding in nonplanar structures. The effect of rehybridization is also felt in the bond distances of inner and outer W−L bonds in puckered structures. The inner W−L bond is shorter while the outer one is longer. Thus the bond distances of W_1−L_5 and W_1−L_6 differ by 0.039 Å (**2**), 0.032 Å (**4**), 0.038 Å (**6**), and 0.018 Å (**8**).

The fact that $[(Me_3SiCH_2)_2W(\mu\text{-}CSiMe_3)]_2$ is more reactive than $[(Pr^iO)_2W(\mu\text{-}CSiMe_3)]_2$ could be a consequence of the puckering in the former. A puckered geometry might give an easier opening for another ligand to approach the metal and trigger the reaction. The present study points to the existence of a structure−reactivity relationship according to the inference obtained from the results on the model W complexes investigated here. Though the observation of puckered structures might seem to contradict the X-ray structures for complexes such as $[(Me_3SiCH_2)_2W(\mu\text{-}CSiMe_3)]_2$, it may be possible to observe the puckering distinctively from diffraction experiments at sufficiently low temperatures. Thus the ab initio and density functional theoretical studies provide a complementary approach for structural studies when traditional experimental methods are not feasible.

The comparison between the cyclobutadiene dication and **1** extends beyond the π-system. The major cause

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[23] The model $[TaH_2(\mu\text{-}CH)]_2$ complex with D_{2h} symmetry was optimized fully at the B3LYP/LANL2DZ level, and a frequency analysis showed it to be a minimum. The corresponding total energy is −195.332 59 au.

Table 4. Wiberg Bond Indices of Structures 1–11 at the HF Level

molecule: no., sym	W(1)–W(2)	C(3)–C(4)	W(1)–C(3)	W(1)–C(4)	W(2)–C(3)	W(2)–C(4)	W(1)–L(5)	W(1)–L(6)	C(3)–R(9)
1, D_{2h}	0.972	0.056	1.299	1.299	1.299	1.299	0.750	0.750	0.949
2, C_{2v}	0.996	0.048	1.306	1.306	1.306	1.306	0.773	0.718	0.950
3, D_{2h}	0.972	0.033	1.308	1.308	1.308	1.308	0.751	0.751	0.818
4, C_{2v}	1.017	0.034	1.290	1.290	1.290	1.290	0.784	0.714	0.838
5, C_s	0.987	0.044	1.249	1.293	1.293	1.249	0.737	0.737	1.067
6, C_2	1.017	0.042	1.264	1.264	1.264	1.264	0.760	0.706	1.075
7, C_{2h}	0.854	0.064	1.289	1.289	1.289	1.289	0.742	0.742	0.951
8, C_2	0.867	0.058	1.297	1.297	1.297	1.297	0.762	0.710	0.951
9, D_{2h}	0.786	0.051	1.337	1.337	1.337	1.337	0.589	0.589	0.948
10, C_{2v}	0.796	0.051	1.338	1.338	1.338	1.338	0.589	0.583	0.948
11, D_{2h}	0.682	0.056	1.290	1.290	1.290	1.290	0.720	0.720	0.953

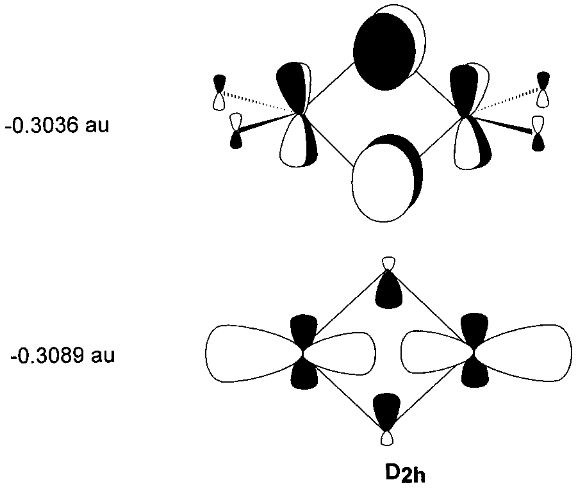

Figure 3. HOMO and HOMO-1 of $[W(OH)_2(\mu$-$CH)]_2$ in D_{2h} symmetry.

for the nonplanarity of cyclobutadiene dication is the release of antibonding (1,3) σ-interactions. In the tungsten complexes the (1,3) M–M interaction is bonding. This is enhanced by puckering. The (1,2) M–C interaction present in the HOMO is antibonding. Puckering decreases this antibonding interaction. The planarity of the $[WF_2(\mu$-$CH)]_2$ complex, **9**, is reminiscent of the observation of cyclobutadiene dication becoming planar on perfluorination. The preference for lower symmetry even while higher symmetry is possible has been known in other organotungsten compounds also. For example, a reduced symmetry has been observed recently for a d^0 homoleptic tungsten compound at low temperature;[24] WMe_6 has C_{3v} symmetry instead of the expected D_{3h}.

Conclusions

The present study shows that the puckering of the W_2C_2 ring in the $[WL_2(\mu$-$CR)]_2$ systems is a function of the ligands connected to the metal centers. Thus the electron-withdrawing ligands along with their π-donor character tend to make the four-membered ring planar while σ-electron donating ligands preferentially make the ring nonplanar. The calculated nonplanar structures contradict the general perception from the X-ray studies that $[WL_2(\mu$-$CR)]_2$ complexes are always planar. The preference for lower symmetry is analogous to those observed in the cyclobutadiene dication. The observed puckering is expected to be very significant in the investigation of reactivity and mechanisms involving these complexes.

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Supporting Information Available: A table of the Hartree–Fock geometries of structures **1**–**11** (1 page). Ordering information is given on any current masthead page.

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