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Bent *vs.* linear metal alkylidynes. An electronic reason for bending the W≡C–H angle in tungsten alkylidynes

Karl Anker Jørgensen

Department of Chemistry, Aarhus University, DK-8000 Aarhus C (Denmark)

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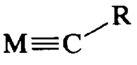
Abstract

The electronic structure of the alkylidyne group in tungsten alkylidynes has been investigated. On the basis of the shape and symmetry of the frontier orbitals of tungsten alkylidyne complexes with a W≡C–H fragment it is argued that the W≡C–H angle is slightly bent, in agreement with the published structures of these complexes. The frontier orbitals of the tungsten alkylidyne complexes are discussed, and it is proposed that the bending of the W≡C–H fragment is due to electronic rather than steric factors. The electronic spectra of the tungsten alkylidyne complexes are discussed. The structure of similar M≡C–R fragments in transition-metal alkylidyne complexes is briefly discussed.

Key words: Tungsten; Alkylidyne; Electronic

1. Introduction

Transition-metal alkylidyne (or carbyne) complexes have been extensively studied because of their chemical properties [1]. The structures of these complexes have also been the subject of numerous studies [2]. In many of these structural studies attention has been focused on the structure of the alkylidyne group, **1** [2].



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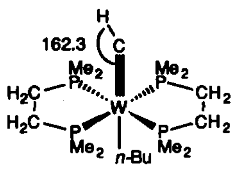
The angle in the M≡C–R fragment, where R ≠ H, in the transition-metal alkylidynes is found to be in the range 171°–180° [2], except for W(≡CPh)I(CO)$_4$, in which the angle is 162° [3]. This slight bending of the alkylidyne moiety has been attributed to steric and crystal packing effects [4], and to asymmetric π-bonding between the metal centre and the carbon atom [5]. Recently, Hopkins *et al.* have determined two structures of tungsten alkylidyne complexes with R = H, and these show a significant bending of the W≡C–H fragment [6]. One of these structures is shown in **2** [6].

Previously, a very similar bending of the W≡C–H fragment has been found in a related tungsten complex, but in this complex the carbon- and tungsten atoms of the W≡C–H fragment were coordinated to a (CH$_3$)$_2$AlCl molecule, as shown in **3** [7].



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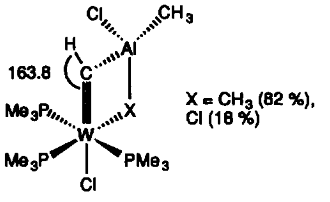

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The W≡C–H bond angle for the three alkylidyne complexes which have been characterized varies between 162.3° and 164.4° [6,7]. The bending of the W≡C–H fragment in these complexes is more pronounced than the observed bending in the similar alkyl- or aryl substituted ones. In the tungsten alkylidyne complexes with a hydrogen atom then bending is probably not due to steric or crystal packing effects in view of the hydrogen atom being smaller than alkyl- and aryl substituents.

We discuss below the structure of the W≡C–H fragment of tungsten alkylidyne complexes. The electronic

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Correspondence to: Professor K.A. Jørgensen.

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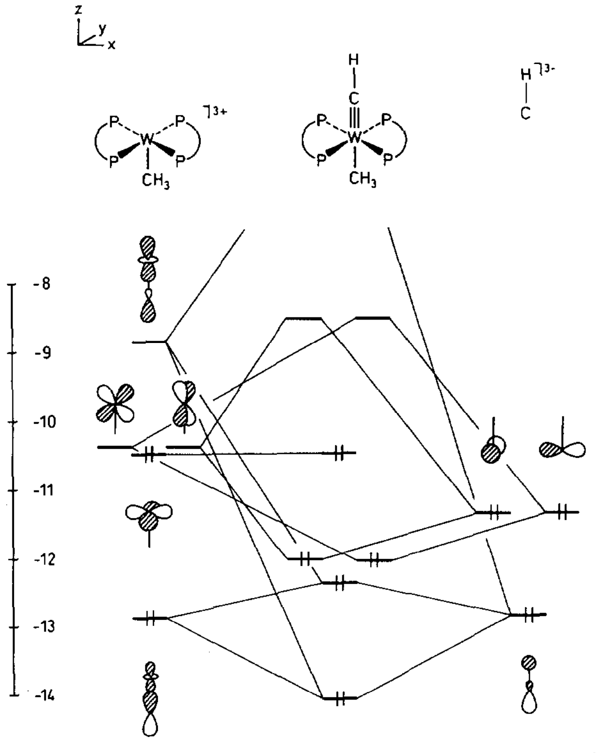


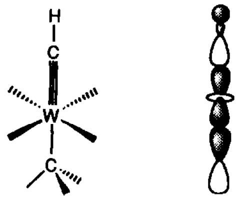
Fig. 1. Interaction diagram for the interaction of $[W(Me)(dmpe)_2]^{3+}$ to the left with HC^{3-} to the right.

structure of the W≡C–H fragment in complex **2** is discussed, and it will be argued that bending of the W≡C–H fragment is probably not due to steric and crystal-packing effects, but rather to electronic effects. The electronic structure of transition-metal alkylidyne complexes has, to the best of our knowledge, not been investigated theoretically in relation to geometrical changes in the alkylidyne part of these systems. The calculations were by the Extended Hückel method [8]. Although this method is considered "old-fashioned", it can still give important insights into the electronic structure of transition-metal complexes thus allowing a better understanding of the geometrical structure of these systems.

2. Results and discussion

The tungsten-alkylidyne complex, **2**, is first considered. The linear W≡C–H complex can be considered as being formed by interaction of a $[W(n\text{-}Bu)(dmpe)_2]^{3+}$ fragment with an alkylidyne, HC^{3-}, fragment. The axial butyl ligand is replaced by a methyl ligand in the calculations. An interaction diagram for the interaction of $[W(Me)(dmpe)_2]^{3+}$ with HC^{3-} is outlined in Fig. 1.

The frontier orbitals of the $[W(Me)(dmpe)_2]^{3+}$ fragment are shown to the left of Fig. 1. The HOMO is located on the tungsten atom as a $d_{x^2-y^2}$ orbital and found at −10.48 eV. The LUMO is a degenerate set of orbitals, d_{xz} and d_{yz}, at −10.40 eV. The antibonding combination of the tungsten d_{z^2} orbital and carbon p_z orbital at the methyl group is found at −8.68 eV. The largest contribution to this orbital emerges from the tungsten d_{z^2} orbital. The bonding combination of the tungsten d_{z^2} orbital and carbon p_z orbital is found at −12.82 eV, to which the carbon p_z orbital makes the largest contribution. Three frontier orbitals of the HC^{3-} fragment are outlined to the right of Fig. 1. The HOMO is a degenerate set of the carbon p_x and p_y orbitals, located at −11.40 eV. At −12.58 eV an orbital, mainly located on the carbon atom of z-character is found, mixed in with the hydrogen s orbital; this orbital can be considered as the σ_{C-H} orbital. The result of the interaction is shown in the middle of the interaction diagram in Fig. 1. The carbon p_x and p_y orbitals of the HC^{3-} fragment interact with the tungsten d_{xz} and d_{yz} orbitals giving the expected bonding and antibonding combinations, the latter being the LUMO of the resulting tungsten alkylidyne complex. The tungsten $d_{x^2-y^2}$ orbital remains untouched by this interaction, thus giving the HOMO of a linear $HC{\equiv}W(Me)(dmpe)_2$ complex. The interesting feature of the interaction of $[W(Me)(dmpe)_2]^{3+}$ with HC^{3-} is that between the bonding combination of the tungsten d_{z^2} orbital and the carbon p_z orbital of the $[W(Me)(dmpe)_2]^{3+}$ fragment and the σ_{C-H} orbital of the HC^{3-} fragment. This is a two orbital four electron interaction resulting in occupied bonding and antibonding combinations. The antibonding tungsten-carbon (alkylidyne) orbital resulting from this interaction is schematically depicted in **4**.



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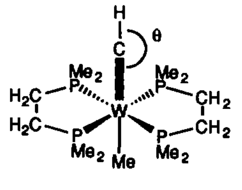
The more the tungsten d_{z^2} orbital and the axial ligand p_z orbital mix, the more important becomes the latter interaction with the alkylidyne fragment since the metal d_{z^2} orbital contribution is found in the resulting occupied orbital of the metal fragment, which is the one involved in the two orbital four electron interaction with the alkylidyne ligand. It should also be noted that the antibonding combination of the tungsten d_{z^2} orbital and the carbon p_z orbital, the third LUMO of the $[W(Me)(dmpe)_2]^{3+}$ complex, is also involved in the latter interaction.

Bending the hydrogen atom from the linear position (W≡C–H bending angle is 163°) as shown in **5** can



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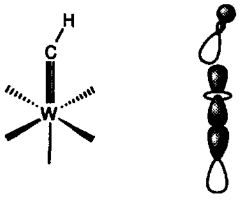

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compensate for this unfavourable occupation of the antibonding $\sigma^*_{\text{W-C}}$ orbital, thus destabilizing the system. But it is a narrow balance, because bending the system also results in weaker $\sigma_{\text{W-C}}$ and $\pi_{\text{W-C}}$ bonds to the alkylidyne. The tungsten-alkylidyne σ-type bonding for a bent W≡C–H complex is schematically outlined in **6**.

In Fig. 2 are shown contour plots of the antibonding $\sigma^*_{\text{W-C}}$ orbital for the HC≡W(Me)(dmpe)$_2$ complex. The linear (Fig. 2a) and the bent (Fig. 2b) W≡C–H extremes are shown. The orbital change leading to the reduced antibonding $\sigma^*_{\text{W-C}}$ orbital character upon going from the linear to the bent form of the W≡C–H fragment is easily seen in Fig. 2.

If the W≡C–H angle is reduced from 180.0° to 162.3°, small orbital overlap population changes are observed for the σ bond between the carbon atom in the alkylidyne fragment and the tungsten atom. The W≡C overlap population for the linear HC≡W(Me)(dmpe)$_2$ complex is calculated to be 0.7520, while that calculated for the bent complex is 0.7715. The increase in the σ orbital overlap population upon going from the linear to the bent form of HC≡W(Me)(dmpe)$_2$ can be attributed to a reduction of the $\sigma^*_{\text{W-C}}$ orbital population.

The frontier orbitals of the linear HC≡W(Me)(dmpe)$_2$ complex provides also a description of the frontier orbitals of a closely related complex. The electronic spectra of the PhC≡W(Br)(dmpe)$_2$ complex have been studied, and it was concluded that the HOMO of this complex is a nonbonding tungsten $d_{x^2-y^2}$ orbital, while the LUMO is a $\pi^*_{\text{C≡W}}$ orbital [9]. This assignment of the frontier orbitals is similar to that obtained by extended Hückel calculations for the linear HC≡W(Me)(dmpe)$_2$ complex. The contributions from the tungsten and the carbon atoms in the LUMO are 56% and 44%, respectively; these numbers are said to be important and unresolved [9].

On the basis of the electronic structure of the [W(Me)(dmpe)$_2$]$^{3+}$ shown to the left in Fig. 1 one might be able to make some tentative predictions about the influence of the axial ligands, *trans* to the alkylidyne ligand, which is suggested to influence the transition-metal–alkylidyne bond angle. Ligands with a high lying HOMO of σ symmetry will interact with the transition-metal d_{z^2} orbital to form the bonding and antibonding $\sigma_{\text{M-C}}$ and $\sigma^*_{\text{M-C}}$ orbitals, respectively. Those ligands possessing a high HOMO energy will interact more strongly with the transition-metal d_{z^2} orbital than those with a low lying HOMO energy, owing to the energy difference. The former ligands

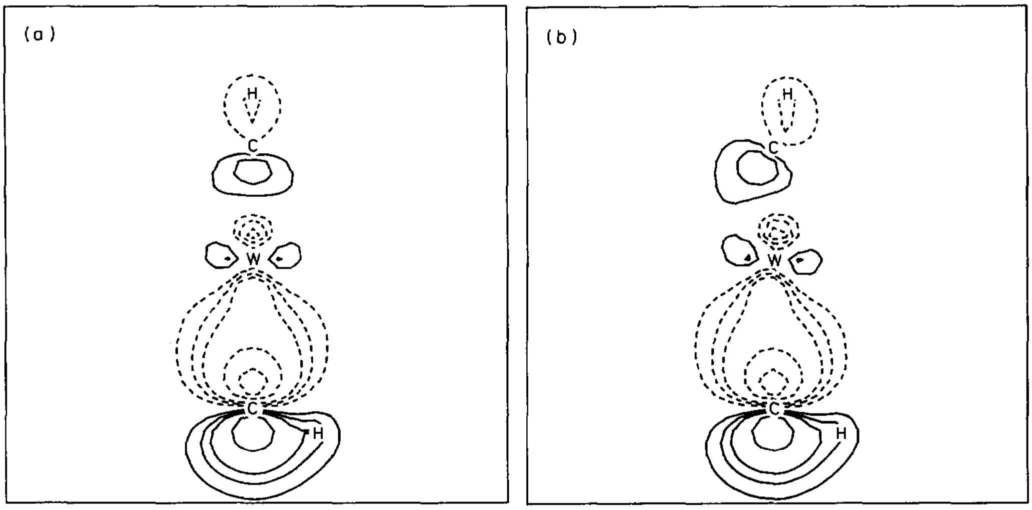

Fig. 2. Contour plots of the antibonding $\sigma^*_{\text{W-C}}$ orbital for the HC≡W(Me)(dmpe)$_2$ complex with a linear (a) and a bent (b) W≡C–H fragment. The contours Ψ are: 0.04, 0.07, 0.10, 0.20 and 0.30.

TABLE 1. Atomic parameters

Atom	Orbital	H_{ii}, eV	ζ_1	ζ_2	c_1 [a]	c_2 [a]
W	6s	−8.26	2.341			
	6p	−5.17	2.309			
	5d	−10.57	4.9820	2.0680	0.66853	0.54244
P	2s	−18.60	1.60			
	2p	−14.00	1.60			
C	2s	−21.40	1.625			
	2p	−11.40	1.625			
H	1s	−13.60	1.300			

[a] Coefficients used in a double-zeta expansion of the metal d orbitals.

thus give a better mixing of the d_{z^2} and p_z orbitals. If the bonding combination of this interaction has an orbital energy similar to that of the alkylidyne orbital it is interacting with there can be an interaction similar to that outlined in Fig. 1, and therefore a bending of the alkylidyne ligand may take place. In other words "soft ligand" *trans* to the alkylidyne ligand would be expected to cause more bending of the M≡C–R fragment, than "hard ligands" *trans* to the alkylidyne ligand. To the author's knowledge no systematic study of the change in the bond angle of the M≡C–R fragment as a function of different axial ligands has been carried out.

3. Calculations

The extended Hückel molecular method [8] was used throughout. The bond distances and angles in the HC≡W(Me)(dmpe)$_2$ complex are in accordance with literature data [6b], with an axial methyl ligand replacing the butyl ligand. Atomic parameters are listed in Table 1.

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