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An investigation into the relative influence of alkoxide and thiolate ligands on the metal–carbon triple bond in $X_3M{\equiv}CH$ compounds, where $M = Cr$, Mo and W and $X = OH$, SH, OCH_3, SCH_3, OCF_3 and SCF_3 from electronic structure calculations☆

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Abstract

Electronic structure calculations using density functional theory with the aid of the GAUSSIAN-98 package have been employed on the model Group 6 metal alkylidyne complexes $X_3M{\equiv}CH$, where $M = Cr$, Mo and W and $X = OH$, SH, OCH_3, SCH_3, OCF_3 and SCF_3. Collectively, these calculations reveal that the relative energies of the metal–carbon π-bonding molecular orbitals are greatly influenced by the metal and the ancillary ligand X. In comparing the bonding in related O and S containing molecules, the effect of oxygen is to increase the relative energy of the M–C π bond by approximately 1 eV as a result of M–O π antibonding interactions. In contrast, the ligand-based lone-pair orbitals lie higher in energy for sulfur and for the series where $X = SH$, SCH_3 and SCF_3, the HOMO is a sulfur lone-pair combination of a_2 symmetry in the C_{3v} point group. The relative influence of H, CH_3 and CF_3 within each series is as expected based on their electron releasing properties. A comparison is made with related compounds having metal to metal or metal to nitrogen triple bonds.

Keywords: Tungsten alkylidyne; Molybdenum alkylidyne; Electronic structure; Frontier molecular orbitals; Alkoxide; Thiolate

1. Introduction

In previous studies, the influence of replacing alkoxide ligands by thiolate ligands in $X_3M{\equiv}MX_3$ ($M =$ Mo, W) [1] and in $X_3Mo{\equiv}N$ compounds [2] has been examined. A natural extension of this work is presented here to include a study of the relative influence of alkoxide and thiolate ligands on compounds having metal–carbon triple bonds. Compounds of the form $X_3M{\equiv}CR$ are known for $M =$ Mo and W where X is an alkoxide or thiolate ligand [3]. $W({\equiv}C^tBu)(O^tBu)_3$ metathesizes a variety of alkynes, while the molybdenum analogue reacts only slowly with RC≡CR' complexes, but reacts rapidly with terminal alkynes. The thiolate complexes, $M({\equiv}C^tBu)(S^tBu)_3$ ($M =$ Mo, W), do not react with 3-heptyne and readily decompose via S–C bond cleavage. $M({\equiv}C^tBu)(SAr)_3$ are also inactive towards alkyne metathesis [4]. At this time no related $X_3Cr{\equiv}CR$ compounds are known.

Peter Hofmann has previously considered the general situation wherein a d^4-ML_3^- fragment interacts with a CR^+ fragment to form a M–C triple bond [5]. The highest occupied molecular orbitals are found to be the M–C π-bonding orbitals, followed by the M–C σ bonding orbital. The lowest unoccupied orbitals are primarily metal $d_{xy}/d_{x^2-y^2}$ in character.

Furthermore, Frenking and coworker have considered various $X_3W{\equiv}CR$ compounds ($X = F$, Cl, OH; $R = H$, CH_3, F, NH_2) as part of a computational study of Fischer and Schrock carbynes [6]. Their results show that Schrock carbynes have stronger W-carbyne bonds

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☆ In celebration of Polyhedron's 21st birthday.

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and that CR substituents have a large effect on the W–C bond strength for both classes of carbynes.

These studies form the background to the present work which aims to elucidate the influence of M = Cr, Mo and W and X = OH, SH, OCH_3, SCH_3, OCF_3 and SCF_3 on the nature of the electronic structure of the metal–carbon triply bonded compounds.

2. Results and discussion

Table 1 gives selected bond lengths and angles for the $M(\equiv CH)X_3$ molecules. The crystal structures of relatively few alkylidyne complexes of the form $M(\equiv CH)X_3$ have been determined. $W(CPh)(O^tBu)_3$ has an average W–O bond length of 1.865(4) Å and a W–C bond length of 1.758(5) Å [7]. The W–O–C bond angles were found to range from 139° to 143°, the W≡C–C bond angle was determined to be 175.8(4)° and the C≡W–O angles were found to be 108(1)°. Similar structural parameters were found for $[(^tBuO)_3W(CMe)]_2$ in which the W–C distance is 1.759(6) Å, the average W–O–C angle 137.8(6)°, the W≡C–C angle 179.8(6)° and the average C≡W–O angle 102.1(3)° [8]. The calculated W alkylidynes with alkoxide groups are in reasonable agreement with a W–C distance of 1.75 Å for X = OH and OCH_3 and W–O distances of 1.90 Å and 1.89 Å for X = OH and OCH_3, respectively. The calculated W–O–H bond angle in $W(\equiv CH)(OH)_3$ is only 121.1°, which is more than 10° less than the observed values for the alkoxides. However, substitution for X = OCH_3 gives a W–O–C angle of 136.6° which is in good agreement with the experimental value.

For a given metal and substituent on E, the calculated M–E–H and M–E–C angles are larger for E = O than E = S. This difference in angles about oxygen and sulfur is observed experimentally for many different alkoxide and thiolate complexes [9].

2.1. $(HO)_3M\equiv CH$ molecules, where M = Mo, Cr and W

As a starting point, the calculated frontier molecular orbitals for the series $(HO)_3M\equiv CH$, where M = Cr, Mo and W, are compared to reveal the influence of the metal. As shown in Fig. 1, the relative ordering of the

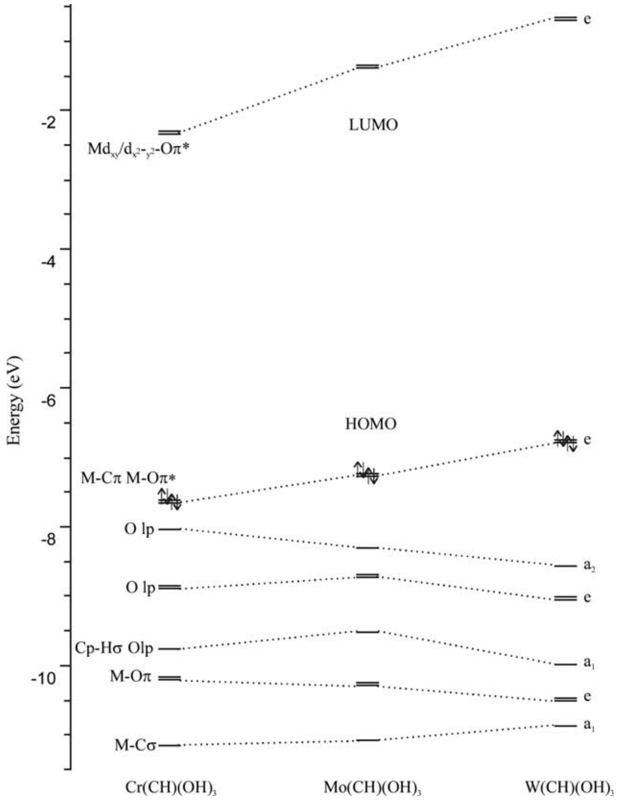


Fig. 1. Orbital energy level diagram for $M(\equiv CH)(OH)_3$, where M = Cr, Mo and W.

Table 1
Calculated structural parameters (Å and °) for the $M(\equiv CH)X_3$ model compounds

	M–C	C–H	M–E	E–C	M–C–H	M–E–C/H	E–M–E	C–M–E
$Cr(CH)(OH)_3$	1.60	1.09	1.76	N/A	180.0	119.0	112.4	106.3
$Cr(CH)(SH)_3$	1.59	1.09	2.19	N/A	180.0	104.9	115.2	102.8
$Mo(CH)(OH)_3$	1.73	1.09	1.91	N/A	180.0	120.0	113.4	105.2
$Mo(CH)(SH)_3$	1.72	1.09	2.35	N/A	180.0	103.8	115.4	102.5
$W(CH)(OH)_3$	1.75	1.09	1.90	N/A	180.0	121.1	112.3	106.4
$W(CH)(SH)_3$	1.74	1.09	2.35	N/A	180.0	103.4	114.5	103.7
$Mo(CH)(OCH_3)_3$	1.74	1.09	1.90	1.41	180.0	135.2	113.8	104.7
$Mo(CH)(SCH_3)_3$	1.73	1.09	2.33	1.84	180.0	113.4	115.4	102.6
$W(CH)(OCH_3)_3$	1.75	1.09	1.89	1.42	180.0	136.6	112.5	106.2
$W(CH)(SCH_3)_3$	1.75	1.09	2.33	1.84	180.0	112.9	114.3	104.0
$Mo(CH)(OCF_3)_3$	1.72	1.09	1.93	1.35	180.0	130.5	114.7	103.5
$Mo(CH)(SCF_3)_3$	1.72	1.09	2.34	1.83	180.0	109.0	116.4	101.2
$W(CH)(OCF_3)_3$	1.74	1.09	1.92	1.36	180.0	132.7	113.3	105.3
$W(CH)(SCF_3)_3$	1.74	1.09	2.34	1.84	180.0	109.2	115.4	102.6

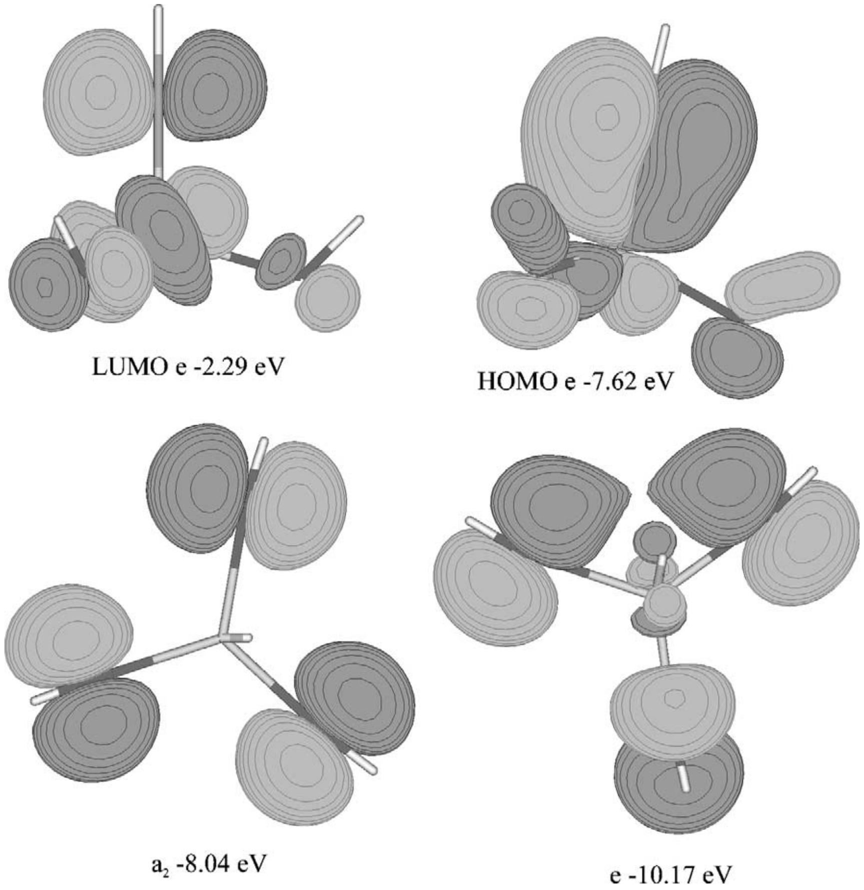
Table 2
Frontier molecular orbitals for M(≡CH)(EH)$_3$ (M = Cr, Mo, W; E = O, S)

	Sym	Energy (eV)	Description
Cr(CH)(OH)$_3$			
LUMO	e	−2.29	Md$_{xy}$/d$_{x^2-y^2}$–Oπ* Cp$_x$/p$_y$
HOMO	e	−7.62	M–Cπ M–Oπ*
	a$_2$	−8.04	Olp
	e	−8.86	Olp
	a$_1$	−9.76	Cp–Hσ Olp
	e	−10.17	M–Oπ
	a$_1$	−11.16	M–Cσ (some Olp)
Cr(CH)(SH)$_3$			
LUMO	e	−3.22	Md$_{xy}$/d$_{x^2-y^2}$–Sπ* Cp$_x$/p$_y$
HOMO	a$_2$	−6.80	Slp
E	e	−7.69	Slp
	e	−8.30	M–Cπ M–Sπ*
	e	−8.81	M–Sπ
	a$_1$	−8.89	Slp
	a$_1$	−11.33	M–Cσ
Mo(CH)(OH)$_3$			
LUMO	e	−1.35	Md$_{xy}$/d$_{x^2-y^2}$–Oπ* Cp$_x$/p$_y$
HOMO	e	−7.24	M–Cπ M–Oπ*
	a$_2$	−8.30	Olp
	e	−8.68	Olp
	a$_1$	−9.52	Cp–Hσ Olp
	e	−10.24	M–Oπ
	a$_1$	−11.07	M–Cσ (some Olp)
Mo(CH)(SH)$_3$			
LUMO	e	−2.77	Md$_{xy}$/d$_{x^2-y^2}$–Sπ* Cp$_x$/p$_y$
HOMO	a$_2$	−6.95	Slp
	e	−7.74	Slp
	e	−8.03	M–Cπ M–Sπ*
	a$_1$	−8.93	Slp
	e	−9.00	M–Sπ
	a$_1$	−11.40	M–Cσ
W(CH)(OH)$_3$			
LUMO	e	−0.67	Md$_{xy}$/d$_{x^2-y^2}$–Oπ* Cp$_x$/p$_y$
HOMO	e	−6.75	M–Cπ M–Oπ*
	a$_2$	−8.57	Olp
	e	−9.01	Olp
	a$_1$	−9.98	Cp–Hσ Olp
	e	−10.47	M–Oπ
	a$_1$	−10.88	M–Cσ (some Olp)
W(CH)(SH)$_3$			
LUMO	e	−2.37	Md$_{xy}$/d$_{x^2-y^2}$–Sπ* Cp$_x$/p$_y$
HOMO	a$_2$	−7.04	Slp
	e	−7.67	M–Cπ M–Sπ*
	e	−7.92	Slp
	e	−9.05	M–Sπ
	a$_1$	−9.33	Slp
	a$_1$	−11.27	M–Cσ

Table 3
Frontier molecular orbitals for W(≡CH)(ECH$_3$)$_3$ and W(≡CH)(ECF$_3$)$_3$

	Sym	Energy (eV)	Description
W(CH)(OCH$_3$)$_3$			
LUMO	e	−0.28	Md$_{xy}$/d$_{x^2-y^2}$–Oπ* Cp$_x$/p$_y$
HOMO	e	−6.36	M–Cπ M–Oπ*
	a$_2$	−7.52	Olp Cp–Hsσ
	e	−7.79	Olp Cp–Hsσ
	a$_1$	−8.48	Cp–Hσ Olp Cp–Hsσ
	e	−9.08	M–Oπ Cp–Hsσ
	a$_1$	−10.43	M–Cσ (some Olp)
W(CH)(SCH$_3$)$_3$			
LUMO	e	−1.79	Md$_{xy}$/d$_{x^2-y^2}$–Sπ* Cp$_x$/p$_y$
HOMO	a$_2$	−6.25	Slp
	e	−6.94	M–Cπ M–Sπ* Slp
	e	−7.23	M–Cπ M–Sπ* Slp
	e	−8.20	M–Sπ (some C–Hσ)
	a$_1$	−8.25	Slp C–Hσ
	e	−10.44	Md–Spσ Sp–Cpσ
	a$_1$	−10.44	Cp–Hsσ Sp–Cpσ Cp–Hsσ
	a$_1$	−11.01	M–Cσ (S–Cσ C–Hσ)
W(CH)(OCF$_3$)$_3$			
LUMO	e	−2.46	Md$_{xy}$/d$_{x^2-y^2}$–Oπ* Cp$_x$/p$_y$
HOMO	e	−8.23	M–Cπ M–Oπ* (Op–Cpσ)
	a$_2$	−10.16	Olp Flp
	e	−10.35	Olp Flp
	a$_1$	−10.85	Cp–Hσ Olp F lp
	e	−11.32	M–Oπ Flp
	a$_2$	−11.42	Flp
	e	−11.43	Flp
	a$_1$	−12.01	M–Cσ (some Olp)
W(CH)(SCF$_3$)$_3$			
LUMO	e	−2.98	Md$_{xy}$/d$_{x^2-y^2}$–Sπ* Cp$_x$/p$_y$
HOMO	a$_2$	−7.70	Slp (Flp)
	e	−8.30	M–Cπ M–Sπ* (S–Cσ)
	e	−8.44	Slp (Flp)
	e	−9.59	M–Sπ (Flp)
	a$_1$	−9.65	Slp Flp
	e	−10.86	Wd–Spσ Sp–Cpσ Flp
	a$_1$	−10.95	Sp–Cpσ Flp
	a$_2$	−11.48	Flp
	e	−11.49	Flp
	a$_1$	−11.97	M–Cσ (Flp)

frontier molecular orbitals is the same, although there are variations in the orbital energies. Table 2 lists the frontier molecular orbitals with their energies, principal orbital character and symmetry labels. The HOMO is the metal–carbon π-bonding orbital with an admixture of metal–oxygen π* character. The HOMO −2 and HOMO −3/−4 are, in all cases, oxygen lone-pair combinations of a$_2$ and e symmetry in the C$_{3v}$ point group. Of note within the series for M = Cr, Mo and W are the relative stabilities of these two orbital sets. In going from W to Mo to Cr, the a$_2$ orbital increases in energy, while the HOMO decreases in energy. The destabilization of the W–C π bond in descending Group 6, Cr → Mo → W, arises as a result of the admixing of M–O π* interactions which are greater for the heavier atoms. Conversely, the a$_2$ orbital for M = Cr is notably higher in energy as a result of increased lone-pair lone-



LUMO e -2.29 eV

HOMO e -7.62 eV

a_2 -8.04 eV

e -10.17 eV

Fig. 2. Selected orbital plots for Cr(≡CH)$(OH)_3$.

pair repulsions. The LUMO is in all cases an orbital of e symmetry which has significant metal $d_{xy}/d_{x^2-y^2}$ character with metal–oxygen π* interactions. The LUMO is also destabilized by the M–O π* interactions which are greatest for W and least for Cr.

A consideration of the orbital energies shown in Fig. 1 leads to the expectation that the chromium compound would be the easiest to reduce and the tungsten compound the easiest to oxidize. The HOMO–LUMO gap is predicted to be 5 eV or greater for all compounds and the polarity of the M–C bond varies slightly down the series based on the Mulliken charges of Cr +0.81 and C −0.19 and W +1.19 and C −0.36.

Selected representations of the frontier molecular orbitals for $(HO)_3Cr{\equiv}CH$ are given in Fig. 2.

The M≡C bond dissociation energies were calculated to be 57 kcal mol^{-1} for Cr, 122 kcal mol^{-1} for Mo and 147 kcal mol^{-1} for W. These values are calculated from the difference in energy of the alkylidyne complex and the fragments CH and $M(OH)_3$. The heats of vaporization for chromium, molybdenum and tungsten metals are 82, 141 and 197 kcal mol^{-1} [10]. The similarities between these energies and the bond dissociation energies indicate that the orbital extension of the metal has a dramatic influence on the M≡C bond strength.

2.2. $(HE)_3W{\equiv}CH$ compounds, where $E = O$ and S

We start our comparison of alkoxide and thiolate ligands by examining the hypothetical $(HE)_3W{\equiv}CH$ molecules, where $E = O$ and S. A comparison of the relative energies of the frontier molecular orbitals is shown in Fig. 3. The ordering of the frontier molecular orbitals of similar character and their energies are markedly different for the OH and SH complexes. In replacing OH by SH, the M–C π bonding molecular orbitals are stabilized by approximately 1 eV as a result of weaker M–S π* mixing. For the $(HS)_3W{\equiv}CH$ molecule, the HOMO is the a_2 orbital of sulfur lone-pair character and the related e sulfur lone–pair is close in energy to the M–C π-bonding molecular orbital. The M–E π-bonding molecular orbital is also higher in energy by approximately 1.5 eV in the SH complex. This destabilization is due to a combination of the differences in electronegativity between oxygen and sulfur and the relative degree of π-bonding to the metal. The LUMO,

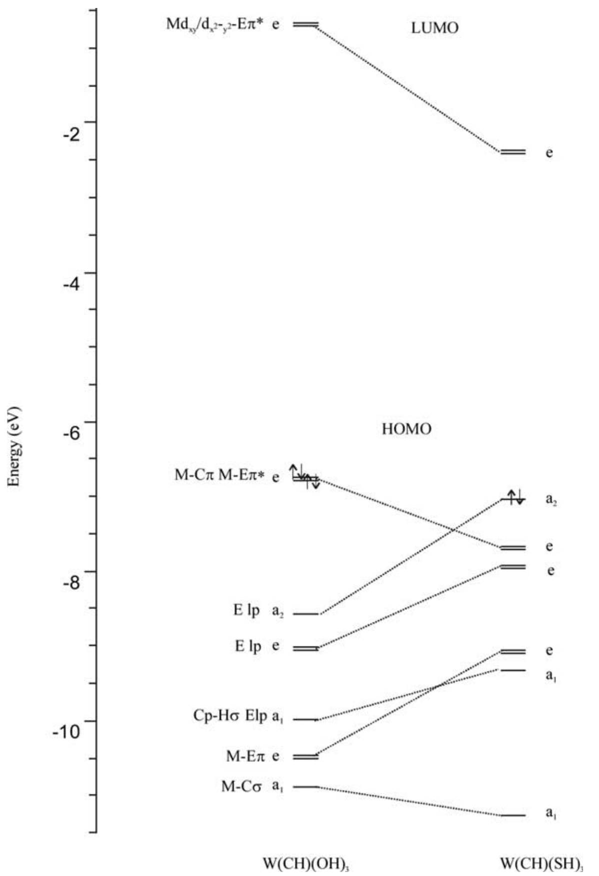


Fig. 3. Orbital energy level diagram for $W(\equiv CH)(EH)_3$, where E = O and S.

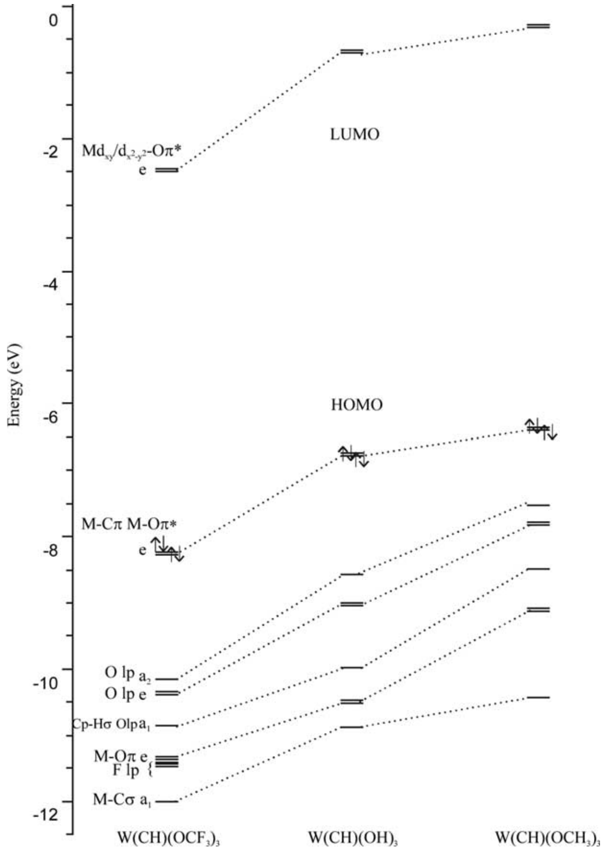


Fig. 4. Orbital energy level diagram for $W(\equiv CH)(OCF_3)_3$, $W(\equiv CH)(OH)_3$ and $W(\equiv CH)(OCH_3)_3$.

which is metal $d_{xy}/d_{x^2-y^2}$ with M–E π* character, is also notably lower in energy in the case of the thiolate leading to a smaller HOMO–LUMO gap.

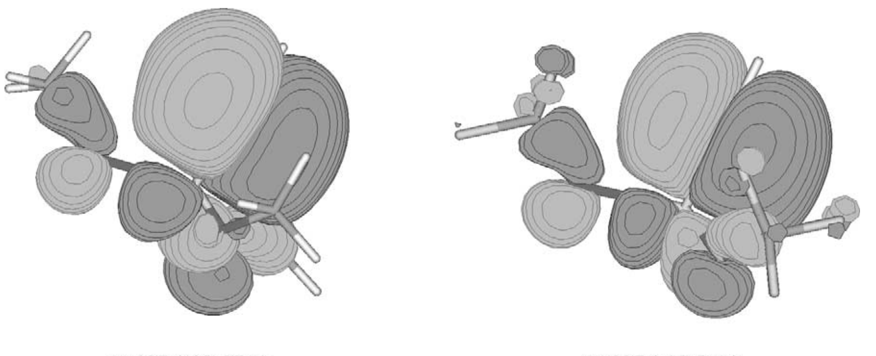
A comparison of the bonding in the compounds $(HE)_3Mo\equiv CH$ and $(HE)_3Cr\equiv CH$ is very similar to the comparison of $(HE)_3W\equiv CH$, although the e sulfur lone-pair molecular orbitals are higher in energy than the M–C π-bonding molecular orbitals in the case of molybdenum and chromium. The lower energy M–O π and primarily S lone-pair orbitals of e and a_1 symmetry are also switched in $(HE)_3M\equiv CH$ for molybdenum compared to tungsten.

2.3. *The influence of methyl and trifluoromethyl substituents*

The calculated orbital energies for the $W(\equiv CH)(ECH_3)_3$ and $W(\equiv CH)(ECF_3)_3$ molecules are given in Table 3. In replacing the EH group by ECH_3 or ECF_3, we observe two significant changes. The first change is that the relative energies of the frontier molecular orbitals reflect the expected electronic influence of the electron donating CH_3 group and the electron withdrawing CF_3 group as is shown in Fig. 4, for the series of compounds $X_3W\equiv CH$, where X = OH, OCH_3 and OCF_3. Namely, the OCH_3 group destabilizes the frontier molecule orbitals, while the OCF_3 group stabilizes the orbitals relative to the OH group. The second difference is that there is now greater mixing of orbitals having the same symmetry. For example, fluorine lone-pairs having a_2 or e symmetry mix with the oxygen lone-pair combinations. In addition, for $(CH_3S)_3W\equiv CH$ there is mixing between the sulfur lone-pair and the metal–carbon π-bonding orbitals that transform as e. This not withstanding, the HOMO for $(CH_3O)_3W\equiv CH$ and $(CF_3O)_3W\equiv CH$ are M–C π bonds, while for the sulfur complexes the HOMO is a sulfur lone-pair combination. Selected representations of these frontier molecular orbitals are given in Figs. 5 and 6.

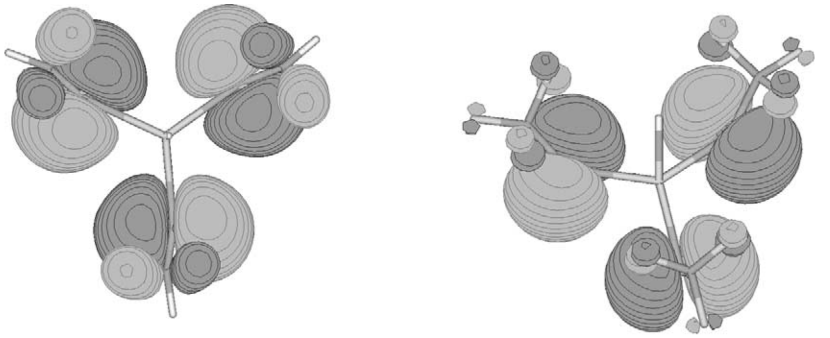
The substituents have little effect on the Mulliken charges on the tungsten atoms with values of 1.19, 1.27 and 1.27 for the OH, OCH_3 and OCF_3 complexes, respectively. A comparison of Mulliken charges on the elements is shown in Table 4.

The calculated orbital energies for the $Mo(\equiv CH)(ECH_3)_3$ and $Mo(\equiv CH)(ECF_3)_3$ complexes are given in Table 5, where it can be seen that the trends described for M = W are also found for M = Mo.



$W(CH)(OCH_3)_3$ $W(CH)(OCF_3)_3$

Fig. 5. Orbital plots of the HOMOs for $W(\equiv CH)(OCH_3)_3$ and $W(\equiv CH)(OCF_3)_3$.



$W(CH)(SCH_3)_3$ $W(CH)(SCF_3)_3$

Fig. 6. Orbital plots of the HOMOs for $W(\equiv CH)(SCH_3)_3$ and $W(\equiv CH)(SCF_3)_3$.

Table 4
Mulliken charges for $M(CH)(EH)_3$, $M(CH)(ECH_3)_3$ and $M(CH)(ECF_3)_3$

	$Cr(CH)(OH)_3$	$Cr(CH)(SH)_3$	$W(CH)(OH)_3$	$W(CH)(SH)_3$
C	−0.19	−0.11		
H	0.18	0.19		
M	0.81	0.23		
E	−0.70	−0.22		
H	0.44	0.12		
	$Mo(CH)(OH)_3$	$Mo(CH)(SH)_3$		
C	−0.32	−0.18	−0.36	−0.21
H	0.16	0.18	0.15	0.17
M	1.13	0.33	1.19	0.27
E	−0.76	−0.25	−0.77	−0.22
H	0.44	0.13	0.45	0.14
	$Mo(CH)(OCH_3)_3$	$Mo(CH)(SCH_3)_3$	$W(CH)(OCH_3)_3$	$W(CH)(SCH_3)_3$
C	−0.36	−0.24	−0.40	−0.27
H	0.16	0.17	0.14	0.15
M	1.19	0.33	1.27	0.25
E	−0.62	−0.10	−0.64	−0.07
C	−0.17	−0.57	−0.17	−0.57
H	0.15	0.20	0.16	0.20
	$Mo(CH)(OCF_3)_3$	$Mo(CH)(SCF_3)_3$	$W(CH)(OCF_3)_3$	$W(CH)(SCF_3)_3$
C	−0.25	−0.18	−0.30	−0.20
H	0.21	0.21	0.19	0.19
M	1.19	0.25	1.27	0.15
E	−0.64	−0.08	−0.66	−0.05
C	1.09	0.77	1.09	0.78
F	−0.28	−0.26	−0.28	−0.26

Table 5
Frontier molecular orbitals for Mo(≡CH)(ECH_3)$_3$ and Mo(≡CH)(ECF_3)$_3$

	Sym	Energy (eV)	Description
Mo(CH)(OCH_3)$_3$			
LUMO	e	−0.97	$\mathrm{Md}_{xy}/\mathrm{d}_{x^2-y^2}$–Oπ* $\mathrm{Cp}_x/\mathrm{p}_y$
HOMO	e	−6.84	M–Cπ M–Oπ* (Op–Cpσ)
	a_2	−7.30	Olp Cp–Hsσ
	e	−7.55	Olp Cp–Hsσ
	a_1	−8.15	Cp–Hσ Olp Cp–Hsσ
	e	−8.94	M–Oπ Cp–Hsσ
	a_1	−10.64	M–Cσ (some Olp)
Mo(CH)(SCH_3)$_3$			
LUMO	e	−2.14	$\mathrm{Md}_{xy}/\mathrm{d}_{x^2-y^2}$–Sπ* $\mathrm{Cp}_x/\mathrm{p}_y$
HOMO	a_2	−6.16	Slp
	e	−6.85	Slp (C–Hσ)
	e	−7.47	M–Cπ M–Sπ* C–Hσ
	a_1	−7.91	Slp C–Hσ
	e	−8.19	M–Sπ (some C–H σ)
	a_1	−10.23	Cp–Hsσ Sp–Cp σ
	e	−10.36	Md–Spσ Sp–Cpσ Cp–Hsσ
	a_1	−10.90	M–Cσ
Mo(CH)(OCF_3)$_3$			
LUMO	e	−3.22	$\mathrm{Md}_{xy}/\mathrm{d}_{x^2-y^2}$–Oπ* $\mathrm{Cp}_x/\mathrm{p}_y$
HOMO	e	−8.82	M–Cπ M–Oπ* (Op–Cpσ)
	a_2	−9.99	Olp Flp
	e	−10.16	Olp Flp
	a_1	−10.61	Cp–Hσ Olp Flp
	e	−11.22	M–Oπ Flp
	a_2	−11.38	Flp
	e	−11.39	Flp
	a_1	−12.09	Cp–Hsσ Olp Flp
	a_2	−12.13	Flp (Olp)
	e	−12.22	Flp (Olp)
	e	−12.28	Flp Md–Opσ
	a_1	−12.43	M–Cσ Olp Flp
Mo(CH)(SCF_3)$_3$			
LUMO	e	−3.40	$\mathrm{Md}_{xy}/\mathrm{d}_{x^2-y^2}$–Sπ* $\mathrm{Cp}_x/\mathrm{p}_y$
HOMO	a_2	−7.65	Slp (Flp)
	e	−8.30	Slp (Flp)
	e	−8.65	M–Cπ M–Sπ* (S–Cσ Flp)
	a_1	−9.37	Slp Flp
	e	−9.59	M–Sπ (Flp)
	a_1	−10.81	Sp–Cpσ Flp
	e	−10.84	Sp–Cpσ Flp Md–Spσ
	a_2	−11.48	Flp
	e	−11.49	Flp
	a_1	−12.02	M–Cσ (Flp)

3. Comparisons with related compounds

The trends observed in replacing O by S in the series of methylidyne complexes considered here directly parallels those seen for the related M≡M and Mo≡N compounds discussed previously. There is a dramatic difference in the ordering and energies of the frontier molecular orbitals of the M≡M, Mo≡N and M≡C molecules with alkoxide and thiolate ligands due to the electronegativity difference between oxygen and sulfur and the extent of M–E π bonding. The greater oxygen to metal π-donation raises the metal–carbon π-bond orbital energy. For the thiolates, the HOMO is a sulfur based lone-pair combination and the LUMO is lower in energy than in the alkoxides and is metal-based. Hopefully, these calculations will stimulate further research into the chemistry of thiolate molybdenum and tungsten alkylidyne complexes which have thus far attracted less attention than their alkoxide analogues.

4. Computational details

The calculations were done with the GAUSSIAN-98 program [11] using the B3LYP [12] method. For molybdenum and tungsten, the LANL2DZ basis set [13] was used and 6-31G* [14] was used for oxygen, sulfur, carbon, fluorine and hydrogen. The geometries of all molecules were optimized and frequency calculations performed to ensure that there were no imaginary frequencies.

Bond dissociation energies were calculated by the difference in energy of the original molecule and the fragments that result from homolytic cleavage of the M≡C bond. The fragment geometries were optimized and frequency calculations were performed to obtain free energy values at 298 K. Both the doublet and quartet fragments were calculated and the lower energy fragment was used to calculate the bond energy. For the CH fragment the ground state was found to be a doublet, while for the M(OH)$_3$ fragments, the quartet state was found to be lower in energy for Cr, Mo and W.

Electron density plots of the orbitals were created using Molden [15].

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