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The bonding of acetylene and ethylene in high-valent and low-valent transition metal compounds [1]

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Abstract

The equilibrium geometries of the transition metal compounds WCl_4L, WCl_5L^- and $W(CO)_5L$ (L = acetylene, ethylene) are theoretically predicted at the HF and MP2 levels of theory using a relativistic effective core potential for tungsten and valence shell basis sets of DZ + P quality. The W–L dissociation energies are calculated at the CCSD(T) level of theory. The calculated geometries are in very good agreement with experimental values. The $W-C_{acetylene}$ and $W-C_{ethylene}$ bond distances of WCl_4L are much shorter than the bond lengths of $W(CO)_5L$. However, the $(CO)_5W-L$ bond dissociation energies are higher than or comparable in magnitude with the Cl_4W-L bond energies. This result can be explained by the different nature of the tungsten–carbon bonds in $W(CO)_5L$ and WCl_4L, as revealed by the charge decomposition analysis (CDA) of the compounds. The W–C bonds of the low-valent carbonyl complexes have donor–acceptor character and the bonding can be understood in terms of the Dewar–Chatt–Duncanson model. The tungsten–carbon bonds of WCl_4L are polar covalent bonds which are formally formed from the triplet states of WCl_4 and L. The dissociation energies of WCl_4L are very low, because the energy which is necessary to promote acetylene and ethylene into the lowest lying triplet state is very high. The CDA results for WCl_5L^- suggest that the anions might also be considered as complexes which can be discussed in terms of closed-shell orbital interactions. The $Cl_5W^- -L$ bond energies are rather low, because there is strong repulsion between the occupied orbitals of the fragments. The breakdown of the donor–acceptor interactions into orbital contributions shows that acetylene is a four-electron donor in $WCl_5(HCCH)^-$, while it is a two-electron donor in $W(CO)_5(HCCH)$. The donation from the out-of-plane CC-bonding π orbital of acetylene is the reason why $WCl_5(HCCH)^-$ is a stable (isolable) compound. This orbital is not available for ethylene, and thus $WCl_5(C_2H_4)^-$ is predicted to have a weak tungsten–ethylene bond.

Keywords: Ab initio calculations; Acetylene complexes; Ethylene complexes; π-bonding

1. Introduction

Transition metal (TM) complexes with alkenes and alkynes as π-bonded ligands may either be considered as (i) metallacyclic compounds or (ii) donor–acceptor complexes (Fig. 1). The metal–ligand interactions of the latter species are frequently discussed in the framework of the Dewar–Chatt–Duncanson (DCD) model [2]. The DCD model considers the metal–ligand bonding to arise from the synergetic ligand → metal donation and metal → ligand back donation between two closed-shell fragments.

Textbooks of inorganic chemistry usually introduce

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[1] Theoretical studies of organometallic compounds, Part XXII. Part XXI: see Ref. [1].

the two models (i) and (ii) as complementary to each other, where the real molecule is on a continuum between the two extreme situations, for example see Ref. [3]. The two models are very helpful in explaining the chemistry of TM π-complexes. It is well known that TM alkene complexes may react with nucleophiles in different ways. For example, some complexes show addition reactions of the nucleophile to the alkene ligand [4], while others show insertion of the nucleophile into the metal–alkene bond [5]. Metal systems that facilitate addition reactions usually do not show insertion reactions. A previous theoretical study of dichlorotitanacyclopropane using the generalized valence bond (GVB) method found wavefunctions describing both the metallacyclopropane and π-complex forms, depending upon the geometry used for the compound [6]. It was suggested that *some* metal–alkene
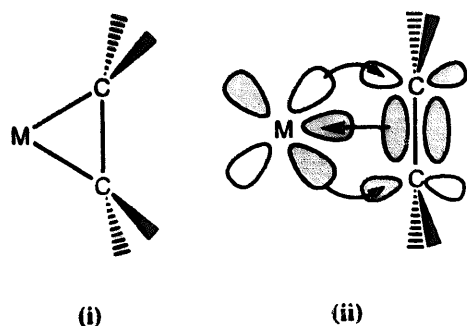
(i)   **(ii)**

Fig. 1. Schematic representation of a metal–olefin complex as (i) a metallacyclic and (ii) a donor–acceptor complex.

complexes should be viewed as metallacycles and others should be viewed as π-complexes, and that the different reactivities of the complexes can be explained by their belonging to one of the two classes of compounds [6].

In the context of studying the bonding properties of TM complexes with π-bonded ligands using high-level ab initio methods, we found that the two situations (i) and (ii) can also clearly be distinguished using modern techniques for analysing ab initio molecular orbital (MO) wavefunctions [7]. The charge decomposition analysis (CDA) [8] of the wavefunction suggests that the donor–acceptor complexes (ii) have semipolar covalent bonds, which are formed from two closed-shell fragments, and that the DCD model is appropriate for the description of the metal–ligand bonding. However, metallacyclic compounds (i) have normal covalent metal–carbon bonds with mainly sd^x-hybridized metal orbitals, [9] where the metal and the ligand contribute with one electron each to the bonding. The same situation is given for high-valent (Schrock-type) and low-valent (Fischer-type) TM carbene and carbyne complexes, see Refs. [10,11]. The term 'complex' is thus not appropriate for such molecules. Furthermore, the CDA results give insight into the orbitals which are relevant for a qualitative and quantitative discussion of the metal–ligand interactions in the framework of the DCD model. This is important for the analysis of metal–alkyne complexes, where the π-ligand can act as a two-electron or four-electron donor [12]. This prompted us to carry out a detailed analysis of the bonding of acetylene and ethylene to TMs in high and low oxidation states. Here we report quantum mechanical ab initio results for WCl$_4$(HCCH) (1), WCl$_4$(C$_2$H$_4$) (2), WCl$_5$(HCCH)$^-$ (3), WCl$_5$(C$_2$H$_4$)$^-$ (4), W(CO)$_5$(HCCH) (5) and W(CO)$_5$(C$_2$H$_4$) (6).

2. Methods

The geometry optimizations have been carried out at the HF and MP2 [13] levels of theory using a relativistic

effective core potential (ECP) in conjunction with a (441/2111/21) split-valence basis set for tungsten developed by Hay and Wadt [14]. The 5s^2 and 5p^6 electrons are treated explicitly as part of the valence space. A 6-31G(d) all electron basis set was used for the ligand atoms C, O and H [15]. A pseudopotential with a (31/31/1) valence basis set was used for Cl [16]. The d polarization function for Cl (orbital exponent $\zeta = 0.65$) has five spherical components. This basis set combination is our standard basis set II [17]. The dissociation energies are calculated using coupled-cluster theory [18] with singles and doubles and a noniterative estimate of triple substitutions (CCSD(T)) [19]. The harmonic vibrational frequencies and the corresponding zero-point vibrational energies (ZPEs) have been estimated at the HF/II level of theory using numerical second derivatives. Unless otherwise noted, the geometries are discussed at MP2/II and the bond energies at CCSD(T)/II using MP2/II optimized geometries. The calculations have been carried out using the program packages TURBOMOLE [20], ACES II [21] and GAUSSIAN 92 [22].

In order to further investigate the ab initio wavefunctions obtained for the energy minimum structures, we used the CDA [8]. In the CDA method the (canonical or natural) MOs of the complex are expressed in terms of the MOs of appropriately chosen fragments. In the present case, the natural orbitals (NOs) of the MP2/II wavefunction of MX$_n$L are formed by a linear combination of the MOs of MX$_n$ and L in the geometry of MX$_n$L. Charge donation d_i from L to MX$_n$ for each NO φ_i of MX$_n$L is then given by

$$d_i = \sum_k^{occ.A} \sum_n^{vac.B} b_i c_{ki} c_{ni} \langle \varphi_k | \varphi_n \rangle$$

Similarly, the back donation b_i from MX$_n$ to L is given by

$$b_i = \sum_l^{occ.B} \sum_m^{vac.A} b_i c_{li} c_{mi} \langle \varphi_l | \varphi_m \rangle$$

Finally, the repulsive polarization r_i between the occupied orbitals of MX$_n$ and L is given by

$$r_i = \sum_k^{occ.A} \sum_m^{occ.B} b_i c_{ki} c_{mi} \langle \varphi_k | \varphi_m \rangle$$

There is also the rest term Δ_i given by the mixing of the unoccupied orbitals of the two fragments. This term is a consequence of the mathematical ansatz of the CDA method which should not contribute to the charge distribution of a complex.

$$\Delta_i = \sum_m^{vac.A} \sum_n^{vac.B} b_i c_{mi} c_{ni} \langle \varphi_m | \varphi_n \rangle$$

$A = $ L, $B = $ MX$_n$, $b = $ occupation number, $c = $ fragment orbital coefficient, $\varphi = $ fragment MO.

The sum of the orbital contributions d_i, b_i and r_i gives the total amount of donation, back donation and charge repulsion respectively. The CDA calculations have been performed using the program CDA 2.1 [2] [23].

3. Geometries and bond energies

Fig. 2 shows the theoretically predicted geometries of the compounds 1–6 in the eclipsed (1a–6a) and staggered (1b–6b) conformations. The corresponding total and relative energies are given in Table 1. The calculated geometry of the more stable form 1b of WCl₄(HCCH) is in very good agreement with experimental values for WCl₄ complexes of substituted acetylenes, which have W–C distances of ca. 2.00 Å [24–26]. The X-ray structure analysis of complexes WCl₄(RCCR′) shows that the compounds have a dimeric structure with two chlorine atoms bridging the tungsten atoms [24–26]. The neutral dimeric alkyne complexes react with chloride anions to give the anionic complexes WCl₅(RCCR′)⁻ as monomers. The X-ray structure analysis of WCl₅(PhCCH)⁻ shows that the average W–C distance is slightly longer in the anion (2.015 Å) [24] than in the neutral compound [WCl₄(PhCCPh)]₂ (1.990 Å) [25]. Fig. 2 shows that the calculated geometry of 3 is in excellent agreement with experimental observations. The theoretically predicted W–C distance of the more stable form 3b of WCl₅(HCCH)⁻ is slightly longer (2.016 Å) than in 1b (2.001 Å). The W–Cl_trans bond in 3b is calculated to be clearly longer (2.446 Å) than the W–Cl_cis bonds (2.398 Å). The experimental values for WCl₅(PhCCH)⁻ are W–Cl_trans = 2.490 Å and W–Cl_cis = 2.370 Å [24].

There are no experimental geometries for compounds related to the alkene complexes 2 and 4 known to us. On the basis of previous experience we expect that the calculated geometries reported here should be quite accurate. The alkene complexes 2 and 4 have longer W–C bond lengths than the respective alkyne complexes 1 and 3. The negatively charged compound WCl₅(C₂H₄)⁻ has a slightly longer W–C bond than neutral WCl₄(C₂H₄) (Fig. 2).

The calculated W–C_alkyne and W–C_alkene bond lengths of the carbonyl complexes 5 and 6 are significantly longer and the C–C bonds are clearly shorter than the respective interatomic distances of 1–4 (Fig. 2). The complexes W(CO)₅(HCCH) (5) and W(CO)₅(C₂H₄) (6) have been observed and the infrared spectra of 5 and 6 are reported [27], but the geometry of 5 and 6 has not been determined experimentally. The theoretically predicted W–C_alkyne distance of 5a (2.330 Å) is in good

agreement with the recently published first X-ray structure analysis of a tungsten pentacarbonyl–alkyne complex reported by Fischer et al. [28]. The measured metal–alkyne bond lengths of W(CO)₅(HCCPh) are 2.481 and 2.389 Å. It is noteworthy that the X-ray structure analysis of W(CO)₅(HCCPh) shows that the alkyne ligand nearly eclipses two CO ligands in the cis position [28]. The calculations predict that the eclipsed conformation 5a is lower in energy than the staggered form 5b (Table 1). The calculations also predict that the trans CO group of 5a has a shorter W–CO bond (2.020 Å) than the cis carbonyl groups (W – CO_cis = 2.057 and 2.059 Å). The same trend is found in the X-ray structure analysis of W(CO)₅(HCCPh), where the W–CO_trans bond length is 1.969 Å, while the average W–CO_cis bond length is 2.047 Å [28]. The calculated W–C_alkene distance of the ethylene complex 6a is also in good agreement with the experimental average value of ten different alkene complexes of W(0), $r = 2.386$ Å [29].

Table 2 shows the calculated metal–acetylene and metal–ethylene bond dissociation energies D_e for the stable conformations of 1–6 predicted at CCSD(T)/II//MP2/II. Previous studies have shown that metal–ligand bond energies calculated at CCSD(T)/II//MP2/II are quite reliable [17,30–32]. The bond energies of 5 and 6 could not be calculated at CCSD(T)/II for technical reasons (less than 2 GB single file size limit). We used the relative bond energies calculated at MP2/II in conjunction with the metal carbonyl bond energy of W(CO)₆ predicted at CCSD(T)/II in order to estimate CCSD(T)/II bond energies for 5 and 6. It has recently been shown that the use of isostructural reaction energies predicted at MP2/II gives rather accurate bond energies [33].

There are two remarkable aspects concerning the bond energies. First, for the WCl₄L and WCl₅L⁻ compounds 1–4 the ethylene ligand is predicted to be significantly more weakly bound to the metal ($D_e = 12.1$ kcal mol⁻¹ for 2a, $D_e = 8.5$ kcal mol⁻¹ for 4a) than acetylene ($D_e = 36.6$ kcal mol⁻¹ for 1b, $D_e = 22.3$ kcal mol⁻¹ for 3b), while the opposite trend holds for the W(CO)₅L complexes. The metal–ligand bond energy of the ethylene complex 6a is higher ($D_e = 41.4$ kcal mol⁻¹) than that of the acetylene complex 5a ($D_e = 35.3$ kcal mol⁻¹). (In Ref. [32] we reported a bond energy $D_0 = 28.9$ kcal mol⁻¹ for the metal–acetylene bond of 5a. This is significantly lower than the value reported here ($D_0 = 34.3$ kcal mol⁻¹, Table 2). The value reported in Ref. [32] was obtained at CCSD(T)/II. However, a STO-3G basis set was used for hydrogen in order to meet the less than 2GB single file limit. We believe that the value reported here is more accurate. The relative bond energies given in Table 2 should be reliable in any case, because they have been obtained at the same level of theory.) The

second remarkable aspect concerns the absolute values of the bond energies of 1–4. Although the W–C bond distances of the WCl$_4$L and WCl$_5$L$^-$ complexes are much *shorter* than those of the W(CO)$_5$L complexes,

the W–L bond energies of the tungsten complexes 1–4 are either clearly *lower* than those of the carbonyl complexes 5 and 6, or comparable in magnitude as in the case of 1b and 5a. It follows that there is no
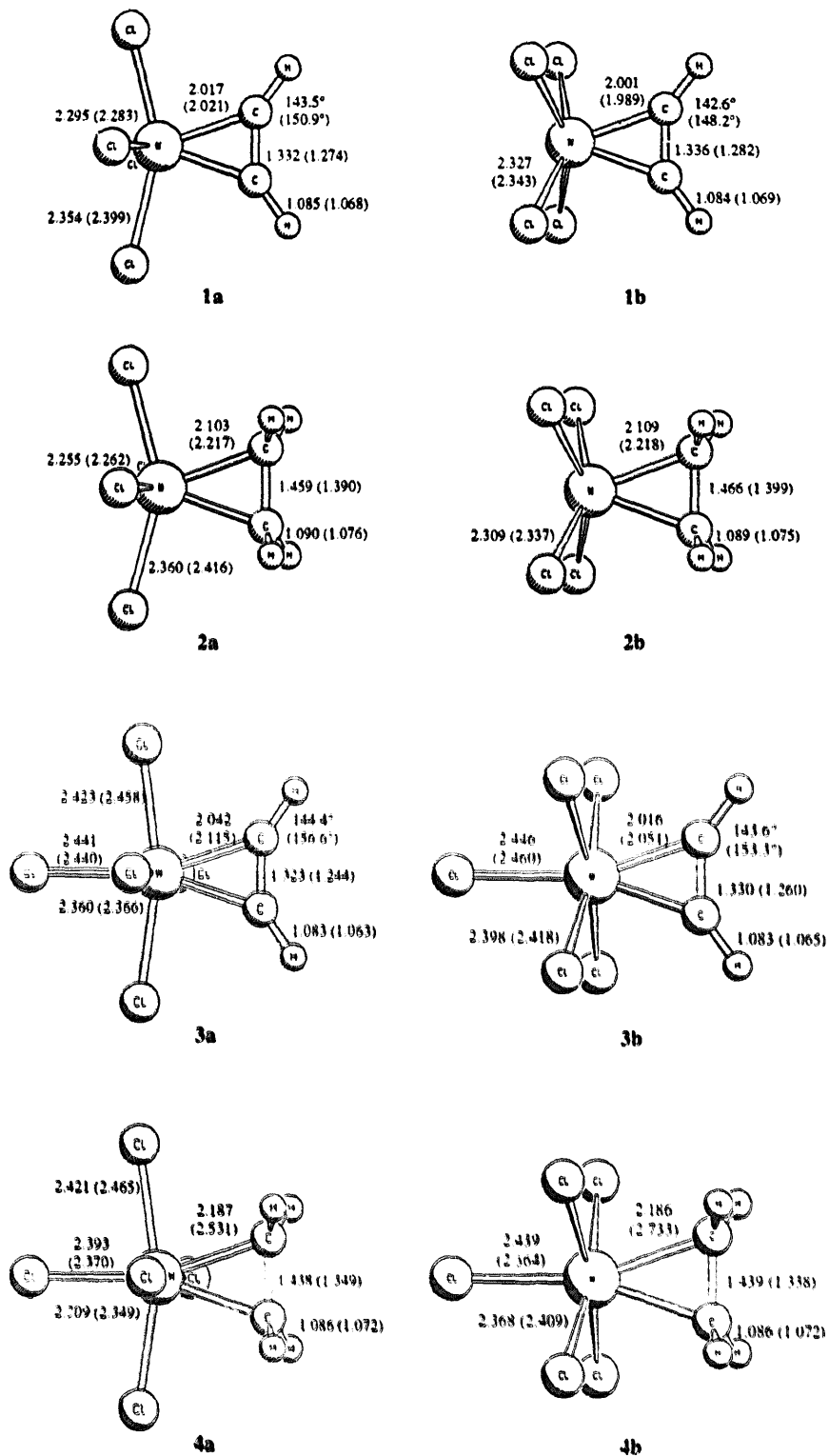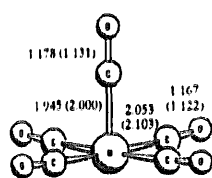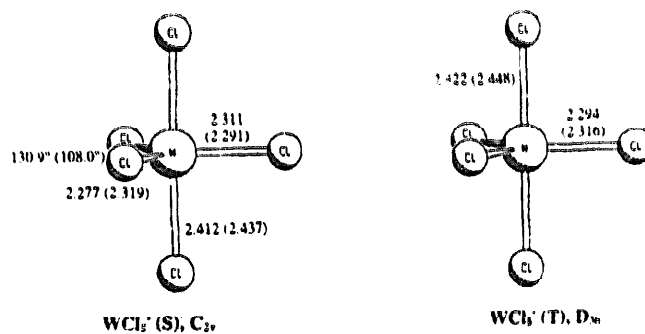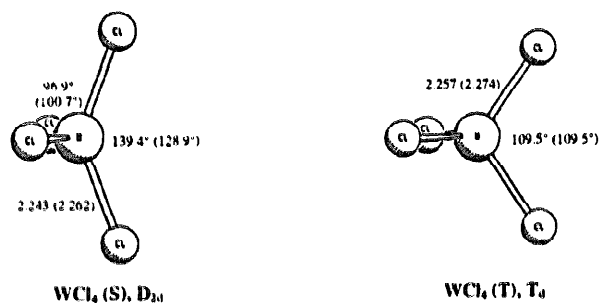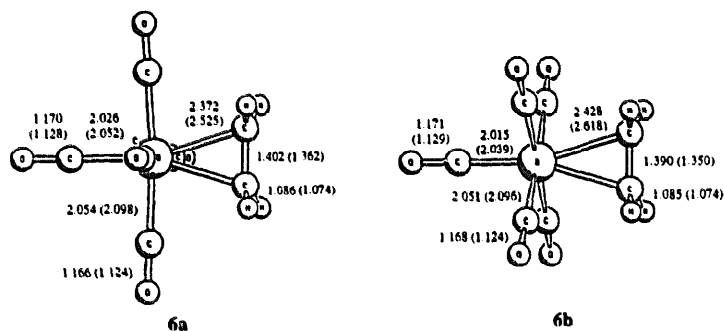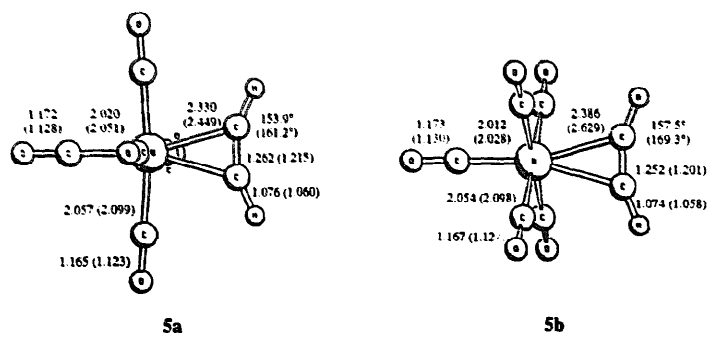

Fig. 2. Optimized geometries of 1a–6b and the fragments. Bond lengths (Å) and bond angles (deg) at MP2/II. Values at HF/II are given in parentheses.

5a

5b

6a

6b

WCl₄ (S), D₂d

WCl₄ (T), T_d

WCl₅⁻ (S), C₂ᵥ

WCl₅⁻ (T), D₃ₕ

W(CO)₅ (S), C₄ᵥ

Fig. 2 (continued).

Table 1
Calculated total energies E_{tot}, relative energies of the eclipsed (a) and staggered (b) conformations E_{rel}, zero point energies (ZPEs) and number of imaginary frequencies i

Molecule	HF/II//HF/II				MP2/II//MP2/II		CCSD(T)/II//MP2/II	
	E_{tot} (au)	E_{rel} (kcal mol^{-1})	ZPE (kcal mol^{-1})	i	E_{tot} (au)	E_{rel} (kcal mol^{-1})	E_{tot} (au)	E_{rel} (kcal mol^{-1})
1a	-203.18545	0.0	23.7	1	-204.25303	0.0	-204.31136	0.0
1b	-203.18842	-1.9	23.8	0	-204.25694	-2.5	-204.31475	-2.1
2a	-204.37039	0.0	40.0	0	-205.42790	0.0	-205.50440	0.0
2b	-204.36340	+4.4	39.8	1	-205.42256	+3.4	-205.49886	+3.5
3a	-218.07531	0.0	23.8	1	-219.28754	0.0	-219.35791	0.0
3b	-218.07802	-1.7	24.2	0	-219.29147	-2.5	-219.36088	-1.9
4a	-219.28789	0.0	40.8	0	-220.47721	0.0	-220.56760	0.0
4b	-219.27496	+8.1	40.0	2	-220.45795	+12.1	-220.54927	+11.5
5a	-707.72044	0.0	47.2	0	-709.75973	0.0	—	—
5b	-707.71714	+2.1	47.1	1	-709.75483	+3.1	—	—
6a	-708.93994	0.0	64.3	0	-710.98794	0.0	—	—
6b	-708.93719	+1.7	64.4	2	-710.98228	+3.6	—	—
WCl$_4$(S)	-126.33544	0.0	3.1	0	-127.06926	0.0	-127.13212	0.0
WCl$_4$(T)	-126.39404	-36.8	3.0	0	-127.10527	-22.6	-127.16568	-21.1
WCl$_5^-$ (S)	-141.24940	0.0	3.5	0	-142.11612	0.0	-142.19298	0.0
WCl$_5^-$ (T)	-141.30913	-37.5	3.7	0	-142.16184	-28.7	-142.23468	-26.2
W(CO)$_5$	-630.87630	—	27.7	0	-632.62396	—	—	—
C$_2$H$_2$	-76.81732	—	18.4	0	-77.06860	—	-77.09074	—
C$_2$H$_4$	-78.03136	—	34.4	0	-78.28701	—	-78.31931	—

bond-length/bond-energy correlation between the high-valent complexes 1=4 and the low-valent complexes 5 and 6. We want to point out that the rather low bond energies of the metal=ethylene compounds 2 and 4, which are much lower than for the metal=acetylene compounds 1 and 3 (Table 2), are in agreement with the experimental observation that alkyne complexes WCl$_4$(RCCR') and WCl$_5$(RCCR')$^-$ are isolable as stable molecules [24-26], while the corresponding alkene complexes have not been reported yet.

The bond energies are calculated as the energy difference between the complex on the one hand and the ligand and the respective fragment on the other hand in their respective electronic ground states. In the case of WCl$_4$ and WCl$_5^-$ the ground state is a triplet state. However, even the dissociation of WCl$_4$L into L and singlet WCl$_4$ gives bond energies which are only 21.1 kcal mol^{-1} higher (see the relative energy of the

Table 2
Calculated bond dissociation energies D_e (kcal mol^{-1}) of the complexes relative to the fragments in their electronic ground state; ZPE-corrected values D_0 (kcal mol^{-1}) in parentheses

Molecule	HF/II// HF/II	MP2/II// MP2/II	CCSD(T)/II// MP2/II
1b	-14.4	52.1	36.6 (34.4)
2a	-34.5	22.4	12.1 (9.6)
3b	-30.4	38.3	22.3 (20.2)
4a	-33.0	17.8	8.5 (5.7)
5a	16.8	42.2	35.3 (34.3) [a]
6a	20.3	48.3	41.4 (39.1) [a]

[a] Estimated values using isostructural reactions, see text.

singlet and triplet state of WCl$_4$ in Table 1). If 1 and 2 were donor-acceptor complexes, the W-L bond energies should be much higher, because WCl$_4$ should be a clearly stronger acceptor than W(CO)$_5$. The calculated geometries and bond energies indicate that the bonding situations in WCl$_4$L and W(CO)$_5$L are quite different, while WCl$_5$L$^-$ seems to be a borderline case.

4. Analysis of the electronic structure

The puzzling aspects of the calculated bond energies can be explained by the different nature of the W-L bonds in the WCl$_4$L, WCl$_5$L$^-$ and W(CO)$_5$L compounds, which is elucidated by the CDA of the MP2/II wavefunctions of the compounds. The CDA expresses the wavefunction of the complex in terms of the MOs of the closed-shell fragments (FMOs) whose interactions ought to be analysed [8]. The sum over the FMOs is divided into (i) mixing of the occupied FMOs of the ligand and the unoccupied FMOs of the metal fragment yielding the L → W donation d; (ii) mixing of the unoccupied FMOs of the ligand and the occupied FMOs of the metal fragment yielding the L ← W back donation b; (iii) mixing of the occupied orbitals of both fragments yielding the repulsive polarisation r; and (iv) mixing of the unoccupied/unoccupied FMOs yielding the 'rest' term Δ. The term Δ is virtually zero for donor-acceptor complexes. It has been shown that the CDA results correlate nicely with the DCD model for donor-acceptor complexes [31,32].

Table 3 shows the CDA results for the energy minimum conformations of 1-6. We begin the discussion with the $W(CO)_5L$ complexes 5 and 6. The calculated $L \rightarrow W$ charge donation and $L \leftarrow W$ back donation are slightly higher for the acetylene complex 5a than for the ethylene complex 6a. We want to point out that there is generally *no* direct correlation between the calculated donation and back donation terms and the bond energy. Ethylene is a *better* donor and a better acceptor than acetylene *energetically*, because ethylene has a higher-lying HOMO and a lower-lying LUMO than acetylene. The repulsive polarization terms are negative for both complexes, because electronic charge is removed from the overlapping region of the occupied/occupied orbitals. As expected, the Δ term is nearly zero for 5a and 6a. The CDA results demonstrate that the bonding in 5 and 6 can be interpreted in terms of the DCD model. Since ethylene is, from an energetic point of view, a better donor and a better acceptor than acetylene, it is reasonable that 6a has a stronger W-L bond than 5a. The longer $W-C_{ethylene}$ bond of 6a compared with the $W-C_{acetylene}$ bond of 5a is due to the radius of the sp^2-hybridized carbon atom of ethylene being larger than the radius of the sp-hybridized carbon atom of acetylene.

The CDA results for 1b and 2a demonstrate that these compounds should *not* be interpreted in terms of the DCD model. The calculated $L \leftarrow W$ back donation for 1b and 2a and the $L \rightarrow W$ donation for 2a are *negative*, which is an unphysical result within the model of charge exchange between closed-shell fragments. Another indication that 1b and 2a should not be considered as donor-acceptor complexes is given by the 'rest' term Δ, which is even more discriminating. In contrast to the results for the complexes 5 and 6 and for other donor-acceptor complexes [7,8,31,34], the contribution from the mixing of the unoccupied fragment orbitals to the charge distribution is very large; it is even the largest among the four terms (Table 3). It follows that the bonding in 1b and 2a cannot be described in a reasonable way by a mixing between the occupied and unoccupied orbitals of the closed shell fragments WCl_4 and ethylene or acetylene respectively. This demonstrates clearly that 1 and 2 should not be considered as

acetylene and ethylene complexes, but rather as metallacyclic compounds with covalent metal-ligand bonds.

The calculated W-C bond lengths and bond dissociation energies can now easily be explained if the different type of metal-ligand bonding is considered. The W-C bonds of the complexes 5 and 6 break in a *heterolytic* way, yielding $W(CO)_5$ and L in the singlet ground state. The WCl_4L compounds have covalent metal-ligand bonds, the W-C bonds dissociate in a *homolytic* way. The dissociation products of the spin-allowed reactions are triplet WCl_4 and triplet C_2H_2 and C_2H_4 respectively. Ethylene and acetylene have formally to be electronically excited before the covalent W-C bonds of 1 and 2 can be formed. The excitation energies from the singlet ground state to the first excited triplet state of acetylene and ethylene are very high. The energetically lowest lying ($^3B_2$) triplet state of acetylene, which has a cis-bent geometry, is calculated to be $82.6 kcal mol^{-1}$ higher in energy than the ($^1\Sigma_g^-$) singlet ground state [35]. This value and the calculated dissociation energy of $36.6 kcal mol^{-1}$ for 1b (Table 2) give a theoretically predicted Cl_4W-acetylene interaction energy of $119.2 kcal mol^{-1}$, which correlates nicely with the short W-C bond length (Fig. 1). For ethylene, only the vertical excitation energy into the first excited triplet state is available. The experimental value is $100.5 kcal mol^{-1}$ [36], which shows that the triplet states of ethylene are much higher in energy than the singlet ground state. The W-C bonds of 1 are clearly stronger than those of 2, because the metallacyclopropene compound 1 has formally sp^2-hybridized carbon atoms, while the carbon atoms of the metallacyclopropane compound 2 are sp^3-hybridized. It is well known that a covalent bond of a given atom or group to $C(sp^2)$ is much stronger than to $C(sp^3)$.

From the above discussion, it follows that ligands with a low singlet $\rightarrow$ triplet excitation energy, or even a triplet ground state, should form strong bonds to metal fragments in a triplet state. This is indeed the case. Carbene ligands with a triplet ground state like methylene form stable high-valent (Schrock-type) TM compounds with strong M-C double bonds, while low-valent (Fischer-type) carbene complexes are only stable when the carbene ligand has a singlet ground state [11,37].

Now we discuss the CDA results for $WCl_5(HCCH)^-$ (3b) and $WCl_5(C_2H_4)^-$ (4a). Table 3 shows that the CDA method gives positive values for the $L \rightarrow W$ donation and $L \leftarrow W$ back donation. The rest term Δ is very small. The CDA results indicate that 3 and 4, unlike 1 and 2, can be considered as donor-acceptor complexes. The most interesting feature of the CDA results for 3b and 4a are the large values for the repulsive polarization r. This shows that there are strong repulsive interactions between the occupied orbitals of WCl_5^- and acetylene and ethylene respectively. This is

Table 3

MP2-CDA of the complexes in their MP2 geometries (donation d, backdonation b, repulsive part r and residual part Δ)

Molecule	d	b	r	Δ
1b	0.057	-0.140	-0.189	0.382
2a	-0.263	-0.194	-0.318	0.351
3b	0.308	0.234	-0.760	-0.048
4a	0.041	0.138	-0.900	-0.045
5a	0.297	0.165	-0.391	-0.004
6a	0.225	0.148	-0.422	-0.025

reasonable, because both fragments WCl_5^- and L are electron rich. The large numbers for the repulsive polarization explain why the W–L bond energies of 3b and 4a are rather low (Table 2). The shorter W–C$_{acetylene}$ and W–C$_{ethylene}$ bond lengths of 3b and 4a, compared with those of 5a and 6b, can be explained by the smaller radius of the high-valent tungsten atom of the former complexes compared with the W(0) atom of the carbonyl complexes.

The breakdown of the CDA results for the donor–acceptor interactions into orbital contributions gives further insight into the metal–ligand interactions, particularly for the acetylene complexes. Since alkynes have two π-bonds, alkyne ligands can act as two-electron or four-electron donors in TM complexes. The participation of the alkyne π orbital, which is orthogonal to the metal–alkyne plane, to the metal–ligand interactions has been discussed on a qualitative level before [12]. The CDA results make it possible to study the effect quantitatively. Table 4 gives the most important orbital interactions for the donation, back donation and repulsive polarization of 3b and 5a. Fig. 3 shows qualitatively the shape of the dominant orbitals. There are only

three orbitals of the complexes which are relevant for the metal–acetylene interactions of 3b and 5a. In the case of 3b, there are two MOs, i.e. MO 31 with a_1 symmetry and MO 32 with b_2 symmetry, which are important for the L → W donation. The donation from the in-plane π orbital of acetylene into the d_{z^2} orbital of W amounts to 0.222 electrons, while 0.260 electrons are donated from the out-of-plane π orbital of acetylene into the d_{yz} orbital of W (Table 4). There is only one dominant orbital for the L → W donation of 5a. This is the MO 46 with a_1 symmetry, which describes the
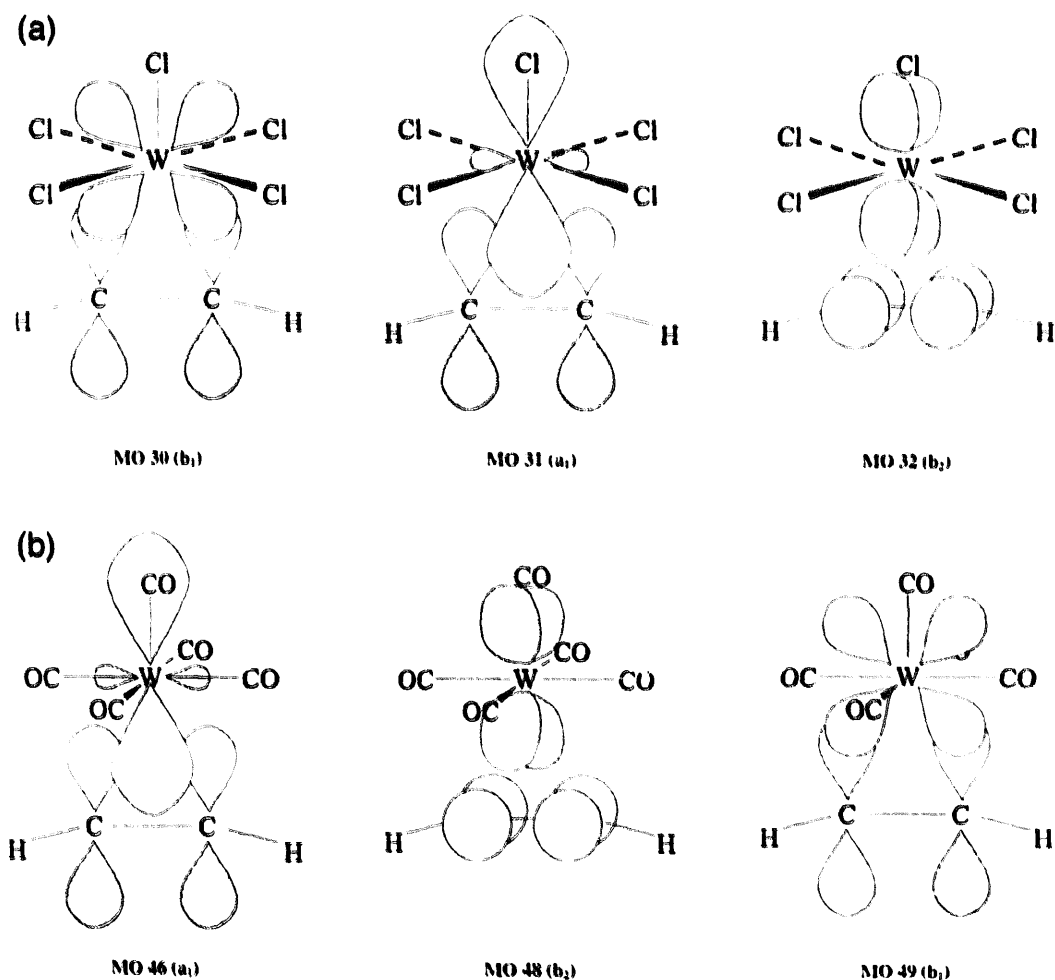
Table 4
Dominant MO contributions to the donation d, backdonation b and repulsion r in the complexes 3b and 5a (MP2/II)

Molecule	MO	d	b	r
3b	MO 30 (b_1)		+0.282	
	MO 31 (a_1)	+0.222		−0.375
	MO 32 (b_2)	+0.260		
5a	MO 46 (a_1)	+0.326		−0.194
	MO 48 (b_2)			−0.272
	MO 49 (b_1)		+0.195	

Fig. 3. Schematic representation of the most important complex orbitals for the metal–acetylene interactions of 3b and 5a as revealed by the CDA.

donation from the in-plane π orbital of acetylene into the d_{z^2} orbital of W (Fig. 3). The absence of electron donation from the out-of-plane π orbital of acetylene into the $W(CO)_5$ fragment orbitals of **5a** is reasonable, because there is no empty d_{yz} orbital at tungsten in $W(CO)_5(HCCH)$. It follows that acetylene is a four-electron donor in **3b** but a two-electron donor in **5a**. The CDA results also show that the L $\leftarrow$ W back donation in **3b** and **5a** occurs mainly through one orbital with b_1 symmetry, i.e. MO 30 of **3b** and MO 49 of **5a**. This is the electron donation from the d_{xz} orbital of W into the in-plane π^* orbital of acetylene. The CDA result is in agreement with chemical intuition. The repulsive polarization of **3b** is given mainly by the orbital 31 (a_1), while the a_1 orbital 46 and the b_2 orbital 48 are involved in the repulsive polarization of **5a** (Table 4).

A similar breakdown of the orbital contributions to the metal–ligand interaction for the ethylene complexes **4a** and **6a** shows that the π and π^* orbitals of ethylene are clearly dominating among the ligand orbitals. The weakness of the metal–alkene bond of **4a** is due to the strong repulsive polarization between the in-plane orbitals (Table 3). The ethylene complex **4a** cannot have an out-of-plane L $\rightarrow$ W π donation like the acetylene complex **3b**, which appears to be the main reason why compounds $WCl_5(RCCR')^-$ are stable, while $WCl_5(C_2R_4)^-$ are not.

5. Summary

The geometry optimization at the MP2/II level of theory of the high-valent and low-valent acetylene and ethylene complexes 1–6 yields structures which are in good agreement with experimental values. The $W-C_{ethylene}$ and $W-C_{acetylene}$ bonds of WCl_4L are much shorter than those of the $W(CO)_5L$ complexes. However, the W–L dissociation energies of $W(CO)_5L$ are higher than or comparable with those of WCl_4L. This is explained by the different nature of the W–L bonds in the two classes of compounds as revealed by the CDA results. The carbonyl complexes **5** and **6** have donor–acceptor bonds which can be interpreted in terms of the DCD model. The covalent W–C bonds of **1** and **2** are formally formed from triplet fragments WCl_4 and ligands L. The energetically lowest-lying triplet states of acetylene and ethylene are much higher in energy than the singlet ground states. Since it takes much energy to promote the ligands from the singlet ground state into the triplet valence state, the net bond energy of the WCl_4–L bond is low, although the interaction energy between tungsten and acetylene or ethylene is high. The CDA suggests that the negatively charged compounds WCl_5L^- might also be considered as donor–acceptor complexes. The repulsive polarization between WCl_5^-

and acetylene or ethylene is very high. This explains why the W–L bond energies of **3** and **4** are rather low. The CDA results show that the acetylene ligand in $WCl_5(HCCH)^-$ is a four-electron donor, while it is a two-electron donor in $W(CO)_5(HCCH)$. The L $\rightarrow$ W donation through the out-of-plane π orbital of acetylene is the main reason why **3** is a stable compound, while **4** has not been isolated so far.

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