DALTON

Theoretical study of the metathesis-like reaction between ditungsten hexaalkoxides and alkynes †

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Density-functional calculations have been carried out on a metathesis-like reaction between $W_2(OR)_6$ (R = alkyl) and alkynes to give tungsten alkylidyne complexes. Two possible pathways have been taken into consideration: (i) a parallel approach between the reactants to give 1,2-ditungstenacyclobutadiene; (ii) a perpendicular approach to yield a ditungstenatetrahedrane which then flattens giving a 1,3-ditungstenacyclobutadiene. The electronic structure of the compounds involved in the reaction, as well as several energy profiles corresponding to the formation and decomposition of these species, have been investigated in order to study the thermodynamics and kinetics of the metathesis-like reaction. The inclusion of relativistic effects is crucial in order to understand how the reaction proceeds.

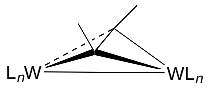
The metathesis of triple bonds is one of the most impressive synthetic methodologies in organometallic chemistry.[1–4] Of particular interest are the dinuclear systems of the type $M_2(OR)_6$ (M = Mo or W; R = Pr^i or Bu^t) which react with small unsaturated organic molecules C≡E (*e.g.* RC≡CR, C≡O or RC≡N), leading to cleavage of the C≡E bond or to a reduction of its bond order.[5] One of the most remarkable classes of such reactions, and one that has been extensively studied, is that between $W_2(OR)_6$ and a wide variety of alkynes.[1–5]

The ditungsten hexaalkoxide reacts with alkynes in a metathesis-like manner to give tungsten alkylidyne complexes [equation (1)]. The situation is actually quite complex, with the

$$(RO)_3W{\equiv}W(OR)_3 + R'C{\equiv}CR' \longrightarrow 2(RO)_3W{\equiv}CR' \quad (1)$$

extent of the reaction depending on (i) the steric bulk of alkoxide and alkyne substituents, (ii) the presence of a base, and (iii) the reaction temperature. An increase in steric bulk of both the alkoxide and alkyne substituents favours the alkylidyne products, although excessive steric crowding may hinder the reaction. It is interesting that when pyridine (py) is added to slow the reaction, alkyne adducts of the type $[W_2(OR)_6(py)_2(\mu\text{-}C_2H_2)]$ have been structurally characterised.[4] In these compounds the acetylene is bound to both metal atoms, with the carbon–carbon bond axis oriented perpendicular to the W–W bond, a co-ordination mode well known in other $M_2L_m(\mu\text{-alkyne})$ complexes (where M is a metal in a low oxidation state).[6] On the basis of the C–C, M–M and M–C bond lengths, these adducts have been formulated as dimetallatetrahedranes **1**. Moreover, NMR studies have shown the existence of a direct equilibrium between a dimetallatetrahedrane and a methylidyne complex when reaction (1) is carried out in the presence of pyridine.[4]

An analogous $[W_2(OR)_6(\mu\text{-}C_2R'_2)]$ adduct has been therefore assumed as the immediate precursor in the metathesis reaction (1).[4] No direct information is, however, available on either the reaction path that leads to breaking of the metallatetrahedrane into two alkylidyne units, or on the reverse reaction. Two possible intermediates with a planar W_2C_2 core have been postulated[7] as 1,2-dimetallacyclobutadiene **2** or 1,3-dimetallacyclobutadiene **3**. Compounds of type **2** are also known as parallel acetylene dinuclear complexes and many examples are known,[6] although almost all are characterised by a 10-electron M_2C_2 unit, and not 12 as would be the case in the tungsten complex **2**. The interconversion **1** ⇌ **2** has been invoked to account for the facile racemisation of chiral tetrahedral complexes of type **1** with different substituents on the alkyne unit.[8] The 1,3-dimetallacyclobutadiene complex **3** can be considered as a head-to-tail dimer of a tungsten alkylidyne. Compounds of this type are known[9–12] for a series of systems of formula $[\{M(\mu\text{-}CSiMe_3)(CH_2SiMe_3)_2\}_2]$ with the structure **4**.



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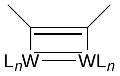

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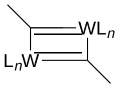

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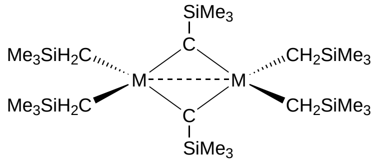

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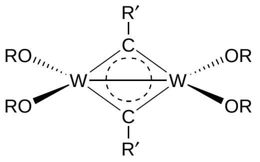

5 R = Pr^i, R′ = $SiMe_3$
R = Bu^t, R′ = Ph

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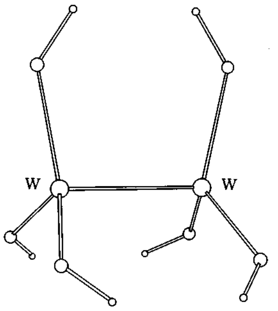
† *Non-SI unit employed*: eV ≈ 1.60×10^{-19} J.

Table 1 Formal bond orders for metal–metal bonds

M	Configuration	Bond order
Nb, Ta[9]	d^0	0
W[10,11]	d^1	1
Re[12]	d^2	2



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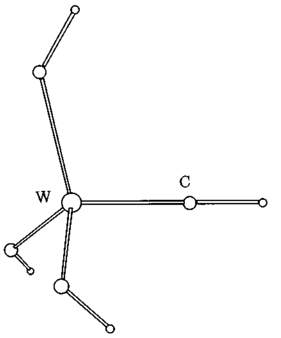


II

Depending on the electron count on the metal centres, a metal–metal bond can be present with formal bond order 0, 1 or 2 (Table 1). More pertinent to reaction (1) are analogous compounds with alkoxo ligands **5**, which are characterised by a formal single tungsten–tungsten bond. In particular such compounds have been isolated by Cotton *et al.*[13] in the reaction between $W_2(OBu^t)_6$ and PhC≡CPh, and can be considered as a side product in reaction (1). The interconversion **1** $\rightleftharpoons$ **3** with successive cleavage of **3** into two alkylidyne molecules, either spontaneously or induced by a base, has been proposed heuristically as the key step for reaction (1).[2]

The situation is therefore far from being fully resolved, suggesting that a theoretical investigation would be helpful in elucidating the relative stability of these possible intermediates, and the energy profile of the pathways leading to them, either from the W≡W and C≡C reactants or from the two alkylidyne products. Some of these systems have been examined previously at the extended Hückel[14] and Fenske–Hall[15] levels, but emphasis was given to a qualitative study of the bonding in the isolated complexes. No previous study has appeared that considers either the thermodynamics of the possible intermediates of reaction (1), or the energy profile for the reaction paths connecting them.

In the present investigation we employ a density-functional theory (DFT) approach to study the geometry and the energetics of the possible intermediates **1**–**3**. We also perform a detailed examination of the energy profile for the interconversions **1** $\rightleftharpoons$ **2** and **1** $\rightleftharpoons$ **3**, and consider the formation of **1**–**3** from the reactants $W_2(OR)_6$ and RC≡CR and the products $[W(OR)_3(\equiv CR)]$. In order to reduce the computational cost we have used hydrogens in place of alkyl groups, both in the alkoxide ligands and in the alkyne units. This reduces the computational effort without changing the main bonding interactions within the W_2C_2 unit. Moreover we will evaluate the relative energetics including relativistic effects, calculations at this level having been carried out on the species involved in the metathesis-like reaction and on the stationary points on the reaction energy profiles.

Computational Details

Calculations were conducted using the ADF (Amsterdam density functional) program package described in detail elsewhere.[16–18] The molecular orbitals were expanded in an uncontracted double-ζ Slater atomic orbital (STO) basis set[19] for all the atoms with the exception of tungsten, where we used a double-ζ STO basis set for the 3s and 3p orbitals, and a triple-ζ STO basis set for the 3d and 4s. Single 4p, 3d and 2p STOs were used as polarisation functions for tungsten, O and C, and H respectively. The cores (W 1s–5p; C, O 1s) have been kept frozen.[16] The local density approximation (LDA) exchange correlation potential was used, together with the Vosko–Wilk–Nusair parametrisation[20] for homogeneous electron gas correlation. Non-local corrections included Becke's correction[21] for local exchange and Perdew's correction[22] to the local correlation energy (NLDA). It has been demonstrated that excellent metal–metal and ligand–metal bond energies are obtained using this density-functional based approach.[23]

Molecular structures were optimised by the NLDA method using analytic energy derivatives. It had been shown that non-local corrections significantly improve the optimised geometries of transition-metal complexes, particularly metal–ligand bond lengths. In the absence of these corrections, such bonds are uniformly too short (by about 0.05 Å).[23]

Relativistic effects have been taken into account by the Pauli formalism, the Pauli Hamiltonian including first-order scalar relativistic corrections (Darwin and mass-velocity) while neglecting spin–orbit corrections.[18,24] Single-point relativistic calculations have been performed at the minima derived from non-relativistic geometry optimisations.

Results and Discussion

The ditungsten hexaalkoxide and the tungsten carbyne

We begin our discussion with a brief analysis of the electronic and molecular structure of the multiply bonded metal–metal compound, $(HO)_3W\equiv W(OH)_3$, and the $[W(OH)_3(\equiv CH)]$ metal carbyne. The former compound has been optimised under D_{3h} symmetry constraints, with the optimised structure **I** close to those observed for a variety of structurally characterised $W_2(OR)_6$ complexes.[25] In particular the calculated W–W bond length of 2.27 Å is comparable to the value of 2.31 Å in $W_2(OPr^i)_6$. The metal–metal bond in this complex can be best described by a $\sigma^2\pi^4$ configuration which, in agreement with earlier calculations,[26] clearly reflects the triple-bond character. The tungsten carbyne complex, **II**, has been optimised under C_{3v} constraints; the optimised geometry is in good agreement with that observed experimentally for several $[W(OBu^t)_3(\equiv CR)]$ complexes.[27] The main frontier orbitals are the occupied $5a_1$ and $5e_1$, and the empty $6e_1$; the $5a_1$ is of σ character, while the highest occupied molecular orbital (HOMO) $5e_1$ represents a pair of π orbitals describing the triple metal–carbon bond, and the $6e_1$, the lowest unoccupied molecular orbital (LUMO), is the pair of empty π* orbitals.

The ditungstenatetrahedrane complex

The first step in the metathesis-like reaction (1) has been postulated to be co-ordination of the alkyne to the dinuclear tungsten alkoxide to give a ditungstenatetrahedrane species of type **1**. As this species has been observed and structurally characterised only when at least one of the tungsten centres is co-ordinated by a Lewis base such as pyridine,[4] we have examined in detail the geometry and bonding of such a plausible adduct, $[W_2(OH)_6(\mu\text{-}C_2H_2)]$. This molecule has been optimised under C_{2v} constraints, **III**. The resulting geometrical parameters are fairly close to those observed for structurally characterised complexes in which one or two pyridines are co-ordinated to tungsten (see Table 2). In particular, **III** was calculated to have a C–C bond distance of 1.40 Å, a W–C bond distance of 2.05 Å, which is in the range of a typical tungsten–carbon single bond, and a W–W bond length of 2.93 Å, corresponding to a tungsten–tungsten single bond.[28]

The best way to discuss the bonding interactions between the alkyne and the ditungsten units in the $[W_2(OH)_6(\mu\text{-}C_2H_2)]$ complex is to consider the interactions between the frontier orbitals of the $W_2(OH)_6$ and C_2H_2 fragments in the distorted geometry

Table 2 Main experimental parameters[4] (Å)

Complex	r(C–C)	r(W–W)	r(W–C)
$[W_2(OPr^i)_6(py)_2(\mu\text{-}C_2H_2)]$	1.39	2.57	2.10
$[W_2(OCH_2Bu^t)_6(py)_2(\mu\text{-}C_2Me_2)]$	1.37	2.60	2.13
$[W_2(OBu^t)_6(py)(\mu\text{-}C_2H_2)]$	1.44	2.67	2.10

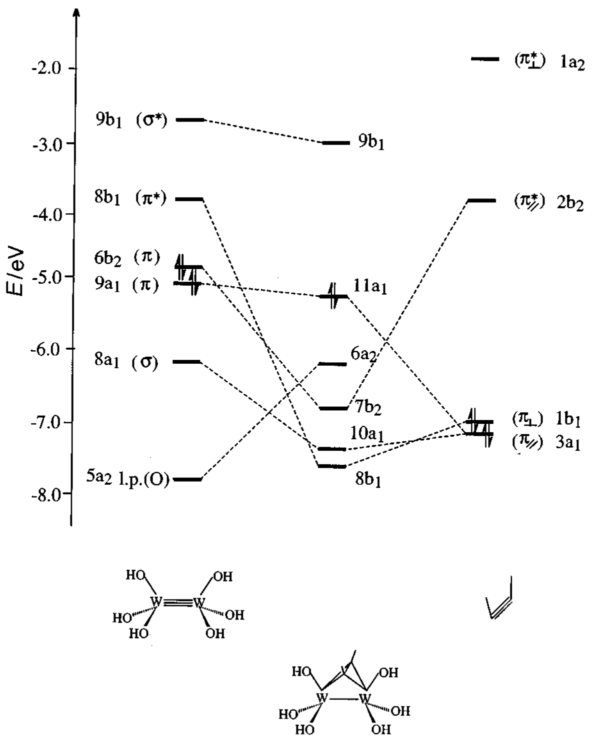
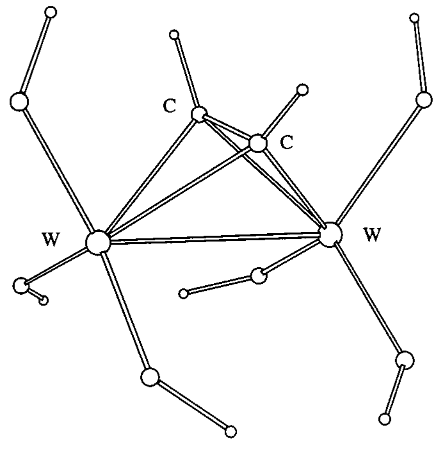
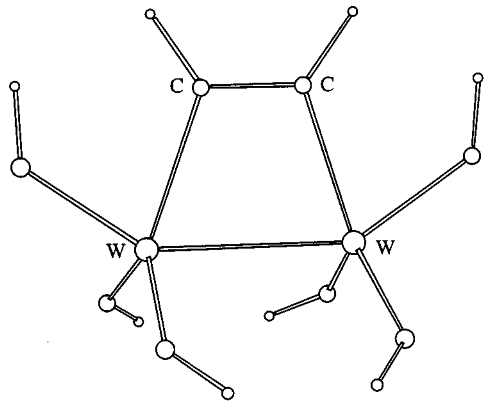


Fig. 1 Orbital interaction diagram for $W_2(OH)_6$ with C_2H_2 in the perpendicular acetylene geometry



III

of complex **III** (see Fig. 1). The frontier orbitals of the C_2H_2 fragment (at the right) comprise two fully occupied low-lying π orbitals and two high-lying π* orbitals: the bending distortion of the C_2H_2 fragment acts to split the degeneracy of the acetylene π and π* orbitals in components perpendicular ($1b_1$, $1a_2$) and parallel ($3a_1$, $2b_2$) to the plane of bending. The frontier orbitals of the $W_2(OH)_6$ fragment (shown at the left in Fig. 1) consist essentially of σ and π metal–metal bonding and antibonding orbitals. The orbitals of **III** which describe the strongest interactions are $8b_1$ and $7b_2$; the former shows mixing between the $8b_1$ [π* orbital of the $W_2(OH)_6$ fragment] and the $1b_1$ ($\pi_\perp$ orbital of the C_2H_2 fragment), while $7b_2$ describes the interaction between the $2b_2$ ($\pi^*_\parallel$ of C_2H_2) and the $6b_2$ [π orbital of $W_2(OH)_6$]. The $11a_1$, the HOMO, is essentially $9a_1$ [π of $W_2(OH)_6$ fragment].



IV

A study of the formation of the dimetallatetrahedrane from acetylene and the ditungsten hexahydroxide, $W_2(OH)_6$, has been carried out in a least-motion pathways in which the acetylene molecule approached the ditungsten complex in such a way that the C–C and the W–W bond axis remained perpendicular during the reaction within C_{2v} symmetry. The reaction coordinate, chosen to be the distance between the centres of the C–C and the W–W bonds, was decreased from 5.0 (when the two molecules are essentially non-interacting) to 1.26 Å (the distance in the final metallatetrahedrane). The energy profile for this reaction, obtained in ten steps by fixing the reaction coordinate and optimising all the other degrees of freedom within C_{2v} symmetry, suggests that the ditungstenatetrahedrane is 23 kJ mol^{-1} less stable than the two reacting molecules and that the reaction barrier is not higher than 290 kJ mol^{-1}.

The ditungstenacyclobutadiene complexes

We now consider the computed geometries and energetics of the two postulated ditungstenacyclobutadiene structures **2** and **3**. The structure of 1,2-ditungstenacyclobutadiene optimised under C_{2v} symmetry, **IV**, reveals a W–W bond distance of 2.69 Å, a C–C bond distance of 1.31 Å, and a W–C bond distance of 2.13 Å (see Table 3); quite surprisingly, the most stable structure is that with the W–C bonds eclipsed with two of the OH groups. Based on corresponding crystallographic data, these values suggest the presence of tungsten–carbon and –tungsten single bonds, and a carbon–carbon double bond.

A frontier orbital analysis of the 1,2-ditungstenacyclobutadiene electronic structure has been performed in terms of the orbitals of the fragment moieties, C_2H_2 and $W_2(OH)_6$, each at the distorted geometry of the optimised butadiene structure, under C_{2v} symmetry. A correlation diagram showing the orbitals of the complex in terms of those of the fragments is given in Fig. 2, where the orbitals of the C_2H_2 and $W_2(OH)_6$ fragments lie to the right and left, respectively. Only ten of the twelve electrons characterising the W_2C_2 valence core of 1,2-ditungstenacyclobutadiene are shown in Fig. 2; the $6a_1$ C–C σ-bond orbital is not reported since it lies at significantly lower energy compared to the other valence orbitals. The $9b_2$ and $10a_1$ orbitals describe the W–C σ bonds and correspond to the interactions between the $\pi^*_\parallel$ and $\pi_\parallel$ of the C_2H_2 fragment with the $\pi_\parallel$ and σ orbitals of $W_2(OH)_6$, respectively. The $11a_1$ describes essentially the W–W σ bond of the $W_2(OH)_6$ moiety. The four electrons of the $7b_1$ and $6b_1$ orbitals are of π character and depict a partially delocalised π system. However they describe a two-orbital four-electron interaction which gives essentially no contribution to W–C π bonding.

To determine if 1,2-ditungstenacyclobutadiene is indeed an intermediate in the metathesis reaction (1), we have analysed the possibility of obtaining the complex from either (i) the

Table 3 Relative energies (kJ mol^{-1}) with respect to $W_2(OH)_6$ and C_2H_2 at the non-relativistic (nr) and relativistic levels (r), distances (Å) and angles (°) optimised at the non-local level

Complex	Symmetry	*E*(nr)	*E*(r)	*r*(C–C)	*r*(W–W)	*r*(W–C)	C–C–W	C–W–W	C–W–C	W–C–W
I $W_2(OH)_6 + C_2H_2$	D_{3h}	0	0	1.20	2.63					
II 2[W(OH)$_3$(CH)]	C_{3v}	154	115			1.75				
III [$W_2(OH)_6(C_2H_2)$]	C_{2v}	23	46	1.40	2.93	2.05	70.1	44.4	39.8	91.2
IV [$W_2(OH)_6(C_2H_2)$]	C_{2v}	168	182	1.31	2.69	2.13	108.9	71.1		
V [$W_2(OH)_6(C_2H_2)$]	C_{2h}	174	123			2.40/1.79			85.7	94.3

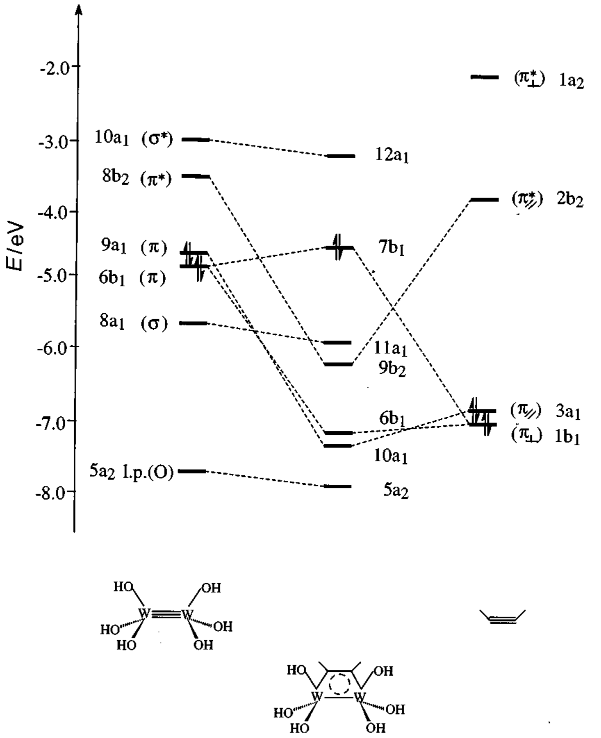


Fig. 2 Orbital interaction diagram for $W_2(OH)_6$ with C_2H_2 in the parallel acetylene geometry

parallel approach of the two reactants, or (ii) from ditungstenatetrahedrane by a twisting mode. The formation-energy profile of the complex from the acetylene and ditungsten moieties has been carried out in such a way that the C–C and W–W bonds remain coplanar throughout the reaction. The energy profile was obtained in ten steps by fixing the reaction coordinate, the distance between the centres of the C–C and W–W bonds, and optimising all the other degrees of freedom, subject to the constraint of C_{2v} symmetry. The activation barrier energy for formation of the parallel complex from acetylene and dinuclear tungsten alkoxide is calculated to be not higher than 304 kJ mol^{-1}, only 14 kJ mol^{-1} higher than the activation energy for formation of the ditungstenatetrahedrane from the same reactants. Given that the tetrahedrane complex is 145 kJ mol^{-1} more stable, we have also examined the possibility of obtaining the intermediate through the tetrahedrane. Since the interconversion of tetrahedrane and cyclobutadiene by a twisting mode is known to be 'symmetry forbidden', it seems quite plausible that a high activation barrier might arise in the present 'half-inorganic' analogue given similar symmetry considerations. Controlling the interconversion by a least-motion pathway leads to the energy profile shown in Fig. 3. The reaction coordinate takes into account the change of the dihedral angle between the W–W and C–C bonds and the distance between the centres of the same bonds. The present profile reveals an activation energy not higher than 284 kJ mol^{-1} for the formation of 1,2-ditungstenacyclobutadiene from ditungstenatetrahedrane.

To complete our study of metathesis energetics, the energy curve describing the formation of the two alkylidynes from 1,2-ditungstenacyclobutadiene has been generated, where the reaction coordinate refers to simultaneous bond stretching, with final cleavage of the two bonds. The curve shows that 1,2-ditungstenacyclobutadiene is 14 kJ mol^{-1} less stable than two alkylidynes and that the activation energy is not higher than 248 kJ mol^{-1}, not unreasonable considering that this refers to cleavage of the carbon–carbon bond.

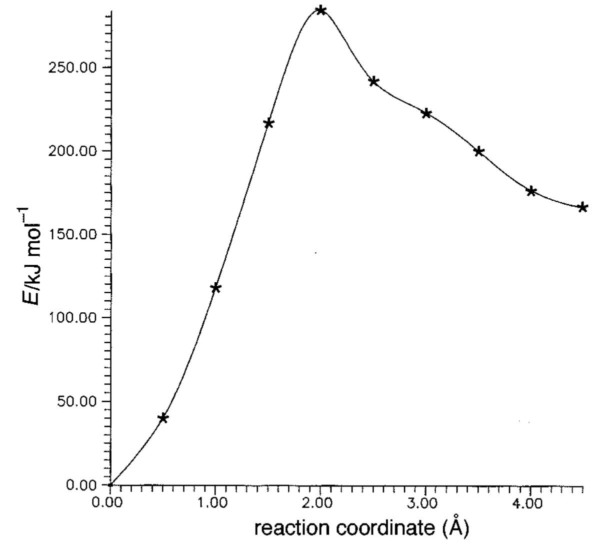


Fig. 3 Energy profile, with respect to ditungstenatetrahedrane, for the formation of 1,2-ditungstenacyclobutadiene by the twisting mode of ditungstenatetrahedrane

The structure of 1,3-ditungstenacyclobutadiene, **V**, has been optimised under C_{2h} symmetry. The calculated geometry reveals quite different W–C bond distances (2.40 and 1.79 Å), values similar to typical tungsten–carbon single and double bonds. An orbital analysis reveals σ bonds between tungsten and carbon described by the a_g and b_u symmetry orbitals in which $d_{x^2-y^2}$ and d_{xy} of tungsten are mixed with the p_x and p_y orbitals of carbon. The frontier orbitals are π bonding and antibonding orbitals; the former, the $6a_u$ and $6b_g$, represent the mixing of the p_z orbitals of the two carbons with a small percentage of tungsten d_{xz} and d_{yz} character. The antibonding orbitals involve the same orbitals but with only a small percentage of carbon. We see that the π system, rather than being delocalised between the W–C bonds, is better represented by two W–C double and two W–C single bonds, an effect confirmed by the quite different bond lengths. This analysis would suggest that this species, formally described as 1,3-ditungstenacyclobutadiene, has few of the properties associated with a metallacyclobutadiene as identified in the introduction, but is better described as a 'stretched' ditungstenacyclobutadiene. Its structure is closer to that of the two alkylidyne molecules, which is supported by the small activation energy of the cleavage step to give the free alkylidynes. Further to study this effect, we have carried out the optimisation of a ditungstenacyclobutadiene complex with the W–C lengths constrained to be equal; this leads to a structure which does not correspond to a true minimum, and is 64 kJ mol^{-1} less stable than the complex described above. Given

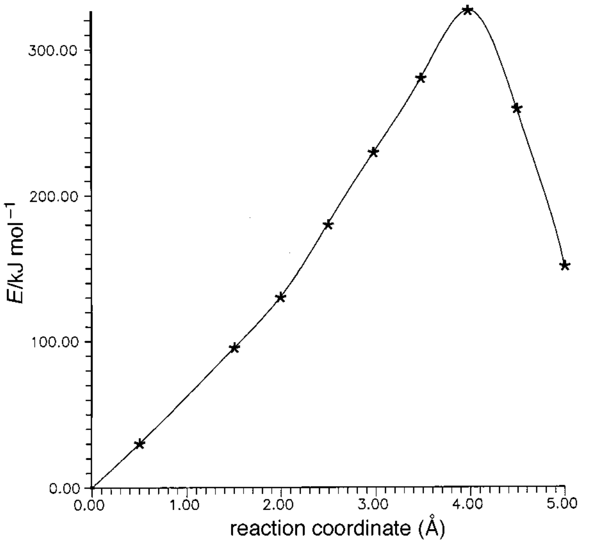
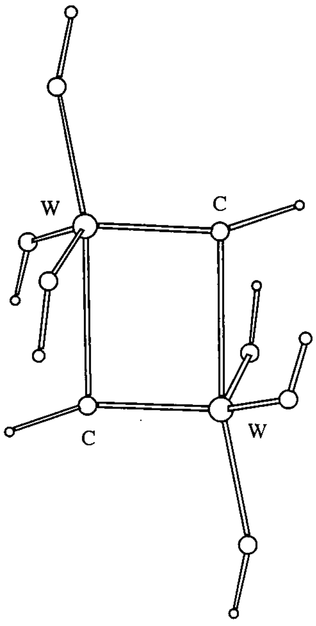


Fig. 4 Energy profile, with respect to ditungstenatetrahedrane, for the formation of 1,3-ditungstenacyclobutadiene by the flattening mode of ditungstenatetrahedrane



V

this effect, we continue to consider the complex with different W–C bonds as a possible intermediate in the metathesis-like reaction, and for convenience continue to refer to this as 1,3-ditungstenacyclobutadiene. The calculated energy of this complex suggests that it is only 151 kJ mol^{-1} less stable than the dimetallatetrahedrane and only slightly less stable than 1,2-ditungstenacyclobutadiene (by 6 kJ mol^{-1}).

A detailed study of the formation of 1,3-ditungstenacyclobutadiene, by a flattening mode of the tetrahedrane with simultaneous stretching of the C–C bond, is shown in Fig. 4. The reaction coordinate takes into account the changes in two parameters: the distance between the centres of the C–C and the W–W bonds and the carbon–carbon distance. The energy profile reveals a reaction barrier of 326 kJ mol^{-1}; such a high activation energy was not expected in light of the similarity of the formation of the dimetallatetrahedrane to the supra-antara $\pi^4 + \pi^4$ symmetry-allowed formation of cyclobutadiene from two acetylene molecules.

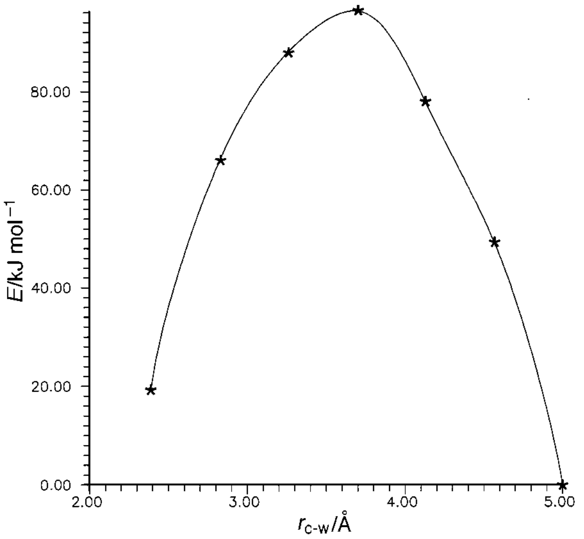


Fig. 5 Energy profile for the cleavage of two W–C bonds of 1,3-ditungstenacyclobutadiene to give two alkylidyne alkoxide complexes, the energy of the alkylidynes being considered as the reference value

The final step of the metathesis-like reaction involving 1,3-ditungstenacyclobutadiene is cleavage of two of the W–C bonds to give two alkylidynes. The 1,3-ditungstenacyclobutadiene has been stretched in a least-motion pathway, fixing as reaction coordinate the longest W–C distance, and varying the other degrees of freedom within C_{2h} symmetry (see Fig. 5). The activation barrier energy for the formation of two alkylidyne molecules by a cleavage reaction is predicted to be 77 kJ mol^{-1}.

All of the energetics described above refer of course to non-relativistic calculations and may well not describe accurately the path of a metathesis-like reaction from alkyne and dinuclear tungsten alkoxide to the alkylidyne complex. From the results presented we can see that the product of the perpendicular approach of reactants, the ditungstenatetrahedrane, is more stable than the product arising from the parallel approach, the 1,2-ditungstenacyclobutadiene, and that its activation energy is only slightly smaller, by 14 kJ mol^{-1}. This strongly suggests that the formation of tetrahedrane represents the first step of the metathesis. The absolute energies and the activation barriers associated with the formation of the ditungstenacyclobutadienes from the ditungstenatetrahedrane do not allow us to differentiate between the two complexes, for: (i) the optimised 1,2-ditungstena- and 1,3-ditungstena-cyclobutadiene are less stable than ditungstenatetrahedrane and have approximately the same energy, with a difference of only 6 kJ mol^{-1}; (ii) the activation-energy barrier for formation of 1,2-ditungstenacyclobutadiene by the twisting of tetrahedrane is 42 kJ mol^{-1} smaller than that associated with flattening of tetrahedrane to yield the 1,3-ditungstenacyclobutadiene; (iii) on the other hand, the cleavage reaction of 1,3-ditungstenacyclobutadiene has an activation barrier of 77 kJ mol^{-1}, smaller than that for cleavage of 1,2-ditungstenacyclobutadiene.

The above data lead us to predict, at the non-relativistic level, that the two ditungstenacyclobutadienes are equivalent intermediates in the metathesis-like reaction (1); we will see below how the inclusion of relativistic effects modifies these conclusions.

Relativistic effects

In addition to the energetic picture described above, comparable relativistic calculations have been carried out at the minima of the complexes obtained at the non-relativistic level. We might expect relativistic effects to play an important role in describing the electronic structure and relative energetics of the species under investigation given the presence of tungsten.

Initially we focus attention on the electronic structure of the $W_2(OH)_6$ and $[W(OH)_3(CH)]$ species, and use these as the reference point for considering relativistic effects in the other

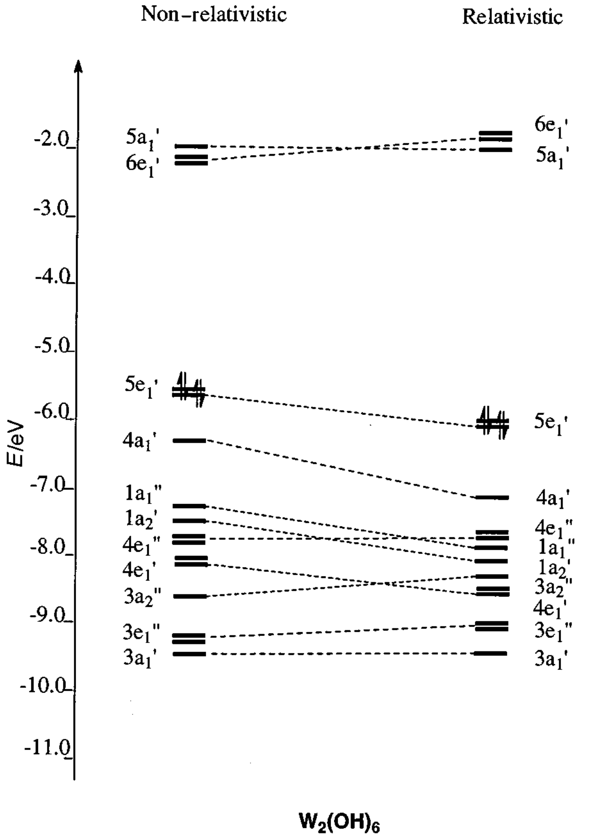


Fig. 6 Non-relativistic (left) and relativistic (right) orbitals of $W_2(OH)_6$

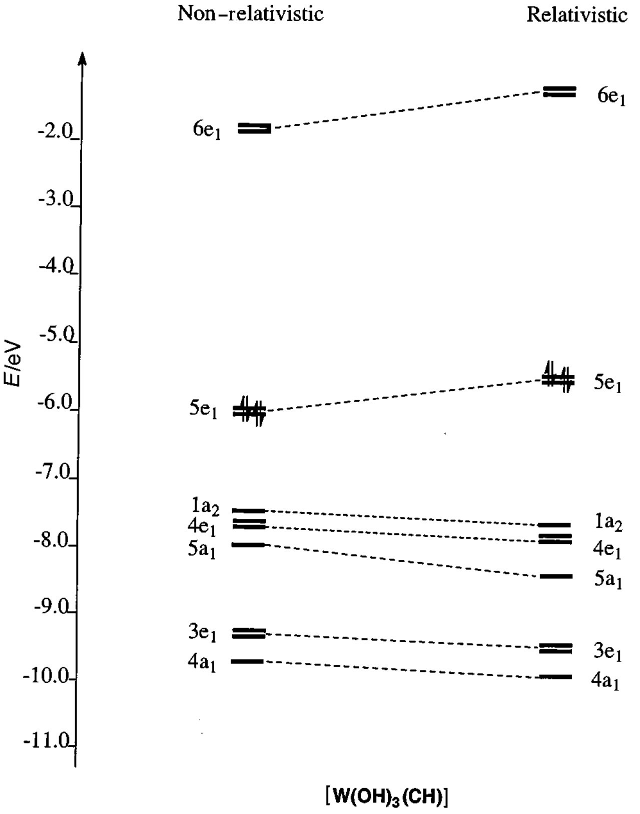


Fig. 7 Non-relativistic (left) and relativistic (right) orbitals of $[W(OH)_3(CH)]$

complexes involved in the metathesis-like reaction (1). To a first approximation the valence orbitals characterised by significant tungsten character are expected to be more affected than those orbitals of carbon, oxygen or hydrogen character, a view consistent with the expected influence of mass-velocity corrections on the tungsten atomic orbitals. The inner s orbitals, characterised by the highest classical velocities, are those most affected, the effective increase in relativistic mass inducing a contraction of such orbitals and a stabilisation of their energy; the p orbitals are less affected by this contraction and stabilisation. The metal d and f orbitals, in contrast, can achieve classical velocities close to *c*, and are strongly influenced by contraction of the s and p orbitals, leading to an expanded character and an associated rise in energy.

Fig. 6 shows the energy levels for the tungsten–tungsten triply bonded complex, with the non-relativistic and relativistic energy levels at the left and right, respectively. We note the substantial relativistic stabilisation of the $4a'_1$ orbital, the tungsten–tungsten σ bond, which involves a significant s-orbital character. The difference in energy and in spatial character between the s and d orbitals decreases at the relativistic level, thereby increasing the associated s–d interaction. The bonding in ditungsten complex **I** is dominated by the 5d orbitals which, while showing an energy destabilisation, become more diffuse leading to an enhanced overlap in the molecular orbitals. Thus the e'_1 symmetry orbitals, comprising tungsten $d_{x^2-y^2}$ and d_{xz} orbital character are, with the exception of the $6e'_1$, slightly stabilised at the relativistic level. In contrast, the e''_1 orbitals, involving the d_{xy} and d_{yz}, are seen to exhibit a slight destabilisation at this level. The net effect of all the orbital changes on the bonding is to lead to a somewhat higher energy, with $W_2(OH)_6$ 102 kJ mol^{-1} less stable than at non-relativistic level.

Turning to $[W(OH)_3(\equiv CH)]$, we show the relativistic and non-relativistic orbital energies, at the right and left, respectively, of Fig. 7. The most relevant energy changes, in the range of ≈0.2 to ≈0.4 eV, are observed for the $5a_1$, the $5e_1$ (the HOMO π orbitals) and for the $6e_1$ (the LUMO π* orbitals). The $5a_1$ orbital, comprising a small percentage of tungsten 6s, is stabilised at the relativistic level, while the remainder, the π and the π* orbitals, which exhibit a mixing of the tungsten $5d_{xz}$ and $5d_{yz}$ orbitals with the carbon $2p_x$ and $2p_y$, are destabilised. The orbitals not involved in the tungsten–carbon triple bond are little affected by the inclusion of relativistic effects. The net result of including these effects is to increase the computed energy of alkylidyne, but only by 29 kJ mol^{-1}, a significantly smaller increase than that found in ditungsten hexahydroxide.

The sensitivity of the species involved in the metathesis-like reaction (1) to the inclusion of relativistic effects might be expected to correlate with the associated degree of multiply bonded W–W character noted above. Thus relativistic calculations carried out on ditungstenatetrahedrane and 1,2-ditungstenacyclobutadiene show an energy destabilisation respectively of 120 and 111 kJ mol^{-1}. In contrast, the absence of W–W bonding in 1,3-ditungstenacyclobutadiene leads to a smaller degree of relativistic destabilisation, and this species is only 46 kJ mol^{-1} less stable than at the non-relativistic level. Total energies calculated at both relativistic (– – –) and non-relativistic levels (——) are reported in Fig. 8. We see that introducing relativistic effects produces significant changes in the relative energetics. With such effects, 1,3-ditungstenacyclobutadiene is 59 kJ mol^{-1} more stable than 1,2-ditungstenacyclobutadiene and only 77 kJ mol^{-1} less stable than ditungstenatetrahedrane. Instead, at the relativistic level, 1,2-ditungstenacyclobutadiene is 136 kJ mol^{-1} less stable than the tetrahedrane.

The above data strongly suggest that 1,3-ditungstenacyclobutadiene may indeed be considered as a plausible intermediate in the metathesis-like reaction (1), at least from thermodynamic considerations. To investigate this effect further we have performed a series of relativistic calculations at the maxima of the energy profiles describing the possible steps in the metathesis-like reaction. The introduction of relativistic effects will clearly act to modify the activation energies, the general trend being towards the prediction of higher barriers. Somewhat different

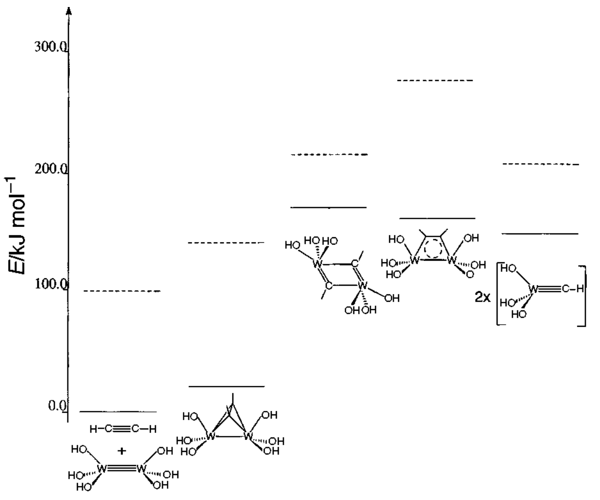


Fig. 8 Comparison of the energies of the species involved in metathesis-like reaction (1); the solid line refers to non-relativistic, the dashed line to relativistic treatment

behaviour is shown however for the flattening of ditungstenatetrahedrane and the cleavage of 1,2-ditungstenacyclobutadiene. The former process is characterised by relativistic and non-relativistic activation energies of 265 and 326 kJ mol^{-1} respectively, while the latter has a relativistic barrier of 201 kJ mol^{-1} to be compared with the value of 248 kJ mol^{-1} at the non-relativistic level. In the metathesis (1) the flattening of tetrahedrane is an endothermic step, with the transition state closer to the products than to the reactants. The product, 1,3-ditungstenacyclobutadiene, is less destabilised by relativistic effects than is the tetrahedrane reactant, leading to a smaller activation barrier.

The activation energies for the other steps described above are raised at the relativistic level. The barrier for the formation of ditungstenatetrahedrane from acetylene and triply bonded ditungsten is 299 kJ mol^{-1}, only 9 kJ mol^{-1} higher than at the non-relativistic level. The relativistic barrier for the formation of 1,2-ditungstenacyclobutadiene from reactants is computed to be 29 kJ mol^{-1} higher than at the non-relativistic level. A similar difference, 23 kJ mol^{-1}, is found in the formation of 1,2-ditungstenacyclobutadiene by ditungstenatetrahedrane twisting. The relativistic activation barrier for the last possible step in the metathesis-like reaction, the formation of the alkylidyne complex from 1,3-ditungstenacyclobutadiene, is computed to be 89 kJ mol^{-1}, only 12 kJ mol^{-1} higher than at the non-relativistic level, but it is yet smaller than that for formation of alkylidynes from 1,2-ditungstenacyclobutadiene.

We can thus conclude that the study of reaction kinetics supports the suggestion that 1,3-ditungstenacyclobutadiene is indeed the intermediate of the metathesis-like reaction (1). We may thus consider the reaction to proceed in three steps, (i) the formation of ditungstenatetrahedrane from the reactants by a perpendicular attack, (ii) the flattening of the tetrahedrane to give 1,3-ditungstenacyclobutadiene, and (iii) the cleavage of the two ditungstenacyclobutadiene W–C bonds to give two alkylidyne complexes. The first and the second steps are the slow ones, although at the relativistic level the activation barrier for the second step is reduced by 61 kJ mol^{-1}; the activation energy for the first step is only increased slightly and remains less than the activation energy for the formation of 1,2-ditungstenacyclobutadiene. Finally, the third step activation barrier increases at the relativistic level, but remains small compared to the activation energy of alkylidyne formation from 1,2-ditungstenacyclobutadiene, 89 as opposed to 201 kJ mol^{-1}.

Conclusion

In this paper, we have performed a detailed study of the electronic and geometric structures of the compounds and possible intermediates involved in metathesis-like reaction (1), generating a variety of energy profiles associated with the formation and decomposition of these species. Initial calculations performed at the non-relativistic level provide no coherent explanation of the steps involved in (1); we find that the inclusion of relativistic effects is necessary to discriminate between the possible pathways involved in reaction (1).

The first pathway studied in the metathesis-like reaction has been the reduction of the C≡C bond, either through a parallel interaction between the reactants, acetylene and the ditungsten hexahydroxide, to yield 1,2-ditungstenacyclobutadiene, or by a perpendicular approach to yield the ditungstenatetrahedrane. Considering the perpendicular complex of acetylene as a plausible intermediate, two possible mechanisms for breaking off the tetrahedrane have been considered, a 'twisting' mode leading to 1,2-ditungstenacyclobutadiene and a 'flattening' mode resulting in 1,3-ditungstenacyclobutadiene. Finally, we have examined the cleavage of the two ditungstenacyclobutadienes to yield the alkylidyne alkoxide complex.

Results at the non-relativistic level lead us to prefer the perpendicular complex since the tetrahedrane is more stable than 1,2-ditungstenacyclobutadiene (Fig. 8) and the activation energies of the two processes are similar. However these data do not allow us to distinguish between 1,2- and 1,3-ditungstenacyclobutadiene as a possible intermediate in the metathesis-like reaction. The two species that we have referred to as ditungstenacyclobutadienes are actually minima corresponding to distorted structures in which the four bonds are different and in which the π system is only partially delocalised. These two dimetallacyclobutadienes have similar non-relativistic energies, with 1,2-ditungstenacyclobutadiene slightly more stable, and their formation processes have similar activation energies.

The introduction of relativistic effects has altered this energy picture (Fig. 8), changing the conclusions derived from the non-relativistic calculations. The 1,3-ditungstenacyclobutadiene is now found to be more stable than 1,2-ditungstenacyclobutadiene, with an activation barrier for the flattening of ditungstenatetrahedrane of 265 kJ mol^{-1}, to be compared with that for the twisting mode of 307 kJ mol^{-1}. The former is further facilitated by the evident ease of bond breaking, given that the two W–C bonds are already stretched. These calculations lead us to prefer 1,3- to 1,2-ditungstenacyclobutadiene as the intermediate, and to suggest that the inclusion of relativistic effects has provided a complete picture of the energetics involved, and hence an understanding of how the metathesis reaction proceeds. This study has emphasised the importance of the inclusion of relativistic effects in the study of reactions involving species containing heavy atoms, such as tungsten.

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