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Spectroscopic properties of conjugated metal–carbon multiple bonds: synthesis and absorption spectra of the "dialkylidynes" $(RO)_3W\equiv C-C\equiv W(OR)_3$ $(OR = OCMe_3, OCMe_2CF_3, OCMe_2Et)$

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Abstract

"Dialkylidyne" (μ-dicarbido) complexes $(RO)_3W\equiv C-C\equiv W(OR)_3$ ($OR = OCMe_3$, **1**; $OCMe_2CF_3$, **2**; $OCMe_2Et$, **3**) have been synthesized. A single crystal X-ray diffraction study performed on the t-butoxy complex **1** demonstrates that the molecule exists in a staggered D_{3d} form in the solid state at −50 °C. Complex **1** crystallizes in the rhombohedral space group $R\bar{3}$, $a = 11.301(4)$ Å, $\alpha = 52.93(3)°$, $Z = 1$. Data were collected in the $\omega-2\theta$ mode and refined to $R = 0.039$ and $R_w = 0.055$. Absorption spectra of **1**–**3** in 2-methylpentane show a surprisingly large number of transitions as compared to the alkylidyne $Me_3CC\equiv W(OCMe_3)_3$ and the triply bonded dimer $W_2(OCMe_3)_6$; while assigning the bands is not currently feasible due to the three-fold symmetry of the molecules, these observations suggest that the π clouds in **1**–**3** are conjugated in the excited state rather than localized.

Organic polyenes and polyynes are of current interest due to their potential applications to photonics [1]. The ability of such molecules and polymers to act as harmonic generators clearly arises from the presence of the conjugated π chain, which allows electronic communication between donor and acceptor sites within the chain. This being so, it seems plausible that systems which incorporate transition metals into the chain will display similar, and possibly enhanced, activity. Additionally, the design flexibility available in transition metal substituted systems arising from variation in the *d*-electron configuration and the electronic and solubility properties of the ancillary ligands suggests that these systems could prove more important than purely organic polymers. Along these lines, several poly(metal acetylides) $\left[C\equiv C-(ML_2)-C\equiv C\right]_n$, (M = Ni, Pd, Pt), the properties of which can be modified through choice of the phosphine ligand L, have been described [2].

We are interested in systems where the metal acts as an integral part of the π chain through metal–carbon multiple bonding, for example, $[L_xM\equiv C)-$

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$(L_xM{\equiv}C)\!\!\rfloor_n$, which we term polymetalynes. In this regard, we were intrigued by the report from Listemann and Schrock that, while monomeric alkylidynes $RC{\equiv}W(OCMe_3)_3$ are colorless or pale yellow, the "dialkylidyne" [3] $(Me_3CO)_3W{\equiv}C{-}C{\equiv}W(OCMe_3)_3$ is dark red [4]. Such dialkylidynes appeared excellent starting points for both spectroscopic and synthetic studies of polymetalynes, and for assessing π conjugation through transition metal-carbon multiple bonds. We therefore report the synthesis and electronic spectra of the ditungsten dialkylidynes $(RO)_3W{\equiv}C{-}C{\equiv}W(OR)_3$ ($OR = OCMe_3$, **1**; $OCMe_2CF_3$, **2**; $OCMe_2Et$, **3**), and the single crystal X-ray diffraction study of the highly symmetric **1**.

Listemann and Schrock prepared t-butoxide complex **1** from the triply bonded dimer $W_2(OCMe_3)_6$ and 3,5-octadiyne. We found this reaction works equally well with the slightly bulkier 4,6-decadiyne. However, treatment of the trifluoro-t-butoxy dimer $W_2(OCMe_2CF_3)_6$ [5] with 4,6-decadiyne provides a mixture of the alkylidynes $Pr{-}C{\equiv}C{-}C{\equiv}W(OCMe_2CF_3)_3$ and $Pr{-}C{\equiv}W(OCMe_2CF_3)_3$; these materials do not further metathesize at room temperature to provide the expected dialkylidyne **2**. Similarly, use of 2,4-hexadiyne in this synthesis leads to $Me{-}C{\equiv}C{-}C{\equiv}W(OCMe_2CF_3)_3$ and $Me{-}C{\equiv}W(OCMe_2CF_3)_3$. Treatment of the t-butoxy complex **1** with stoichiometric or excess CF_3Me_2COH also does not provide **2**, but leads to as yet uncharacterized products. We attempted to assess whether the differences between alkoxy and fluoroalkoxy systems lay in steric or electronic factors by treating the dimer $W_2(OCMe_2Et)_6$ [6], which we anticipated would be electronically similar to the t-butoxide dimer but sterically more demanding, with 4,6-decadiyne and 2,4-hexadiyne. In both cases the expected dialkylidyne **3** formed, but only very slowly (several days at room temperature). Thus it appears that both steric and electronic effects dictate product formation.

Ultimately, we were able to prepare **2** and **3** in good yield rapidly at room temperature through treatment of the appropriate dimer with 3-hexyne in pentane, thereby preforming the less hindered propylidynes $EtC{\equiv}W(OR)_3$, and treatment of these with 2,4-hexadiyne. As expected, the compounds are orange-red (**2**) or red (**1** and **3**) crystalline substances, with solubilities in pentane of $OR = OCMe_2Et \gg OCMe_3 > OCMe_2CF_3$. As observed previously in comparing the dimer $W(OCMe_3)_6$ with the monomeric alkylidynes $RC{\equiv}W(OCMe_3)_3$, the ^1H NMR spectra indicate that the formation of the dialkylidynes from the dimers generally results in upfield shifts of ca. δ 0.05 of the resonances corresponding to the alkoxide group protons from those of the dimers [7].

A single crystal X-ray diffraction study of **1** [8] shows this compound to crystallize in the high symmetry space group $R\bar{3}$, corresponding to the D_{3d} orientation likely to exist in solution (Fig. 1). The bond length and angle data suggest that **1** is most correctly described as a dialkylidyne, as the tungsten–alkylidynyl carbon bond distance is similar to that seen in monomeric W^{VI} alkylidynes [10] and the alkylidynyl carbon–alkylidynyl carbon bond distance is similar to that observed in organic polyynes (ca. 1.37 Å) [11]. Thus **1** appears distinct [12a] from the other possible μ-dicarbide structures, e.g. the bridging ethynediyl $L_nM{-}C{\equiv}C{-}ML_n$ [12b], and the dimetallocumulene $L_nM{=}C{=}C{=}ML_n$ [12c].

The electronic nature of these dialkylidyne complexes is of interest due to the possibility of conjugation of the metal–carbon multiple bonds. The length of the alkylidynyl C–C bond suggests conjugation in the ground state, but could simply represent the increased s-orbital character of this bond. To explore the question of

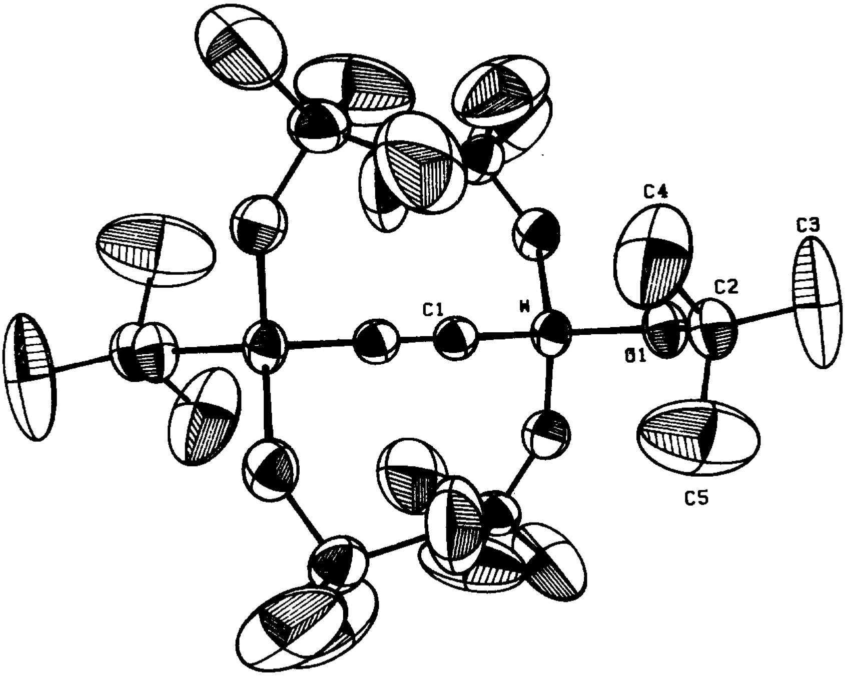

Fig. 1. ORTEP drawing of **1**. Selected bond distances (Å) and angles (°): W–O(1): 1.865(5); W–C(1): 1.79(1); C(1)–C(1)′: 1.38(2); O(1)–W–C(1): 108.3(1); O(1)–W–O(1)′: 110.6(1).

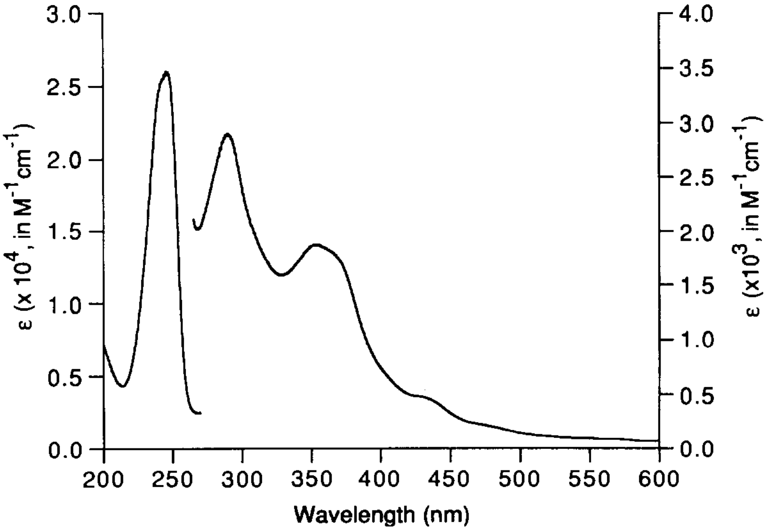

Fig. 2. Absorption spectrum of **2** in 2-methylpentane. The portion of the spectrum from 260–600 nm was obtained at a concentration of 3.8×10^{-4} *M* and a 1-cm path length. The portion of the spectrum from 190–260 nm was obtained at a concentration of 7.9×10^{-4} M and a 0.1-cm path length. The data were not corrected for solvent absorption.

Table 1

Absorption data [a] for $W_2C_2(OR)_6$ complexes in 2-methylpentane

OR = $OCMe_3$	$OCMe_2CF_3$	$OCMe_2Et$
470 (170)	460 (220)	464 (210)
425 (460)	420 (460)	428 (520)
370 (1800)	373 (1700)	370 (2300)
350 (2100)	354 (1900)	353 (2500)
295 (3100)	289 (2900)	296 (3700)
248 (24000)	247 (26000)	249 (30000)
	241 (26000)	

[a] Values are given in nm (ϵ in M^{-1} cm^{-1}).

conjugation in the excited state, we obtained the absorption spectra of **1**–**3** in 2-methylpentane. The spectrum of **2** appears in Fig. 2; spectroscopic data for **1**–**3** appear in Table 1. Surprisingly, despite the presumably dissimilar electron-donating properties of the six trifluoro-t-butoxide ligands at the tungsten centers in **2**, and of the t-butoxide and t-pentoxide ligands in **1** and **3**, respectively, the spectra are essentially identical. Apparently, the ground state and excited states between which observable transitions occur are perturbed equally by the electronic properties of the alkoxide group, so that the energy gaps remain nearly constant. Comparing these spectra to those of the monomeric C_{3v} alkylidyne $Me_3CC{\equiv}W(OCMe_3)_3$ [13a] and the D_{3d} dimer $W_2(OCMe_3)_6$ [13b] provides us with evidence for the presence of significant excited state conjugation in **1**–**3**. While the three-fold symmetry of the system makes interpretation and assignment of the bands difficult [14], the fact that the alkylidyne and dimer display simple, well-resolved spectra essentially containing two bands while **1**–**3** display considerably more complex spectra with at least six bands above 200 nm suggests that the tungsten-carbon triple bonds in the dialkylidynes do not act in isolation, but mix strongly with each other. In this respect, the alkylidyne/dialkylidyne comparisons resemble those between alkenes and polyenes, and alkynes and polyynes: as the chain length increases, the absorption bands shift to lower energies [15]. It seems reasonable that similar electronic behavior occurs in the dialkylidynes, with the electrons delocalized through the MCCM framework.

Experiments designed to extend the metal-carbon multiply bound chain and to utilize the conjugative properties of these molecules are in progress.

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3 Such molecules are also correctly termed μ-dicarbides. We use the term dialkylidynes to reflect that they are prepared by methodologies used to prepare monomeric "Schrock-type", formally d^0W^{VI} alkylidynes [4], and that we consider these molecules "extended" examples of Schrock-type systems.

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7 **2**: ^{1}H NMR (C_6D_6): δ 1.44 (s). $W_2(OCMe_2Et)_6$: ^{1}H NMR (C_6D_6): δ 1.83 (q, J(HH) = 7.5 Hz, CH_2CH_3); 1.61 (s, CH_3); 1.02 (t, J(HH) = 7.5 Hz, CH_2CH_3). **3**: ^{1}H NMR (C_6D_6): δ 1.84 (q, J(HH) = 7.5 Hz, CH_2CH_3); 1.53 (s, CH_3); 0.97 (t, J(HH) = 7.5 Hz, CH_2CH_3).

8 Complex **1** crystallizes in the rhombohedral space group $R\bar{3}$, $a = 11.301(4)$ Å, $\alpha = 52.93(3)^\circ$, $Z = 1$. Data were collected on an Enraf–Nonius CAD-4 diffractometer at $-50\,^\circ$C with Mo-K_α radiation in the ω–2θ mode and were refined using SHELX and SHELXS [9] to $R = 0.039$ and $R_w = 0.055$. Complete structural details will be published in due course.

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13 (a) The absorption spectrum of this molecule in 2-methylpentane exhibits bands at 330 (shoulder, ϵ 550 M^{-1} cm^{-1}), 297 (shoulder, ϵ 1200) and 253 (ϵ 4100) nm; T.M. Gilbert and M.D. Hopkins, unpublished work; (b) M.H. Chisholm, D.L. Clark, E.M. Kober and W.G. Van der Sluys, Polyhedron, 6 (1987) 723.

14 If the ground state has an e_g HOMO and and e_u LUMO [12a], then excited states generated by the HOMO–LUMO excitation are A_{2u}, E_u, and A_{1u}. Transitions $A_{1g} \rightarrow A_{2u}$ and $A_{1g} \rightarrow E_u$ are LaPorte allowed in D_{3d} point symmetry. Including vibronic and spin–orbit coupling, both of which are probably substantial effects for **1**–**3**, would increase the number of possible transitions.

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