Reduction of α,β-Unsaturated Ketones and Aldehydes by Tungsten–Tungsten Triple Bonds: Formation of 1,2 and 1,4 Adducts as opposed to C=O Cleavage

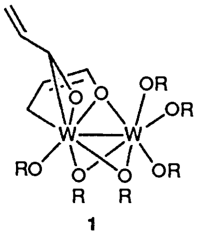
Malcolm H. Chisholm,* Eric A. Lucas, Aaron C. Sousa, John C. Huffman, Kirsten Folting, Emil B. Lobkovsky and William E. Streib

Department of Chemistry and Molecular Structure Center, Indiana University, Bloomington, Indiana 47405, USA

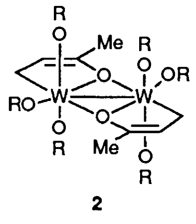
Whereas reactions between sterically unencumbered aldehydes RCHO and $[W_2(OCH_2Bu^t)_6(py)_2]$ (py = pyridine) yield μ-alkylidene oxo ditungsten compounds, similar reactions with the α,β-unsaturated organic carbonyls CH_2=CHCH=O, MeCH=CHCH=O and CH_2CHC(Me)=O give 2 : 1 adducts of three different structural types; the presence of the neighbouring C–C double bond allows chelate behaviour by ring-closure, thereby providing a kinetic diversion from the otherwise facile C=O bond cleavage.

Previously we have shown[1] that ketones and $[W_2(OR)_6]$ compounds (R = Pr^i, CH_2Bu^t) react to yield alkenes in a molecular system that superficially mimics the well known McMurry reaction.[2] However, while the latter proceeds *via* initial C–C bond formation giving pinacolate intermediates, the reactions involving $[W_2(OR)_6]$ compounds proceed in the inverse order, namely by initial C=O bond cleavage and subsequent C–C bond formation. In reactions involving $[W_2(OCH_2Bu^t)_6(py)_2]$ (py = pyridine) the reaction is limited by the dissociative step wherein pyridine leaves the dinuclear centre. However, in reactions involving the unligated $[W_2(OR)_6]$ compounds (R = Pr^i, CH_2Bu^t) and ^{13}C labelled benzophenone, $Ph_2{}^{13}CO$, and acetone, $Me_2{}^{13}CO$, carried out in $[^2H_8]$toluene at −80 °C in an NMR tube, there is clear evidence for the formation of a bridging ^{13}C labelled alkylidene, but no evidence for a 1:1 ketone adduct. Evidently the energy of activation for C=O bond cleavage is very small. Reasoning that there must exist a 1 : 1 adduct with some degree of kinetic persistence (*i.e.* subsequent to adduct formation there must be some degree of reorganizational energy leading to C=O cleavage) we have tried to trap the adduct by use of a functionalized aldehyde or ketone that would serve as a chelating ligand. We describe here three types of complexes that have been isolated from reactions employing α,β-unsaturated aldehydes. In each, the carbon–oxygen bond of the aldehyde has been maintained. This is in contrast to the reaction with benzaldehyde, wherein the C–C double bond is part of the aromatic ring and the C=O bond is cleaved.

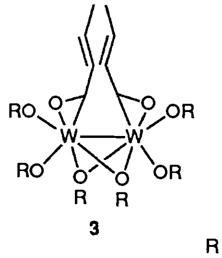
A general reaction procedure was employed wherein a hydrocarbon solution of $[W_2(OCH_2Bu^t)_6(py)_2]$ was allowed to react with the α,β-unsaturated aldehyde (2 equiv.) at room temperature for 30 min. Upon cooling to *ca.* −15 °C crystalline samples of the adducts involving acrolein, **1**, methyl vinyl ketone (MVK), **2**, and crotonaldehyde, **3**, were obtained. In each instance the crystal and molecular structure was determined by a single crystal X-ray study† and the solution behaviour of the complexes in $[^2H_6]$benzene was investigated by NMR spectroscopy. In addition, the labelled compounds derived from $[W_2(OCD_2Bu^t)_6]$ were prepared so that all the ^1H signals of the attendant aldehyde ligands could be observed. When only one equivalent of the aldehyde was added the complexes **1**, **2** and **3** were still formed, but in reduced amounts. Evidently the ditungsten centre is keen to pick up two α,β-unsaturated units since this, as is shown later, represents a four-electron oxidation to give a $W_2{}^{10+}$ centre. By contrast, the addition of one equivalent of benzaldehyde or



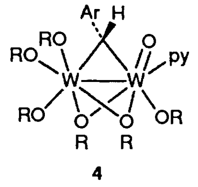
1



2



3



4

R = CH_2Bu^t

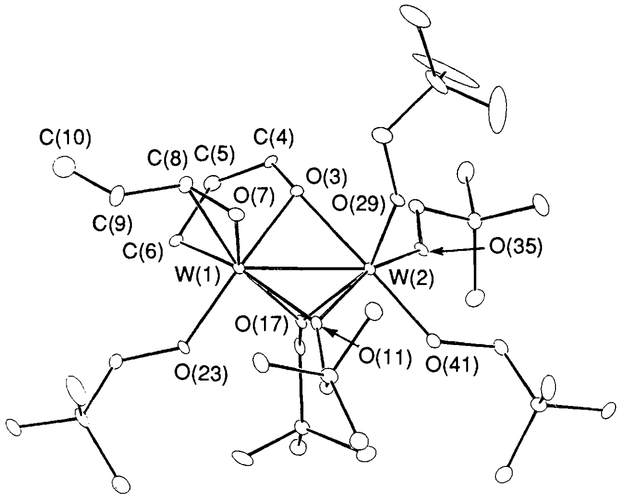


Fig. 1 ORTEP diagram of **1**. Thermal ellipsoids represent 35% probability. Hydrogen atoms have been removed for clarity. Some metric data include: W(1)–W(2) 2.6478(6); average W–OCH_2Bu^t(terminal) 1.88(2); W(1)–O(11) 2.167(6); W(2)–O(11) 2.025(6); W(1)–O(17) 2.127(6); W(2)–O(17) 2.035(6); W(1)–C(6) 2.19(1); W(1)–O(3) 2.073(6); W(2)–O(3) 2.143(6); O(3)–C(4) 1.38(1); C(4)–C(5) 1.32(1); C(5)–C(6) 1.52(1); W(1)–O(7) 1.921(7); W(1)–C(8) 2.09(1); C(7)–C(8) 1.37(1); C(8)–C(9) 1.46(2); C(9)–C(10) 1.29(2) Å; O(3)–C(4)–C(5) 119.3(9); C(4)–C(5)–C(6) 118.0(9); O(7)–C(8)–C(9) 117.3; C(8)–C(9)–C(10) 129(1)°.

---

† *Crystal data* for **1** at −170 °C: space group $P2_1/n$ with a = 14.198(3), b = 15.045(4), c = 20.550(6) Å, β = 106.07(1)°, Z = 4, D_c = 1.542 g cm^{-3}. Final R(F) = 0.0438 and R_w(F) = 0.0428. For **2** at −155 °C: space group $P2_1/n$ with a = 11.048(2), b = 17.558(5), c = 12.806(3) Å, β = 114.29(1)°, Z = 4, D_c = 1.512 g cm^{-3}. Final R(F) = 0.0520 and R_w(F) = 0.0497. For **3** hexane at −128 °C: space group = $P2/a$ with a = 19.367(3), b = 12.386(2), c = 22.090(6) Å, β = 101.07(1)°, Z = 4, D_c = 1.436 g cm^{-3}, final R(F) = 0.0654 and R_w(F) = 0.0677. For **4** (μ-tolylidene) at −155 °C: space group $P\bar{1}$, a = 12.014(2), b = 19.972(6), c = 11.496(3) Å, α = 105.16(1), β = 115.79(1), γ = 89.26(1)°, Z = 2, D_c = 1.520 g cm^{-3}, final R(F) = 0.0571, R_w(F) = 0.0574. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

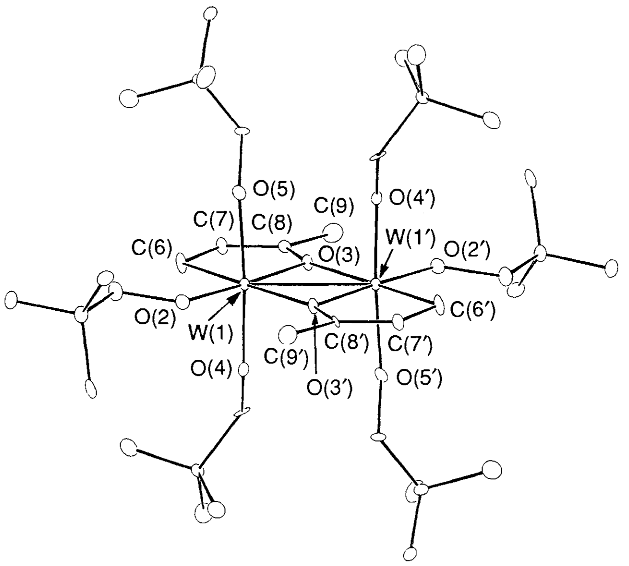


Fig. 2 ORTEP diagram of **2**, showing 35% probability ellipsoids. Primed atoms are related to unprimed atoms by a crystallographic inversion centre. Hydrogen atoms have been removed for clarity. Some metric data include: W(1)–W(1′) 2.792(1); W(1)–O(2) 1.913(8); W(1)–O(4) 1.862(9); W(1)–O(5) 1.840(9); W(1)–O(3) 2.069(7); W(1′)–O(3) 2.146(8); W(1)–C(6) 2.20(1); C(6)–C(7) 1.51(2); C(7)–C(8) 1.33(2); C(8)–O(3) 1.39(2); C(8)–C(9) 1.48(2) Å; C(6)–C(7)–C(8) 120(1); C(7)–C(8)–O(3) 115(1); C(7)–C(8)–C(9) 129(1)°.

para-X-substituted benzaldehydes (X = Me, OMe, CF_3, NMe_2) to $[W_2(OCH_2Bu^t)_6(py)_2]$ under identical conditions yields the μ-benzylidene oxo compound **4** or the appropriate *para*-X-substituted derivative. This too represents a four-electron redox reaction. The molecular structures of the compounds are depicted by the line drawings and ball-and stick drawings giving the atom number scheme are shown in Figs. 1–4

The complex **1** shows two types of acrolein ligands, one behaving both as a chelate and a bridging ligand and the other as an η^2-aldehyde. The MVK adduct **2** adopts a more symmetrical structure in the solid state, with two chelating and bridging MVK ligands. However, in solution (C_6D_6, 22 °C) the ^1H NMR spectrum is consistent with a structure of the type that would be anticipated based on **1**.‡ The crotonaldehyde complex, **3**, is totally different in having two η^2-aldehyde ligands and is somewhat reminiscent of the bis-ethylene adduct $[W_2(OCH_2Bu^t)_6(\eta^2\text{-}C_2H_4)_2]$.[3] The structure of the μ-tolylidene complex **4** is as might have been expected based on previous work[1] (terminal oxo and μ-alkylidene) though in this instance there are three bridging groups to make the structure derived from a confacial bioctahedron. In each structure the W–W distance, *ca.* 2.6–2.8 Å, and the coordina-

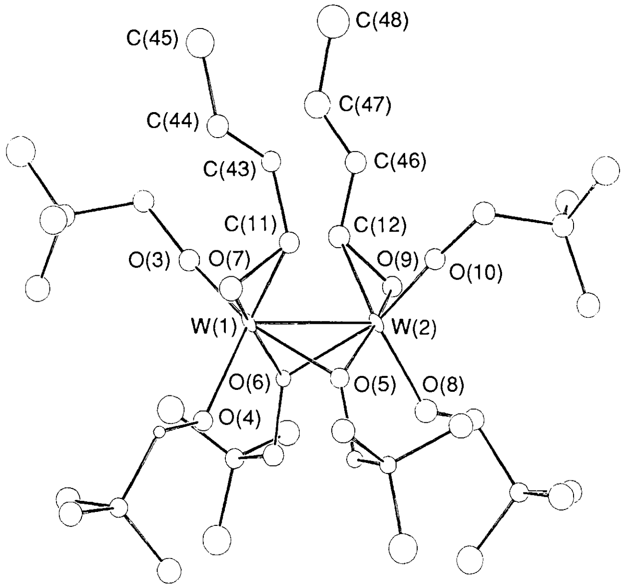


Fig. 3 ORTEP diagram of **3** from a crystal of $\mathbf{3}\cdot C_6H_{14}$, showing 35% probability ellipsoids. Hydrogen atoms have been removed for clarity. Tungsten atoms were refined anisotropically; all other atoms were refined isotropically. Some metric data include: W(1)–W(2) 2.621(2); average W–OCH_2Bu^t (bridging) 2.07(3); W(1)–O(3) 1.76(2); W(1)–O(4) 1.98(2); W(2)–O(8) 1.861(2); W(2)–O(10) 1.82(2); W(1)–O(7) 1.91(2); W(1)–C(11) 2.15(3); W(2)–O(9) 1.93(2); W(2)–C(12) 2.14(3); O(7)–C(11) 1.42(3); C(11)–C(43) 1.49(4); C(43)–C(44) 1.22(4); C(44)–C(45) 1.51(5); O(9)–C(12) 1.39(4); C(12)–C(46) 1.37(4); C(46)–C(47) 1.26(5); C(47)–C(48) 1.52(6) Å; O(7)–C(11)–C(43) 115(3); C(11)–C(43)–C(44) 129(3); C(43)–C(44)–C(45) 130(3); O(9)–C(12)–C(46) 119(3); C(12)–C(46)–C(47) 129(4); C(46)–C(47)–C(48) 131(4)°.

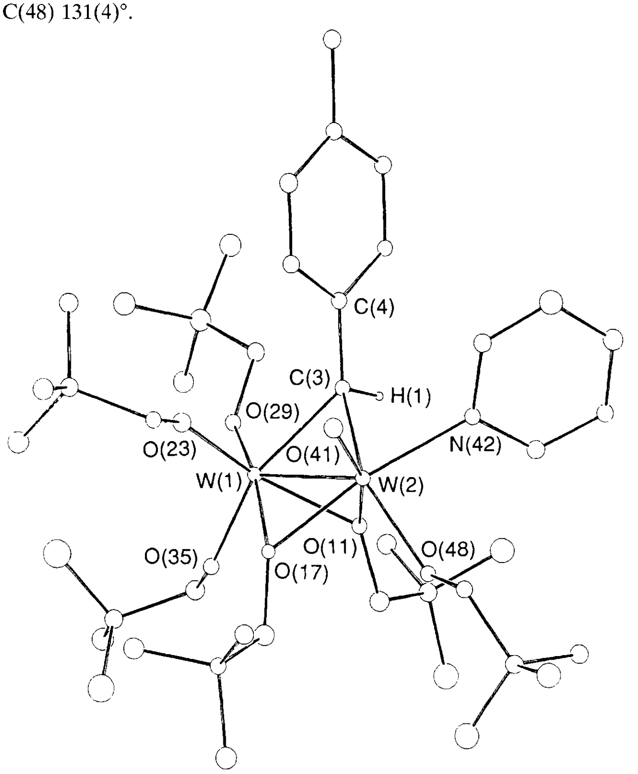


Fig. 4 ORTEP diagram of **4**, showing 35% probability ellipsoids. Except for the hydrogen atom on the alkylidene carbon, hydrogen atoms have been omitted for clarity. The alkylidene hydrogen was not found in the X-ray structure, and is shown in its calculated position. Some metric data are: W(1)–W(2) 2.655(1); W(1)–C(3) 2.16(2); W(2)–C(3) 2.15(2); W(2)–O(41)(oxo) 1.72(1); W(1)–O(23) 1.95(1); W(1)–O(29) 1.85(1); W(1)–O(35) 1.92(1); W(2)–O(48) 1.97(1); W(2)–N(42) 2.19(2); W(1)–O(17) 2.06(1); W(2)–O(17) 2.30(1); W(1)–O(11) 2.12(1); W(2)–O(11) 2.08(1); C(3)–C(4) 1.47(3); C–C(aromatic, min.) 1.37(3) C–C(aromatic, max.) 1.42(3) Å.

---

‡ ^1H NMR data for compounds **1–4** supported by OCD_2CMe_3 ligands (C_6D_6, 360 MHz, δ): **1**: 0.482, 0.643, 0.768, 0.811, 0.971, 1.217 (s, OCD_2CMe_3): 2.032, 2.810 (d, μ-η^1,η^2-OCH=CHCH_2); 4.949, 5.115, 5.981 (d, η^2-OC*H*CH=CH_2); 6.019 (m, μ-η^1,η^2-OCH=C*H*CH_2); 6.289 (m, η^2-OCHC*H*=CH_2); 7.090 (s, μ-η^1,η^2-OC*H*=CHCH_2). **2**: ^1H NMR of $[W_2(\eta^2\text{-}OCMeCH{=}CH_2)(\mu\text{-}\eta^1,\eta^2\text{-}OCMe{=}CHCH_2)(OCD_2CMe_3)_6]$, obtained by dissolving crystals of $[W_2(\mu\text{-}\eta^1,\eta^2\text{-}OCH{=}CHCH_2)_2(OCD_2CMe_3)_6]$ in C_6D_6 at 22 °C: 0.742, 0.891, 0.982, 1.059, 1.151, 1.412, (s, OCD_2CMe_3); 2.180, 2.285, 2.499 (s, OC*Me*CHCH_2); 5.049, 6.052, 6.133 (dd, μ-η^1,η^2-OCMeC*H*=CH_2); 4.947 (m, μ-η^1,η^2-OCMe=CHCH_2); 5.071 (s, μ-η^1,η^2-OCMe=C*H*CH_2). **3**: 0.774, 1.054, 1.142 (s, OCD_2CMe_3); 2.110 (d, η^2-OC*H*CH=CH_2); 5.490, 5.605, 6.197 (m, η^2-OCHC*H*=CH_2). **4**: NMR data for the unsubstituted benzylidene complex, $[W_2(OCD_2CMe_3)_6(O)(py)(\mu\text{-}CHPh)]$: 0.873, 0.878, 0.975, 1.101, 1.293, 1.488 (s, OCD_2CMe_3); 5.695 (s, μ-C*H*Ph); 6.405, 6.693, 7.007, 7.130, 8.513 (m, py + CHC_6H_5).

tion of the ligands is indicative of a four-electron oxidation of the ditungsten centre. In **1**, **2** and **3** a two-electron reduction of each α,β-unsaturated organic carbonyl occurs by either 1,2- or 1,4-coordination to the dinuclear metal centre.

We suggest that in the reactions involving acrolein, MVK and crotonaldehyde, the initial 1 : 1 adduct formed by oxygen-to-tungsten bonding undergoes a rapid ring-closure to generate the bridging type of ligand seen in **1** and **2**. This is apparently faster than the rearrangement required for C=O bond cleavage. In the case of the benzaldehyde this type of ring closure is not favoured on electronic grounds because it would lead to loss of aromaticity. The second uptake of aldehyde then completes the four-electron oxidation of the ditungsten centre and the resultant geometry and coordination of the α,β-unsaturated ligands reflect steric factors. Note that when crotonaldehyde behaves as a chelate with a five-membered ring, the metal–carbon bond involves a secondary alkyl.

Finally we note that, whereas addition of benzaldehyde to **4** leads to the formation of stilbene, **1**, **2** and **3** do not react with benzaldehyde at room temperature. By contrast, addition of acrolein to **4** leads to formation of the alkene, PhCH=CH–CH=CH_2.

We thank the National Science Foundation for support.

Received, 21st March 1991; Com. 1/01363G

References

1 M. H. Chisholm and J. A. Klang, *J. Am. Chem. Soc.*, 1989, **111**, 2324; M. H. Chisholm, K. Folting and J. A. Klang, *Organometallics*, 1990, **9**, 602, 607.

2 J. E. McMurry, *Acc. Chem. Res.*, 1983, **16**, 405; For related reactions involving highly activated metals see: B. E. Kahn and R. T. Rieche, *Chem. Rev.*, 1988, **88**, 733.

3 R. H. Cayton, S. T. Chacon, M. H. Chisholm and J. C. Huffman, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 1026.