# Synthesis and *X*-Ray Crystal Structure of the Tungsten Dimetallatetrahedrane Complex $[W_2Cl_4(\mu\text{-}Cl)_2(\mu\text{-}C_2Me_2)(THF)_2]$ (THF = Tetrahydrofuran)

**Simon G. Bott, David L. Clark, Malcolm L. H. Green,* and Philip Mountford**
*Inorganic Chemistry Laboratory, South Parks Road, Oxford OX1 3QR, U.K.*

Treatment of $\{[W_2Cl_7(THF)_5]Na\}$ with excess of alkyne gives the dimetallatetrahedrane compounds, $[W_2Cl_4(\mu\text{-}Cl)_2(\mu\text{-}C_2RR')(THF)_2]$ (R = R′ = H, Me, Et; R = H, R′ = Ph); the *X*-ray crystal structure of $[W_2Cl_4(\mu\text{-}Cl)_2(\mu\text{-}C_2Me_2)(THF)_2]$ (**1**) reveals a confacial bioctahedral co-ordination environment about the ditungsten centre with a bridging alkyne unit.

There is considerable interest in binuclear μ-alkyne derivatives of the early transition metals,[1] and of compounds containing bridging hydrocarbon ligands in general.[2] Here we describe the synthesis of the first example of a ditungsten halide system containing a μ-alkyne bridge. Previous examples of μ-alkyne ditungsten(III) compounds have invariably been associated with the π-donor ligands OR or $NR_2$.[3] The ditungsten μ-alkyne halide systems described herein are potential new synthons to a wide variety of derivatives of this class of compound.

Treatment of a dilute THF solution of the recently-reported[4] $\{[W_2Cl_7(THF)_5]Na\}$ with excess of but-2-yne at ambient temperature gave green, air-sensitive crystals of $[W_2Cl_4(\mu\text{-}Cl)_2(\mu\text{-}C_2Me_2)(THF)_2]$ (**1**) in *ca.* 40% yield.† The crystal structure of (**1**) (Figure 1)‡ shows that the molecule has virtual $C_{2v}$ symmetry and is isostructural with $[Ta_2Cl_4(\mu\text{-}Cl)_2(\mu\text{-}C_2Bu^t_2)(THF)_2]$.[5] Each tungsten atom in (**1**) achieves pseudo-octahedral co-ordination if the alkyne unit is considered to occupy a single co-ordination site and the metal–metal bond is ignored. The two octahedral units are brought together in a confacial arrangement by the $C_2Me_2$ unit and a pair of bridging Cl ligands, and the W–W distance of 2.5863(6) Å is indicative of metal–metal bonding. Electron counting suggests a formal W–W triple bond, but in compounds of this type the metal–metal and metal–(μ-alkyne) bonding molecular orbitals are extensively mixed. The internal alkyne C(1)–C(1B) distance of 1.39(2) Å, and the increase of the W–W distance from 2.4028(15) Å in the starting material $\{[W_2Cl_7(THF)_5]Na\}$ to 2.5683(6) Å in (**1**) clearly indicates significant back donation of electron density from the dimetal

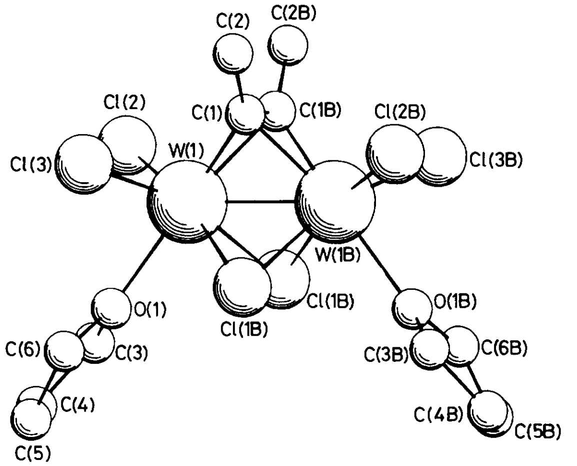
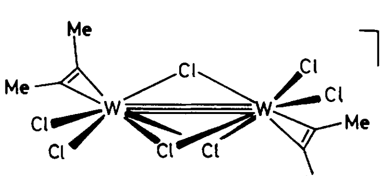


**Figure 1.** The molecular structure of $[W_2Cl_4(\mu\text{-}Cl)_2(\mu\text{-}C_2Me_2)(THF)_2]$ (**1**) viewed nearly perpendicular to the W–W bond. The molecule lies across a crystallographic 2-fold rotation axis. Atoms designated B are related to their counterparts by the symmetry operator [*x*, 1/2 − *y*,*z*]. Selected bond distances (Å) and angles (°) are: W(1)–W(1B) 2.5863(6); W(1)–C(1) 2.01(1); W(1)–C(1B) 2.16(1); C(1)–C(1B) 1.39(2); W(1)–Cl(1) 2.486(2); W(1)–Cl(2) 2.331(2); W(1)–Cl(3) 2.348(2); W(1)–O(1) 2.224(7); Cl(2)–W(1)–Cl(3) 92.65(9); Cl(3)–W(1)–Cl(1) 164.0(1); Cl(3)–W(1)–Cl(1B) 89.80(9); W(1)–Cl(1)–W1(B) 62.70(5); Cl(1)–W(1B)–Cl(1B) 82.34(9); C(1)–W(1)–C(1B) 38.8(6); C(2)–C(1)–C(1B) 134.5(8).



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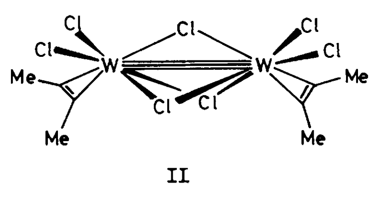

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† Satisfactory analyses have been obtained for all new compounds. N.m.r. data (solvent $[^2H_2]$dichloromethane): $^1H$ n.m.r. at 300 MHz and $^{13}C$ n.m.r. at 75 MHz; chemical shifts (δ) in p.p.m. and coupling constants in Hz.

Compound (**1**): $^1H$ n.m.r. 4.34 (s, 6H, $C_2\mathit{Me}_2$), 4.22 (m, 8H, $OC\mathit{H}_2$), 1.98 (m, 8H, $OCH_2C\mathit{H}_2$); $^{13}C\{^1H\}$ n.m.r. 234.8 ($\mathit{C}_2Me_2$), 74.9 ($O\mathit{C}H_2$), 25.6 ($OCH_2\mathit{C}H_2$), 23.9 ($C_2\mathit{Me}_2$). Analogous n.m.r. data were obtained for the other $[W_2Cl_4(\mu\text{-}Cl)_2(\mu\text{-}C_2RR')(THF)_2]$ compounds.

Compound (**2**): $^1H$ n.m.r. 4.61 and 4.59 (br.s and s, 10H, $OC\mathit{H}_2$ and $C_2\mathit{Me}_2$), 2.14 (br.s, 4H, $OCH_2C\mathit{H}_2$); $^{13}C\{^1H\}$ n.m.r. 270.7 [$J(^{13}C\text{–}^{183}W)$ 26, $\mathit{C}_2Me_2$], 62.9 ($O\mathit{C}H_2$], 20.0 ($OCH_2\mathit{C}H_2$), 15.7 ($C_2\mathit{Me}$).

Compound (**3**): $^1H$ n.m.r. 3.13 (br. m, 8H, $NC\mathit{H}_2$), 3.08 (s, 6H, $C_2\mathit{Me}_2$), 1.62 (m, 8H, $C\mathit{H}_2$ of NBu), 1.44 (m, 8H, $C\mathit{H}_2$ of NBu), 1.02 (t, 12H, $C\mathit{H}_3$ of NBu); $^{13}C\{^1H\}$ n.m.r. 217.8 ($\mathit{C}_2Me_2$), 49.5 ($N\mathit{C}H_2$), 14.3 ($\mathit{C}H_2$ of NBu), 11.4 ($C_2\mathit{Me}_2$), 10.0 ($\mathit{C}H_2$ of NBu), 3.7 ($\mathit{C}H_2$ of NBu). $\lambda_{max.}$ ($CH_2Cl_2$) 240, 341, 430, 540 nm.

‡ *Crystal data* for (**1**): $W_2Cl_6O_2C_{12}H_{22}$, $M$ = 778.72, monoclinic, space group $P2/c$, $a$ = 10.028(3), $b$ = 7.894(1), $c$ = 13.298(2) Å, β = 105.96(2)°, $U$ = 1012 Å$^3$, $Z$ = 2, $D_c$ = 2.56 g cm$^{-3}$, μ(Mo-$K_\alpha$) = 124.10 cm$^{-1}$, crystal size *ca.* 0.1 × 0.2 × 0.4 mm. The data were collected ($2\theta_{max.}$ = 50°) on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo-$K_\alpha$ radiation. An empirical absorption correction was applied and the structure was solved using routine Patterson and Fourier methods. Full-matrix least-squares refinement has led to final agreement factors of $R$ = 0.031 ($R_w$ = 0.037) from 1386 observed reflections with $I/3\sigma(I) > 3.0$ Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

centre to the π*-orbitals of the μ-alkyne fragment. In the $^{13}C$ n.m.r. spectrum† of (**1**), the chemical shift for the internal carbon atoms of the μ-$C_2Me_2$ ligand is observed at δ 234.8 which is the largest reported for this class of $M_2$($μ^2$-alkyne) complexes. {[$W_2Cl_7(THF)_5$]Na} reacts with other alkynes to give the homologous compounds [$W_2Cl_4$(μ-Cl)$_2$(μ-$C_2RR'$)$(THF)_2$] (R = R′ = H, Et; R = H, R′ = Ph)† in similar yield to that obtained for (**1**).

Treatment of (**1**) with an excess of but-2-yne in $CH_2Cl_2$ gives the octahedral complex [W($η^2$-$C_2Me_2$)$Cl_4$(THF)] (**2**) in *ca.* 25% yield.† Compounds of this type have been reported previously.[6] The i.r. spectrum of (**2**) shows a characteristic ν(C–C) stretch at 1754 $cm^{-1}$, and the crystal structure reveals an $η^2$-alkyne internal C–C bond length of 1.30(1) Å.[7] Reaction of {[$W_2Cl_7(THF)_5$]Na} with excess of but-2-yne in $CH_2Cl_2$ also gives (**2**), but if the reaction is carried out in the presence of a source of chloride ion such as $NBu_4Cl$, then another variety of ditungsten–alkyne compound {[$W_2Cl_4$(μ-Cl)$_3$($η^2$-$C_2Me_2$)$_2$][$NBu_4$]} (**3**) is obtained as a purple microcrystalline material in moderate yield.† The spectroscopic data for (**3**) are consistent with either of two possible isomers, I or II.

Both the isomeric structures, I and II, appear to represent a new co-ordination geometry of an alkyne to a dimetallic centre with a confacial bioctahedral arrangement.

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